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CHAPTERWISE SOLUTIONS

CHEMISTRY

- *Multiple Choice Questions* • *Subjective Problems* • *Assertion & Reason Type*
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CHAPTERWISE SOLUTIONS

CHEMISTRY

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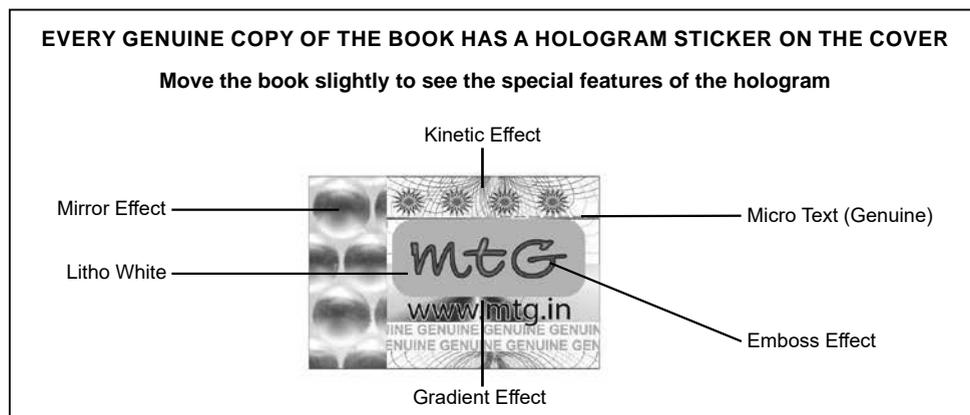
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SYLLABUS*

PHYSICAL CHEMISTRY

General topics :

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

Gaseous and liquid states :

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

Atomic structure and chemical bonding :

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

Energetics :

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

Chemical equilibrium:

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

Electrochemistry :

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

* For latest information please refer to latest JEE Advanced Prospectus.

Chemical kinetics :

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

Solid state :

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

Solutions :

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

Surface chemistry :

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

Nuclear chemistry :

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

INORGANIC CHEMISTRY**Isolation/preparation and properties of the following non-metals :**

Boron, silicon, nitrogen, phosphorus, oxygen, sulphur and halogens; Properties of allotropes of carbon (only diamond and graphite), phosphorus and sulphur.

Preparation and properties of the following compounds :

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

Transition elements (3d series) :

Definition, general characteristics, oxidation states and their stabilities, colour (excluding the details of electronic transitions) and calculation of spin-only magnetic moment; Coordination compounds: nomenclature of mononuclear coordination compounds, *cis-trans* and ionisation isomerisms, hybridisation and geometries of mononuclear coordination compounds (linear, tetrahedral, square planar and octahedral).

Preparation and properties of the following compounds :

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

Ores and minerals :

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

Extractive metallurgy :

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

Principles of qualitative analysis :

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

ORGANIC CHEMISTRY**Concepts :**

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

Preparation, properties and reactions of alkanes :

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

Preparation, properties and reactions of alkenes and alkynes :

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

Reactions of benzene :

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

Phenols :

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

Characteristic reactions of the following (including those mentioned above) :

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

Carbohydrates :

Classification; mono- and di-saccharides (glucose and sucrose); Oxidation, reduction, glycoside formation and hydrolysis of sucrose.

Amino acids and peptides :

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

Properties and uses of some important polymers :

Natural rubber, cellulose, nylon, teflon and PVC.

Practical organic chemistry :

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



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Basic Concepts of Chemistry

Multiple Choice Questions with ONE Correct Answer

- When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volumes of hydrogen evolved is
(a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 9 : 4
(1979)
- 2.76 g of silver carbonate on being strongly heated yields a residue weighing
(a) 2.16 g (b) 2.48 g (c) 2.32 g (d) 2.64 g
(1979)
- A gaseous mixture contains oxygen and nitrogen in the ratio of 1 : 4 by weight. Therefore, the ratio of their number of molecules is
(a) 1 : 4 (b) 1 : 8 (c) 7 : 32 (d) 3 : 16
(1979)
- The total number of electrons in one molecule of carbon dioxide is
(a) 22 (b) 44 (c) 66 (d) 88
(1979)
- The number of neutrons in dipositive zinc ion with mass number 70 is
(a) 34 (b) 36 (c) 38 (d) 40
(1979)
- The largest number of molecules is in
(a) 36 g of water
(b) 28 g of carbon monoxide
(c) 46 g of ethyl alcohol
(d) 54 g of nitrogen pentoxide.
(1979)
- If 0.50 mol of BaCl_2 is mixed with 0.20 mol of Na_3PO_4 , the maximum number of moles of $\text{Ba}_3(\text{PO}_4)_2$ that can be formed is
(a) 0.70 (b) 0.50 (c) 0.20 (d) 0.10
(1981)
- A molal solution is one that contains one mole of a solute in
(a) 1000 g of the solvent
(b) one litre of the solvent
(c) one litre of the solution
(d) 22.4 litres of the solution.
(1986)
- The equivalent weight of MnSO_4 is half its molecular weight when it is converted to
(a) Mn_2O_3 (b) MnO_2 (c) MnO_4^- (d) MnO_4^{2-}
(1988)
- In which mode of expression, the concentration of a solution remains independent of temperature?
(a) Molarity (b) Normality
(c) Formality (d) Molality
(1988)
- The number of moles of KMnO_4 that will be needed to react completely with one mole of ferrous oxalate in acidic solution is
(a) $\frac{3}{5}$ (b) $\frac{2}{5}$ (c) $\frac{4}{5}$ (d) 1
(1997)
- The normality of 0.3 M phosphorous acid (H_3PO_3) is
(a) 0.1 (b) 0.9 (c) 0.3 (d) 0.6
(1999)
- The reaction, $3\text{ClO}^-_{(aq)} \rightarrow \text{ClO}^-_{3(aq)} + 2\text{Cl}^-_{(aq)}$ is an example of
(a) oxidation reaction
(b) reduction reaction
(c) disproportionation reaction
(d) decomposition reaction.
(2001)
- An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this solution is
(a) 40 ml (b) 20 ml (c) 10 ml (d) 4 ml
(2001)
- In the standardization of $\text{Na}_2\text{S}_2\text{O}_3$ using $\text{K}_2\text{Cr}_2\text{O}_7$ by iodometry, the equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ is
(a) (molecular weight)/2
(b) (molecular weight)/6
(c) (molecular weight)/3
(d) same as molecular weight.
(2001)

16. How many moles of electron weigh one kilogram?

- (a) 6.023×10^{23} (b) $\frac{1}{9.108} \times 10^{31}$
 (c) $\frac{6.023}{9.108} \times 10^{54}$ (d) $\frac{1}{9.108 \times 6.023} \times 10^8$

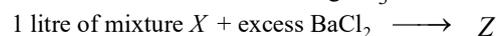
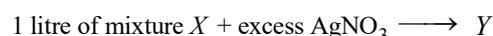
(2001)

17. Which has maximum number of atoms?

- (a) 24 g of C (12) (b) 56 g of Fe (56)
 (c) 27 g of Al (27) (d) 108 g of Ag (108)

(2003)

18. Mixture *X* containing 0.02 mol of $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and 0.02 mol of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ was prepared in 2 litre of solution.



No. of moles of *Y* and *Z* are

- (a) 0.01, 0.01 (b) 0.02, 0.01
 (c) 0.01, 0.02 (d) 0.02, 0.02

(2003)

19. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is

- (a) 3 (b) 4 (c) 5 (d) 6.

(2007)

20. Given that the abundances of isotopes ^{54}Fe , ^{56}Fe and ^{57}Fe are 5%, 90% and 5% respectively, the atomic mass of Fe is

- (a) 55.85 (b) 55.95 (c) 55.75 (d) 56.05.

(2009)

Fill in the Blanks

21. Of the halide ions, is the most powerful reducing agent. (1978)

22. The total number of electrons present in 18 ml of water is (1980)

23. The modern atomic mass unit is based on the mass of (1980)

24. 3 g of a salt of molecular weight 30 is dissolved in 250 g of water. The molality of the solution is..... (1983)

25. The weight of 1×10^{22} molecules of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is (1991)

26. The compound $\text{YBa}_2\text{Cu}_3\text{O}_7$, which shows superconductivity, has copper in oxidation state..... Assume that the rare earth element yttrium is in its usual +3 oxidation state. (1994)

Subjective Problems

27. Account for the following : Limit your answer to two sentences.

Atomic weights of most of the elements are fractional. (1979)

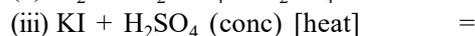
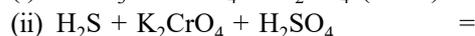
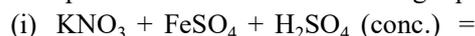
28. In the analysis of 0.500 g sample of feldspar, a mixture of the chlorides of sodium and potassium is obtained, which weighs 0.1180 g. Subsequent treatment of the mixed chlorides with silver nitrate gives 0.2451 g of silver chloride. What is the percentage of sodium oxide and potassium oxide in feldspar? (1979)

29. 5 ml of a gas containing only carbon and hydrogen were mixed with an excess of oxygen (30 ml) and the mixture exploded by means of an electric spark. After the explosion, the volume of the mixed gases remaining was 25 ml. On adding a concentrated solution of potassium hydroxide, the volume further diminished to 15 ml the residual gas being pure oxygen. All volumes have been reduced to NTP. Calculate the molecular formula of the hydrocarbon gas. (1979)

30. (i) 5.5 g of a mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ requires 5.4 ml of 0.1 N KMnO_4 solution for complete oxidation. Calculate the number of gram mole of hydrated ferric sulphate in the mixture.

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

31. Complete and balance the following equations.



32. Find the equivalent weight of H_3PO_4 in the reaction.



33. (a) 1 litre of a mixture of CO and CO_2 is taken. This mixture is passed through a tube containing red hot charcoal. The volume now becomes 1.6 litre. The volumes are measured under the same conditions. Find the composition of the mixture by volume.

(b) A compound contains 28 percent of nitrogen and 72 percent of a metal by weight. 3 atoms of the metal combine with 2 atoms of N. Find the atomic weight of the metal. (1980)

Basic Concepts of Chemistry

3

34. A 1.00 g sample of H_2O_2 solution containing x percent H_2O_2 by weight requires x ml of a KMnO_4 solution for complete oxidation under acidic conditions. Calculate the normality of the KMnO_4 solution. (1981)
35. Hydroxylamine reduces iron(III) according to the equation:

$$2\text{NH}_2\text{OH} + 4\text{Fe}^{3+} \rightarrow \text{N}_2\text{O}_{(g)} \uparrow + \text{H}_2\text{O} + 4\text{Fe}^{2+} + 4\text{H}^+$$
 Iron(II) thus produced is estimated by titration with a standard permanganate solution. The reaction is:

$$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$$
 A 10 ml sample of hydroxylamine solution was diluted to 1 litre. 50 ml of this diluted solution was boiled with an excess of iron(III) solution. The resulting solution required 12 ml of 0.02 M KMnO_4 solution for complete oxidation of iron(II). Calculate the weight of hydroxylamine in one litre of the original solution. (H = 1, N = 14, O = 16, K = 39, Mn = 55, Fe = 56) (1981)
36. The density of a 3M sodium thiosulphate solution ($\text{Na}_2\text{S}_2\text{O}_3$) is 1.25 g per ml. Calculate (i) the percentage by weight of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate and (iii) the molalities of Na^+ and $\text{S}_2\text{O}_3^{2-}$ ions. (1983)
37. 4.08 g of a mixture of BaO and an unknown carbonate MCO_3 was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 ml of 1 N HCl. The excess acid required 16 ml of 2.5 N NaOH solution for complete neutralization. Identify the metal M . (At. wt. H = 1, C = 12, O = 16, Cl = 35.5, Ba = 138) (1983)
38. 2.68×10^{-3} moles of a solution containing an ion A^{n+} acquire 1.61×10^{-3} moles of MnO_4^- for the oxidation of A^{n+} to AO_3^- in acid medium. What is the value of n ? (1984)
39. 5 ml of 8 N nitric acid, 4.8 ml of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made upto 2 litre. 30 ml of this acid mixture exactly neutralise 42.9 ml of sodium carbonate solution containing one gram of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in 100 ml of water. Calculate the amount in gram of the sulphate ions in solution. (1985)
40. (i) What is the weight of sodium bromate and molarity of solution necessary to prepare 85.5 ml of 0.672 N solution when the half-cell reaction is

$$\text{BrO}_3^- + 6\text{H}^+ + 6e^- \rightarrow \text{Br}^- + 3\text{H}_2\text{O}$$
 (ii) What would be the weight as well as molarity if the half-cell reaction is:

$$2\text{BrO}_3^- + 12\text{H}^+ + 10e^- \rightarrow \text{Br}_2 + 6\text{H}_2\text{O}$$
 (1987)
41. A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). Calculate: (i) molal concentration and (ii) mole fraction of sugar in the syrup. (1988)
42. A sample of hydrazine sulphate ($\text{N}_2\text{H}_6\text{SO}_4$) was dissolved in 100 ml of water, 10 ml of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 ml of M/50 potassium permanganate solution. Estimate the amount of hydrazine sulphate in one litre of the solution.
 Reaction:

$$4\text{Fe}^{3+} + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{Fe}^{2+} + 4\text{H}^+$$

$$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$$
 (1988)
43. An equal volume of a reducing agent is titrated separately with 1M KMnO_4 in acid, neutral and alkaline media. The volumes of KMnO_4 required are 20 ml in acid, 33.3 ml neutral and 100 ml in alkaline media. Find out the oxidation state of manganese in each reduction product. Give the balanced equations for all the three half reactions. Find out the volume of 1M $\text{K}_2\text{Cr}_2\text{O}_7$ consumed; if the same volume of the reducing agent is titrated in acid medium. (1989)
44. A mixture of $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) and NaHC_2O_4 weighing 2.02 g was dissolved in water and solution made upto one litre. Ten milliliters of the solution required 3.0 ml of 0.1 N sodium hydroxide solution for complete neutralization. In another experiment, 10.0 ml of the same solution, in hot dilute sulphuric acid medium required 4.0 ml of 0.1 N potassium permanganate solution for complete reaction. Calculate the amount of $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 in the mixture. (1990)
45. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the weight of the residue was constant. If the loss in weight is 28.0 per cent, find the amount of lead nitrate and sodium nitrate in the mixture. (1990)
46. Calculate the molality of 1 litre solution of 93% H_2SO_4 (weight/volume). The density of the solution is 1.84 g/ml. (1990)
47. A solution of 0.2 g of a compound containing Cu^{2+} and $\text{C}_2\text{O}_4^{2-}$ ions on titration with 0.02 M KMnO_4 in presence of H_2SO_4 consumes 22.6 ml of the oxidant. The resultant solution is neutralized with Na_2CO_3 , acidified with dilute acetic acid and treated with excess KI. The liberated iodine requires 11.3 ml of 0.05 M $\text{Na}_2\text{S}_2\text{O}_3$ solution for complete reduction. Find out the molar ratio of Cu^{2+} to $\text{C}_2\text{O}_4^{2-}$ compound. (1991)

48. A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 ml. An aliquot of 25.0 ml of this solution requires 17.0 ml of 0.0167 M solution of an oxidant for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. (1991)
49. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is gently heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123.9 ml. A 1.5 g of the same sample requires 150 ml of (M/10) HCl for complete neutralisation. Calculate the % composition of the components of the mixture. (1992)
50. One gram of commercial AgNO_3 is dissolved in 50 ml of water. It is treated with 50 ml of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with (M/10) KIO_3 solution in presence of 6 M HCl till all I^- ions are converted into ICl . It requires 50 ml of (M/10) KIO_3 solution. 20 ml of the same stock solution of KI requires 30 ml of (M/10) KIO_3 under similar conditions. Calculate the percentage of AgNO_3 in the sample.
(Reaction: $\text{KIO}_3 + 2\text{KI} + 6\text{HCl} \rightarrow 3\text{ICl} + 2\text{KCl} + 3\text{H}_2\text{O}$) (1992)
51. Upon mixing 45.0 ml of 0.25 M lead nitrate solution with 25.0 ml of 0.10 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also, calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble. (1994)
52. The composition of a sample of Wustite is $\text{Fe}_{0.93}\text{O}_{1.00}$. What percentage of the iron is present in the form of Fe (III)? (1994)
53. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of a solution of density 1077.2 kg m^{-3} . Calculate the molarity, molality and mole fraction of Na_2SO_4 in the solution. (1994)
54. A 3.00 g sample containing Fe_3O_4 , Fe_2O_3 and an inert impure substance, is treated with excess of KI solution in presence of dilute H_2SO_4 . The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 ml. A 20 ml of the diluted solution requires 11.0 ml of 0.5 M $\text{Na}_2\text{S}_2\text{O}_3$ solution to reduce the iodine present. A 50 ml of the diluted solution, after complete extraction of the iodine requires 12.80 ml of 0.25 M KMnO_4 solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+} . Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original sample. (1996)
55. An aqueous solution containing 0.10 g KIO_3 (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45.0 ml of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution. (1998)
56. How many milliliters of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper (II) carbonate? (1999)
57. A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm^3/g . If the virus is considered to be a single particle, find its molar mass. (1999)
58. Hydrogen peroxide solution (20 ml) reacts quantitatively with a solution of KMnO_4 (20 ml) acidified with dilute H_2SO_4 . The same volume of the KMnO_4 solution is just decolourised by 10 ml of MnSO_4 in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2 . The brown precipitate is dissolved in 10 ml of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4 . Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2 . (2001)
59. Calculate the molarity of water if its density is 1000 kg/m^3 . (2003)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

60. **Statement-1** : In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume required at the equivalence point is twice that of the acid required using phenolphthalein indicator.

Statement-2 : Two moles of HCl are required for the complete neutralization of one mole of Na_2CO_3 .

(1991)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension - 1

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 ml of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : Na = 23, Hg = 200 ; 1 faraday = 96500 coulombs).

61. The total number of moles of chlorine gas evolved is
(a) 0.5 (b) 1.0 (c) 2.0 (d) 3.0
62. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is
(a) 200 (b) 225 (c) 400 (d) 446.
63. The total charge (coulombs) required for complete electrolysis is
(a) 24125 (b) 48250
(c) 96500 (d) 193000. (2007)

Integer Answer Type

64. A student performs a titration with different burettes and finds titre values of 25.2 ml, 25.25 ml, and 25.0 ml. The number of significant figures in the average titre value is
(2010)
65. Silver (atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm^{-3} . The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^x$. The value of x is
(2010)
66. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is
(2011)
67. The volume (in ml) of 0.1 M AgNO_3 required for complete precipitation of chloride ions present in 30 ml of 0.01 M solution of $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$, as silver chloride is close to
(2011)
68. 29.2%(w/w) HCl stock solution has a density of 1.25 g ml^{-1} . The molecular weight of HCl is 36.5 g mol^{-1} . The volume (ml) of stock solution required to prepare a 200 ml solution of 0.4 M HCl is
(2012)
69. If the value of Avogadro number is $6.023 \times 10^{23} \text{ mol}^{-1}$ and the value of Boltzmann constant is $1.380 \times 10^{-23} \text{ J K}^{-1}$, then the number of significant digits in the calculated value of the universal gas constant is
(2014)
70. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g ml^{-1} . Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is
(2014)

ANSWER KEY

- | | | | | | |
|---|---|---|----------------------------|---------------|---------|
| 1. (a) | 2. (c) | 3. (c) | 4. (a) | 5. (d) | 6. (a) |
| 7. (d) | 8. (a) | 9. (b) | 10. (d) | 11. (a) | 12. (d) |
| 13. (c) | 14. (a) | 15. (b) | 16. (d) | 17. (a) | 18. (a) |
| 19. (d) | 20. (b) | 21. Iodide | 22. 6.023×10^{24} | 23. Carbon-12 | 24. 0.4 |
| 25. 4.14 g | 26. + 7/3 | 27. Presence of different isotopes of the same element. | | | |
| 28. 3.58% Na_2O and 10.62% K_2O | 29. C_2H_4 | 30. $9.5 \times 10^{-3} \text{ g mole}$, 0.437 moles | 32. 49 | | |
| 33. CO_2 and CO are in the ratio of 3 : 2, 24 | 37. Calcium | 34. 0.588 N | 35. 39.6 g | | |
| 36. 37.92, 0.065, 7.732, 3.865 | 40. (i) 1.446 g, 0.112 M (ii) 1.735 g, 0.1344 M | 38. 2 | 39. 6.528 | | |
| 44. 1.12 g, 0.90 g | 45. 1.676 g, 3.324 g | 41. 0.56, 0.0099 | 42. 6.5 g | 43. 16.67 ml | |
| 49. 26.5%, 31.5% | 50. 85% | 46. 10.43 | 47. 1 : 2 | 48. 6 | |
| 52. 15.05% | 53. 4.3×10^{-3} | 51. 0.0075 moles, $\text{Pb}^{2+} = 0.05357 \text{ M}$, $\text{NO}_3^- = 0.3214 \text{ M}$, $\text{Cr}^{3+} = 0.0714 \text{ M}$ | 55. 0.062 | 56. 8.097 ml | |
| 57. $7.09 \times 10^7 \text{ g}$ | 58. 0.1 M | 54. 49.33%, 34.8% | 60. (b) | 61. (b) | 62. (d) |
| 63. (d) | 64. (3) | 59. 55.55 M | 66. (5) | 67. (6) | 68. (8) |
| 69. (4) | 70. (8) | | | | |

Explanations

1. (a): (i) Reaction of zinc and H_2SO_4 (excess)



- (ii) Reaction of zinc and NaOH (excess)



$$\therefore \text{Ratio of volumes of hydrogen evolved} = \frac{1}{1} = 1:1$$

2. (c): $\text{Ag}_2\text{CO}_3 \xrightarrow[\text{-CO}_2]{\Delta} \text{Ag}_2\text{O}$
(2.76 g) (x g)

$$\text{Molecular mass of } \text{Ag}_2\text{CO}_3 = 2(108) + 3(16) = 276$$

$$\therefore \text{Number of moles of } \text{Ag}_2\text{CO}_3 = \frac{2.76}{276} = 0.01 \text{ mol}$$

Now 1 mole of Ag_2CO_3 releases 1 mole of CO_2 and 1 mole of Ag_2O remains as residue.

$$\therefore \text{residue} = 0.01 \times \text{molecular mass of } \text{Ag}_2\text{O} \\ = 0.01 \times 232 = 2.32 \text{ g}$$

3. (c): $\frac{\text{Oxygen}}{\text{Nitrogen}} = \frac{1}{4}$ (by weight)

$$\text{Ratio of number of molecules} = \frac{14}{4 \times 16} = \frac{7}{32}$$

$\therefore 7:32$ is the ratio of their number of molecules.

4. (a): In 1 molecule of CO_2 number of electrons
 $= 6 + 2 \times 8 = 6 + 16 = 22$

5. (d): Neutrons in Zn^{2+}

Atomic weight = 70

Atomic number = 30

$$\therefore \text{Number of neutrons} = 40$$

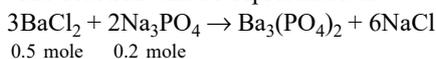
6. (a): Number of moles

$$\frac{36}{18} \text{ of } \text{H}_2\text{O}; \frac{28}{28} \text{ of } \text{CO}; \frac{46}{46} \text{ of } \text{C}_2\text{H}_5\text{OH} \text{ and } \frac{54}{108} \text{ of } \text{N}_2\text{O}_5$$

\therefore 2 moles of H_2O , 1 mole of CO , 1 mole of $\text{C}_2\text{H}_5\text{OH}$ and 0.5 mole of N_2O_5 .

\therefore Largest number of molecules is in (a).

7. (d): The reaction can be represented as



0.5 mole 0.2 mole

From the above balanced equation, 3 moles of BaCl_2 requires 2 moles of Na_3PO_4

$$\therefore 0.5 \text{ moles of } \text{BaCl}_2 \text{ will require moles of } \text{Na}_3\text{PO}_4 = \frac{2}{3} \times 0.5 \\ = 0.33$$

Since only 0.2 moles of Na_3PO_4 are available so Na_3PO_4 is the limiting reagent.

Since 1 mole of $\text{Ba}_3(\text{PO}_4)_2$ is formed when 2 moles of Na_3PO_4 react. So the moles of $\text{Ba}_3(\text{PO}_4)_2$ formed when 0.2 moles of

$$\text{Na}_3\text{PO}_4 \text{ reacts} = \frac{1}{2} \times 0.2 = 0.1$$

8. (a): A molal solution is one that has a molality (m) = 1 i.e. it contains 1 mole (gram molecular mass) of the solute in 1000 g (1 kg) of the solvent.

9. (b): Equivalent weight = $\frac{\text{Molecular weight}}{\text{Change in O.N. of Mn}}$
 $= \frac{\text{Molecular weight}}{2}$

Thus change in oxidation state of Mn must be 2.

Oxidation state of Mn in $\text{MnSO}_4 = +2$.

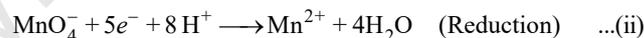
So the oxidation state of Mn in the new compound should be +4.

The oxidation states of Mn in Mn_2O_3 , MnO_2 , MnO_4^- and MnO_4^{2-} compounds are +3, +4, +7 and +6 respectively.

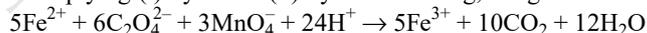
10. (d): Temperature has no effect on molality as it involves only masses and no volumes.

11. (a): $\text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Fe}^{3+} + 2\text{CO}_2 + 3e^-$
 MnO_4^- will oxidise Fe^{2+} to Fe^{3+} and $\text{C}_2\text{O}_4^{2-}$ to CO_2 .

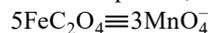
Thus we have,



Multiplying (i) by 5 and (ii) by 3 and adding, we get



From above equation, we have



12. (d): H_3PO_3 is a dibasic acid $[\text{H}-\overset{\text{OH}}{\underset{\text{O}}{\text{P}}}-\text{OH}]$. So, 0.3 M H_3PO_3 will be $2 \times 0.3 \text{ N } \text{H}_3\text{PO}_3$, i.e., it is 0.6 N or its normality is 0.6

13. (c): $3\text{ClO}_3^- \text{(aq)} \longrightarrow \text{ClO}_3^- \text{(aq)} + 2\text{Cl}^- \text{(aq)}$

The oxidation state of chlorine (Cl) in reactant (ClO_3^-) is +1 ($x - 2 = -1$; $x = +1$) and the oxidation states of chlorine (Cl) in products are +5 (in ClO_3^-) and -1 (in Cl^-). From this we find that chlorine gets oxidised (changes from +1 to +5 state) and also reduced (changes from +1 to -1 state). A reaction like this is called a **disproportionation reaction**.

14. (a): Equivalent of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 10 ml
 $=$ Equivalent of NaOH

$$\therefore \frac{6.3}{63} \times \frac{10}{250} = 0.1 \times V \text{ (in litres)}$$

$$\text{(Eq. wt. of } \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 63)$$

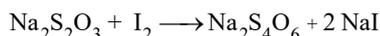
or $V = 0.04 \text{ L}$ or 40 ml

15. (b): In iodometry, $\text{K}_2\text{Cr}_2\text{O}_7$ acts as an oxidising agent to liberate iodine (I_2) from an iodide such as KI or NaI.

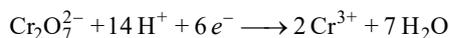
The iodine (I_2) thus liberated is titrated with hypo ($\text{Na}_2\text{S}_2\text{O}_3$) solution.

Basic Concepts of Chemistry

7



We find that one mole of $\text{K}_2\text{Cr}_2\text{O}_7$ accepts 6 moles of electrons as follows:



Thus equivalent weight = $\frac{\text{Molecular weight}}{6}$

16. (d): Weight of 1 mole of electrons = $9.108 \times 10^{-31} \times 6.023 \times 10^{23}$ kg

Or number of moles of electrons in $9.108 \times 10^{-31} \times 6.023 \times 10^{23}$ kg = 1 mole

\therefore Number of moles of electrons in 1 kg =

$$\frac{1}{9.108 \times 10^{-31} \times 6.023 \times 10^{23}} = \frac{1}{9.108 \times 6.023} \times 10^8 \text{ moles}$$

17. (a): Number of atoms in

24 g of carbon = $2 \times 6.023 \times 10^{23}$

56 g of iron = $1 \times 6.023 \times 10^{23}$

27 g of aluminium = $1 \times 6.023 \times 10^{23}$

108 g of silver = $1 \times 6.023 \times 10^{23}$

Hence the maximum number of atoms is in 24 g of carbon (*i.e.* 2 moles of carbon)

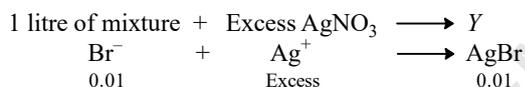
18. (a): Number of moles of Br^- in the mixture = $0.02 / 2$ mol = 0.01 mol/L

{ Br^- ions are produced in case of $[\text{Co}(\text{NH}_3)_5\text{SO}_4]$ Br only and not in case of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ }

Number of moles of SO_4^{2-} in the mixture = $0.02/2 = 0.01$ mol/L

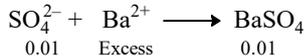
{ SO_4^{2-} ions are produced in case of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ only}

Now



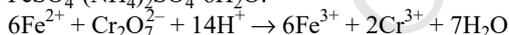
$\therefore Y = 0.01$

Also 1 litre of mixture + Excess $\text{BaCl}_2 \longrightarrow Z$



$\therefore Z = 0.01$

19. (d): In the redox reaction, $\text{Cr}_2\text{O}_7^{2-}$ oxidises Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.



Mohr's salt $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ and dichromate reacts in 6 : 1 molar ratio.

or one mole of $\text{Cr}_2\text{O}_7^{2-}$ will require six moles of Fe^{2+} ions.

20. (b): The average isotopic mass or atomic mass = $\sum m_i \times \frac{x_i}{100}$

where m_i = mass of i^{th} isotope, x_i = abundance of i^{th} isotope

$$\therefore \text{Atomic mass} = 54 \times \frac{5}{100} + 56 \times \frac{90}{100} + 57 \times \frac{5}{100} = 55.95$$

21. Iodide

22. 6.023×10^{24} , 18 ml $\text{H}_2\text{O} = 18$ g $\text{H}_2\text{O} = 1$ mol of H_2O

1 mol of $\text{H}_2\text{O} = 10 \times 6.023 \times 10^{23}$ (\therefore No. of electron in $\text{H}_2\text{O} = 2 + 8 = 10e^-$)

$$= 6.023 \times 10^{24} \text{ electron}$$

23. Carbon-12

24. 0.4 ; Molality (m) = $\frac{3}{30} \times \frac{1000}{250} = 0.4$

25. 4.14 g; Weight of 6.023×10^{23} molecules of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 249$ g (g mol. wt.)

\therefore Weight of 1×10^{22} molecules of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

$$= \frac{249}{6.023} \times \frac{10^{22}}{10^{23}} = 4.14 \text{ g}$$

26. + 7/3 ; Let the oxidation state of Cu be = x , then we have,
 $+3 + 2 \times (+2) + 3 \times x + 7 \times (-2) = 0$

$$\text{or } +3 + 4 + 3x - 14 = 0 \quad \text{or } 3x = 14 - 3 - 4$$

$$\text{or } x = +7/3$$

27. Because of the presence of different isotopes of the same element. These isotopes have different atomic masses.

28. According to the question,



Similarly



Let the amount of NaCl in the mixture be = x g then amount of KCl in the mixture = $(0.118 - x)$ g

Since 58.5 g of NaCl gives AgCl = 143.5

$$\therefore x \text{ g of NaCl gives AgCl} = \frac{143.5}{58.5} \times x \text{ g}$$

Similarly amount of AgCl obtained from KCl

$$= \frac{143.5}{74.5} (0.118 - x) \text{ g}$$

Total weight of AgCl obtained = 0.2451 g

$$\therefore \frac{143.5}{58.5} x + \frac{143.5}{74.5} (0.118 - x) = 0.2451$$

or $x = 0.0338$ g

\therefore Amount of KCl in the mixture = 0.0338 g

\therefore Amount of KCl in the mixture = $0.1180 - 0.0338$ g = 0.0842 g

As $2\text{NaCl} \equiv \text{Na}_2\text{O}$
 $2 \times 58.5 \quad 62$
 $= 117.0$

\therefore 117 g NaCl is equivalent to $\text{Na}_2\text{O} = 62$ g

$$\therefore 0.0338 \text{ NaCl is equivalent to } \text{Na}_2\text{O} = \frac{62}{117} \times 0.0338 \text{ g} = 0.0179 \text{ g}$$

$$\% \text{ of } \text{Na}_2\text{O} \text{ in } 0.5 \text{ g of feldspar} = \frac{0.0179}{0.500} \times 100 = 3.58 \%$$

Similarly, $2\text{KCl} \equiv \text{K}_2\text{O}$
 $2 \times 74.5 \quad 94$
 $= 149$

\therefore 149 g KCl is equivalent to $\text{K}_2\text{O} = 94$ g

$$\therefore 0.0842 \text{ g KCl is equivalent to } \text{K}_2\text{O} = \frac{94}{149} \times 0.0842 \text{ g} = 0.0531 \text{ g}$$

$$\% \text{ of } \text{K}_2\text{O} \text{ in } 0.5 \text{ g feldspar} = \frac{0.0531}{0.5} \times 100 = 10.62 \%$$

Thus the sample of feldspar contains 3.58% Na_2O and 10.62% K_2O .

29. Volume of oxygen added = 30 ml

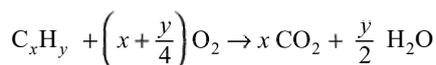
Volume of oxygen left = 15 ml

\therefore Volume of oxygen used = $30 - 15 = 15$ ml

Volume of CO_2 produced = $25 - 15 = 10$ ml

Volume of hydrocarbon = 5 ml

The general equation for combustion is



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

$$\text{or } 5 \text{ ml} \quad \left(x + \frac{y}{4}\right) \text{ ml} \quad 5x \text{ ml}$$

Volume of CO_2 produced = $5x = 10 \text{ ml}$

$$\therefore x = 2$$

Since volume of oxygen used = 15 ml

$$\therefore 5\left(x + \frac{y}{4}\right) = 15 \quad \text{or} \quad x + \frac{y}{4} = 3 \quad \therefore x = 2$$

$$\therefore 2 + \frac{y}{4} = 3 \quad \text{or} \quad \frac{y}{4} = 1 \quad \text{or} \quad y = 4$$

Molecular formula of hydrocarbon is C_2H_4 .

30. (i) $5.4 \text{ ml of } 0.1 \text{ N KMnO}_4 = \frac{5.4 \times 0.1}{1000} \text{ equivalent.}$
 $= 5.4 \times 10^{-4} \text{ equivalent}$

Equivalent weight of $FeSO_4 \cdot 7H_2O = 278$

Amount of $FeSO_4 \cdot 7H_2O = 5.4 \times 10^{-4} \times 278 \text{ g} = 0.150 \text{ g}$

Amount of ferric sulphate = $5.5 - 0.150 \text{ g} = 5.35 \text{ g}$

Molecular weight of ferric sulphate = 562

Moles of ferric sulphate = $\frac{5.35}{562} = 9.5 \times 10^{-3} \text{ g mole}$

(ii) Molecular weight of mixture = $2 \times 38.3 = 76.6$

$$\text{Number of moles in mixture} = \frac{100}{76.6} \quad \dots(i)$$

Let in 100 g of mixture there are $x \text{ g}$ of NO_2

\therefore Weight of N_2O_4 in the mixture = $100 - x$

Molecular weight of $NO_2 = 46$

$$\therefore \text{Number of moles of } NO_2 = \frac{x}{46} \quad \dots(ii)$$

Similarly molecular weight of $N_2O_4 = 92$

$$\therefore \text{Number of moles of } N_2O_4 = \frac{100 - x}{92} \quad \dots(iii)$$

From equations (i), (ii) and (iii)

$$\frac{100}{76.6} = \frac{x}{46} + \frac{100 - x}{92}$$

$$\text{or } 46 \times 92 \times 100 = (92x + 4600 - 46x) \times 76.6$$

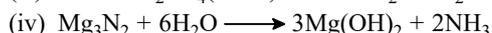
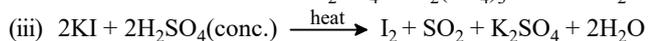
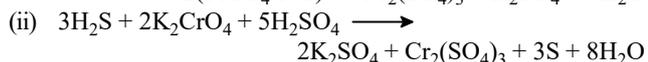
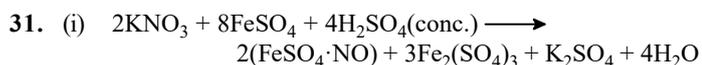
$$\frac{423200}{76.6} = 4600 + 46x$$

$$5524.8 - 4600 = 46x \quad \text{or} \quad 46x = 924.8 \quad \text{or} \quad x = 20.1$$

\therefore Weight of $NO_2 = 20.1 \text{ g}$

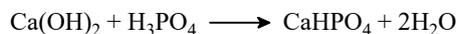
\therefore Weight of $N_2O_4 = 79.9 \text{ g}$

$$\text{Moles of } NO_2 = \frac{20.1}{46} = 0.437 \text{ moles}$$



(v) A thin layer of Al_2O_3 is deposited over aluminium.

32. In the reaction



two hydrogen atoms of H_3PO_4 are replaced, therefore, the equivalent weight of H_3PO_4 is half of its molecular weight.

Molecular weight of $H_3PO_4 = (1 \times 3) + 31 + (4 \times 16) = 98$

$$\therefore \text{Equivalent weight} = \frac{98}{2} = 49$$

33. (a) The reaction is $C + CO_2 \longrightarrow 2CO$

Volume of the mixture of CO and $CO_2 = 1 \text{ litre}$

Let x be the volume of CO_2 in the mixture.

\therefore Volume of CO produced from x of $CO_2 = 2x$

Volume of CO originally present in the mixture = $1 - x$

Total volume of CO after the reaction = $(1 - x) + 2x$
 $= 1 - x + 2x = 1 + x$

Total volume after the reaction = 1.6 litre

$$\therefore 1 + x = 1.6 \quad \text{or} \quad x = 0.6$$

Thus volume of $CO_2 = 0.6 \text{ litre}$ and volume of $CO = 0.4 \text{ litre}$

CO_2 and CO are in the ratio of $3 : 2$.

(b) Formula of the compound M_3N_2

Valency of nitrogen in the compound $M_3N_2 = 3$

$$\therefore \text{Equivalent weight of nitrogen} = \frac{14}{3}$$

28 g Nitrogen combines with metal = 72 g

1 g Nitrogen combines with metal = $\frac{72}{28} \text{ g}$

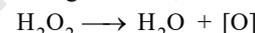
$$\frac{14}{3} \text{ g nitrogen combines with metal} = \frac{72}{28} \times \frac{14}{3} = 12$$

\therefore Equivalent weight of metal = 12

Valency of metal in $M_3N_2 = 2$

\therefore Atomic weight of metal = $12 \times 2 = 24$

34. From the given data, we have



$$\text{Thus equivalent weight of } H_2O_2 = \frac{\text{Molecular weight}}{2}$$

$$= \frac{34}{2} = 17$$

$$\text{Equivalent weight of } KMnO_4 = \frac{\text{Molecular weight}}{5} = \frac{158}{5} = 31.6$$

Calculation of Normality of $KMnO_4$ solution

Let the normality of $KMnO_4 = N_1$ then

$$x \text{ ml of } N \text{ KMnO}_4 = x \text{ ml of } N \text{ H}_2O_2 = \frac{x \times N \times 17}{1000} \text{ g of H}_2O_2$$

From the given data, we have

$$\frac{x \times N \times 17}{1000} \text{ g of H}_2O_2 \text{ is present in } 1 \text{ g of solution}$$

Also 100 g of H_2O_2 solution contains $H_2O_2 = x \text{ g}$

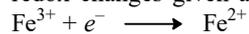
$\therefore 1 \text{ g}$ of H_2O_2 solution contains $H_2O_2 = x/100 \text{ g}$

From the above, we have

$$\frac{x \times N \times 17}{1000} = \frac{x}{100} \quad \text{or} \quad N = \frac{x}{100} \times \frac{1000}{x \times 17} = \frac{10}{17}$$

$$\text{Hence normality of } KMnO_4 \text{ solution} = \frac{10}{17} \text{ N} = 0.588 \text{ N}$$

35. The redox changes given are



Thus meq of Fe^{2+} formed by NH_2OH in 50 ml dilute solution

= Meq of $KMnO_4$ used

$$= 12 \times 0.02 \times 5 = 1.2$$

Meq of NH_2OH in 1000 ml of dilute solution

$$= 1.2 \times \frac{1000}{50} = 24$$

Basic Concepts of Chemistry

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Meq of NH_2OH in 10 ml of original solution
 = Meq of NH_2OH in 1000 ml of diluted solution = 24

$$\text{or, } \frac{W_{\text{NH}_2\text{OH}}}{33/2} \times 1000 = 24 \quad [\text{Molecular wt. of } \text{NH}_2\text{OH} = 33]$$

$$\text{or } W_{\text{NH}_2\text{OH}} = \frac{24 \times 33}{1000 \times 2} = 0.396 \text{ g}$$

Thus weight of NH_2OH in 10 ml of original solution = 0.396 g
 Hence weight of NH_2OH in 1 litre of original solution

$$= \frac{0.396 \times 1000}{10} = 39.6 \text{ g}$$

36. Given $\text{Na}_2\text{S}_2\text{O}_3$ has molarity = 3 mole litre⁻¹

$$\therefore \text{Mole of } \text{Na}_2\text{S}_2\text{O}_3 = 3$$

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

and Volume of solution = 1 litre = 1000 ml

$$\therefore \text{Weight of solution} = 1000 \times 1.25 = 1250 \text{ g}$$

$$\therefore \text{Weight of water} = 1250 - 474 = 776 \text{ g}$$

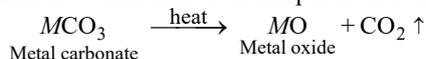
$$\begin{aligned} \text{(i) \% by weight of } \text{Na}_2\text{S}_2\text{O}_3 &= \frac{\text{wt. of } \text{Na}_2\text{S}_2\text{O}_3}{\text{wt. of solution}} \times 100 \\ &= \frac{474}{1250} \times 100 = 37.92 \end{aligned}$$

$$\begin{aligned} \text{(ii) Mole fraction of } \text{Na}_2\text{S}_2\text{O}_3 &= \frac{\text{Mole of } \text{Na}_2\text{S}_2\text{O}_3}{\text{Mole of } \text{Na}_2\text{S}_2\text{O}_3 + \text{Mole of } \text{H}_2\text{O}} \\ &= \frac{3}{3 + 776/18} = 0.065 \end{aligned}$$

$$\begin{aligned} \text{(iii) Molality of } \text{Na}^+ &= \frac{\text{Mole of } \text{Na}^+}{\text{Wt. of water in g}} \times 1000 \\ &= \frac{6 \times 1000}{776} = 7.732 \end{aligned}$$

$$\text{Molality of } \text{S}_2\text{O}_3^{2-} = \frac{3 \times 1000}{776} = 3.865$$

37. The mixture when heated decomposes as follows:



Thus loss of weight occurs due to evolution of CO_2 and the residue consists of MO and BaO .

From the given data,

$$\text{loss of weight in heating} = (4.08 - 3.64) \text{ g} = 0.44 \text{ g}$$

Hence weight of CO_2 evolved = 0.44 g

$$= \frac{0.44}{44} \text{ moles} = 0.01 \text{ moles}$$

From the above equation we find

$$1 \text{ mole of } \text{CO}_2 = 1 \text{ mole of } \text{MCO}_3$$

$$\therefore 0.01 \text{ mole of } \text{CO}_2 = 0.01 \text{ mole of } \text{MCO}_3$$

Hence the given mixture contains 0.01 mole of MCO_3 which will yield 0.01 mole of MO .

From the given data, we also find that

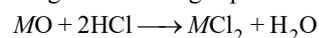
$$\begin{aligned} 16 \text{ ml of } 2.5 \text{ N NaOH} &= 16 \text{ ml of } 2.5 \text{ N HCl} \\ &= 16 \times 2.5 \text{ ml of N HCl} \end{aligned}$$

Hence volume of N HCl that remains unused = 16×2.5 ml
 = 40.0 ml

Total volume of N HCl = 100 ml

Thus volume of N HCl used = $(100 - 40)$ ml = 60 ml

Hence 60 ml of N HCl is used in neutralizing BaO and MO according to following equation



Thus 0.01 mole of MO = 0.02 mole of HCl

$$= 0.02 \times 1000 \text{ ml of N HCl}$$

$$= 20.0 \text{ ml of N HCl}$$

Volume of N HCl used for neutralisation of MO = 20.0 ml

Volume of N HCl still unused = $(60 - 20)$ ml = 40 ml

$$\text{Equivalent weight of BaO} = \frac{138 + 16}{2} = 77$$

$$\left[\therefore \text{Eq. wt.} = \frac{\text{Molecular weight}}{\text{Number of positive charge}} = \frac{\text{Mol. wt.}}{2} \right]$$

Now 40 ml of N HCl = 40 ml of N BaO

$$= \frac{40 \times 77}{1000} \text{ or } 3.08 \text{ g of BaO}$$

Hence total weight of oxides

$$= \text{weight of } \text{MO} + \text{weight of BaO}$$

$$\text{or } 3.64 = \text{weight of } \text{MO} + 3.08$$

$$\text{or weight of } \text{MO} \text{ in mixture} = (3.64 - 3.08) \text{ g} = 0.56 \text{ g}$$

Since residue contains 0.01 mole of MO (already calculated) so we have

$$0.01 \text{ mole of } \text{MO} = 0.56 \text{ of } \text{MO}$$

$$\text{or } 1 \text{ mole of } \text{MO} = \frac{0.56}{0.01} \text{ or } 56 \text{ g of } \text{MO}$$

Let the atomic weight of $M = a$

Then molecular weight of $\text{MO} = a + 16$

Since one mole of $\text{MO} = 56$ g

$$\therefore a + 16 = 56 \text{ or } a = 56 - 16 = 40$$

Thus metal M is Calcium.

38. The change in oxidation state of A when A^{n+} is oxidised to AO_3^- in acidic medium is from $+n$ to $(+5)$ i.e. the change is equal to $(5 - n)$.

The number of electrons added to reduce

$$1.61 \times 10^{-3} \text{ moles of } \text{MnO}_4^- \text{ to } \text{Mn}^{2+}$$

$$(\text{O.S. of Mn changes from } +7 \text{ to } +2 = 1.61 \times 10^{-3} \times 5)$$

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

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

$$\text{or } 5 - n = 3 \text{ or } n = 2$$

39. Let V be the volume of sulphuric acid taken while mixing the given acids. We will have amount of H^+ in 2 L of acid solution

$$= (5 \text{ ml})(8 \text{ M}) + (4.8 \text{ ml})(5 \text{ M}) + (V)(2 \times 17 \text{ M})$$

$$= \left(\frac{5}{1000} \text{ L} \right) (8 \text{ mol L}^{-1}) + \left(\frac{4.8}{1000} \text{ L} \right) (5 \text{ mol L}^{-1}) + (V) (2 \times 17 \text{ mol L}^{-1})$$

$$= \left(\frac{1}{1000} \right) \left[5 \times 8 + 4.8 \times 5 + \left(\frac{V}{\text{ml}} \right) (2 \times 17) \right] \text{ mol}$$

$$= \left(\frac{1}{1000} \right) \left[64 + 34 \left(\frac{V}{\text{ml}} \right) \right] \text{ mol}$$

Amount of H^+ in 30 ml of acids solution

$$= \left(\frac{30}{2000} \right) \left(\frac{1}{1000} \right) \left[64 + 34 \left(\frac{V}{\text{mL}} \right) \right] \text{ mol} \quad \dots(\text{i})$$

Mass of sodium carbonate neutralized by 30 ml of acids solution

$$= \left(\frac{1 \text{ g}}{100 \text{ ml}} \right) (42.9 \text{ ml}) = \frac{42.9}{100} \text{ g}$$

Amount of sodium carbonate neutralized

$$= \frac{(42.9/100) \text{ g}}{286 \text{ g mol}^{-1}} = \frac{42.9}{100 \times 286} \text{ mol} \quad \dots(\text{ii})$$

From the chemical equation $\text{C}_3^{2-} + 2\text{H}^+ \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$ we find that 1 mol $\text{CO}_3^{2-} \equiv 2 \text{ mol H}^+$

Hence, from equations (i) and (ii) we write

$$2 \left(\frac{42.9}{100 \times 286} \right) = \left(\frac{30}{2000} \right) \left(\frac{1}{1000} \right) \left[64 + 34 \left(\frac{V}{\text{ml}} \right) \right]$$

which gives

$$\frac{V}{\text{ml}} = \frac{1}{34} \left[2 \left(\frac{42.9}{100 \times 286} \right) \left(\frac{2000}{30} \right) \left(\frac{1000}{1} \right) - 64 \right] = 4$$

i.e. $V = 4 \text{ ml}$

Finally, mass of SO_4 unit in 4 ml of 17 M H_2SO_4 solution

$$= (4 \text{ ml}) (17 \text{ mol l}^{-1}) (96 \text{ g mol}^{-1}) = \left(\frac{4}{1000} \right) (17) (96) \text{ g} = 6.528 \text{ g}$$

40. (i): From the given data (half-cell reaction), we find $6e^-$ are involved in the reaction.

$$\text{Equivalent weight of NaBrO}_3 = \frac{\text{Molecular wt.}}{6} = \frac{151}{6} \text{ or } 25.17$$

$$\text{We have meq} = \text{Normality} \times V (\text{ml}) = 0.672 \times 85.5 = 57.456 \quad \dots(i)$$

$$\text{Also meq} = \frac{W_{\text{NaBrO}_3}}{\text{Eq. wt. of NaBrO}_3} \times 1000 = \frac{W_{\text{NaBrO}_3}}{25.17} \times 1000 \quad \dots(ii)$$

From (i) and (ii)

$$\therefore \frac{W_{\text{NaBrO}_3}}{25.17} \times 1000 = 57.456$$

$$\text{or } W_{\text{NaBrO}_3} = \frac{57.456 \times 25.17}{1000} = 1.446 \text{ g}$$

$$\text{Molarity of NaBrO}_3 = \frac{\text{Normality}}{6} = \frac{0.672}{6} = 0.112 \text{ M}$$

(ii) From the given half-cell reaction, we find $10e^-$ are involved for 2Br atoms, so the number of e^- involved for each Br atom is $10/2$ or 5.

$$\therefore \text{Eq. wt. of NaBrO}_3 = \frac{\text{Mol. wt.}}{5} = \frac{151}{5} = 30.2$$

Thus amount of NaBrO_3 needed to prepare 1000 ml of 1N $\text{NaBrO}_3 = 30.2 \text{ g}$

Hence amount of NaBrO_3 needed to prepare 85.5 ml

$$\text{of } 0.672 \text{ N NaBrO}_3 = \frac{30.2 \times 0.672 \times 85.5}{1000} = 1.735 \text{ g}$$

$$\text{Molarity} = \frac{0.672}{5} \text{ or } 0.1344 \text{ M.}$$

41. (i): Given,

Weight of sugar syrup = 214.2 g

Weight of sugar in syrup = 34.2 g

$$\therefore \text{Weight of water in sugar syrup} = (214.2 - 34.2) \text{ g} = 180.0 \text{ g}$$

Molecular weight of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) = 342

$$\therefore \text{Molal concentration} = \frac{34.2 \times 1000}{342 \times 180} = 0.56$$

$$\begin{aligned} \text{(ii) Mole fraction of sugar} &= \frac{34.2}{\frac{180}{18} + \frac{34.2}{342}} \quad (\text{Mol. wt of water} = 18) \\ &= \frac{0.1}{10 + 0.1} = \frac{0.1}{10.1} = 0.0099 \end{aligned}$$

42. The reactions given:

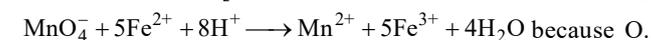


The O. N. of N changes from +2 to 0 i.e. by 2 for each N atom and total electrons involved are 4.

$$\therefore \text{Equivalent weight of N}_2\text{H}_6\text{SO}_4 = \frac{130}{4} = 32.5$$

$$\text{Number of equivalents of KMnO}_4 = \frac{20 \times 5}{50 \times 1000} = \frac{1}{500}$$

[5 electrons are involved in the reaction,



N. of Mn changes from +7 (in MnO_4^-) to +2 (in Mn^{2+})]
If the weight of hydrazine sulphate is $x \text{ g}$, then equivalents of

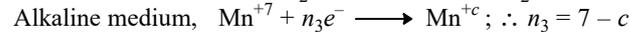
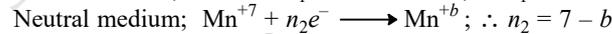
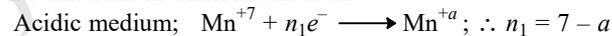
$$\text{hydrazine sulphate} = \frac{x}{32.5}$$

$$\therefore \frac{1}{500} = \frac{x}{32.5} \text{ or } x = \frac{32.5}{500} = 0.065 \text{ g}$$

Hence weight of $\text{N}_2\text{H}_6\text{SO}_4$ in 10 ml solution = 0.065 g

$$\therefore \text{Weight of N}_2\text{H}_6\text{SO}_4 \text{ in } 1000 \text{ ml solution} = \frac{0.065}{10} \times 1000 = 6.5 \text{ g}$$

43. Let us assume that KMnO_4 undergoes following changes in its titrations in different medium.



If $V \text{ ml}$ of reducing agent are used for KMnO_4 (oxidising agent) in different medium,

Then,

$$\begin{aligned} \text{meq. of reducing agent} &= \text{meq of KMnO}_4 \text{ in acidic medium} \\ &= \text{meq of KMnO}_4 \text{ in neutral medium} \\ &= \text{meq of KMnO}_4 \text{ in alkaline medium} \end{aligned}$$

$$\text{or } 1 \times n_1 \times 20 = 1 \times n_2 \times 33.3 = 1 \times n_3 \times 100$$

$$\text{or } n_1 = 1.665 n_2 = 5n_3$$

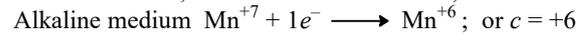
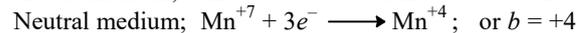
Since n_1, n_2 and n_3 are integers and n_1 is not greater than 7, therefore

$$n_3 = 1 \left[n_3 = \frac{1}{5}, n = \frac{7}{5} \approx 1 \right]$$

$$\text{hence } n_1 = 5 \left[n_1 = 5n_3 = 5 \times 1 = 5 \right]$$

$$\text{and } n_2 = 3 \left[n_2 = \frac{5}{1.665} \approx 3 \right]$$

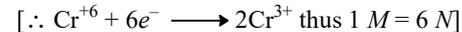
Thus, different oxidation states of Mn in



Moreover, same volume of reducing agent is treated with $\text{K}_2\text{Cr}_2\text{O}_7$, and therefore

$$\text{meq. of reducing agent} = \text{meq. of K}_2\text{Cr}_2\text{O}_7$$

$$\text{or } 1 \times 5 \times 20 = 1 \times 6 \times V$$



$$\text{or } V = \frac{5 \times 20}{6} \text{ or } 16.67 \text{ ml}$$

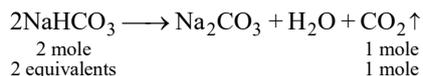
Number of meq of oxidant used = $1.1356 \times n$

Thus, $1.1356 \times n = 6.908$ or $n = \frac{6.908}{1.1356} = 6$

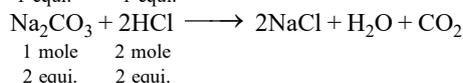
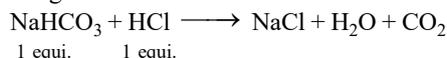
49. Given, 1.5 g of sample require acid = 150 ml of M/10 HCl

\therefore 2 g of sample will require acid = $\frac{150}{1.5} \times 2$ ml of M/10 HCl
= 200 ml of M/10 HCl

When the sample (containing Na_2CO_3 and NaHCO_3 and Na_2SO_4) is heated only NaHCO_3 decomposes to give out CO_2 .



The neutralisation reactions of sample with HCl involves following reactions.



\therefore 2 g sample \equiv 200 ml of M/10 HCl \equiv 200 ml of N/10 HCl
= 20 meq. or 0.02 equi of HCl.

According to ideal gas equation $PV = nRT$ (where n = no. of moles of CO_2 formed)

$$n = \frac{PV}{RT} = \frac{750}{760} \times \frac{123.9}{1000} \times \frac{1}{0.082 \times 298} = 0.005$$

Moles of NaHCO_3 in the sample (2 g) = $2 \times 0.005 = 0.01$

Equivalent of NaHCO_3 in sample = 0.01

Weight of $\text{NaHCO}_3 = 0.01 \times 84$ g (Eq. wt. of $\text{NaHCO}_3 = 84$)
= 0.84 g

% of $\text{NaHCO}_3 = \frac{0.84}{2} \times 100 = 42\%$

Equivalent of Na_2CO_3 in the sample = $0.02 - 0.01 = 0.01$

Weight of $\text{Na}_2\text{CO}_3 = 0.01 \times 53 = 0.53$ g

[Eq. wt. of $\text{Na}_2\text{CO}_3 = 106/2 = 53$]

% of $\text{Na}_2\text{CO}_3 = \frac{0.53}{2} \times 100 = 26.5\%$

% of Na_2SO_4 in the sample = $100 - (42 + 26.5)$
= $100 - 68.5 = 31.5\%$

50. $\text{KIO}_3 + 2\text{KI} + 6\text{HCl} \rightarrow 3\text{ICl} + 3\text{KCl} + 3\text{H}_2\text{O}$

1 mole of $\text{KIO}_3 = 2$ moles of KI

20 ml KI = 30 ml $\frac{M}{10}$ $\text{KIO}_3 = 3$ mmole $\text{KIO}_3 = 6$ mmole KI

\therefore 50 ml KI = $\frac{6}{20} \times 50 = 15$ mmole KI

50 ml $\frac{M}{10}$ $\text{KIO}_3 = 5$ mmole $\text{KIO}_3 = 10$ mmole KI

Amount of KI reacted with $\text{AgNO}_3 = 15 - 10 = 5$ mmole



5 mmole of KI = 5 mmole AgNO_3

= $5 \times 170 \times 10^{-3} = 0.85$ g AgNO_3

% of $\text{AgNO}_3 = 85\%$

51. Moles of $\text{Pb}(\text{NO}_3)_2 = 0.25 \times \frac{45}{1000} = 0.01125$

Initial moles of $\text{Pb}^{2+} = 0.01125$

Moles of $\text{NO}_3^- = 2 \times 0.01125 = 0.02250$

Moles of chromic sulphate,

$\text{Cr}_2(\text{SO}_4)_3 = 0.1 \times \frac{25}{1000} = 0.0025$ moles

Moles of $\text{SO}_4^{2-} = 3 \times 0.0025$ or 0.0075 moles

Moles of PbSO_4 formed = 0.0075

Moles of Pb^{2+} left = $0.01125 - 0.0075 = 0.00375$

Moles of NO_3^- left = 0.02250

Moles of Cr^{3+} left = $0.0025 \times 2 = 0.005$

Total volume of solution = $(45 + 25)$ ml = 70 ml

Molar concentration of species left :

(i) $\text{Pb}^{2+} = \frac{0.00375}{70} \times 1000 = 0.05357$ M

(ii) $\text{NO}_3^- = \frac{0.0225}{70} \times 1000 = 0.3214$ M

(iii) $\text{Cr}^{3+} = \frac{0.005}{70} \times 1000 = 0.0714$ M

52. We know that in pure iron oxide (FeO), iron and oxygen are present in the ratio of 1 : 1.

In Wustite ($\text{Fe}_{0.93}\text{O}_{1.00}$), some of the Fe^{2+} ions are missing and the number of Fe^{2+} ions present is 0.93 instead of 1.

From here we find the number of missing Fe^{2+} ions

$$= 1.0 - 0.93 = 0.07$$

Since each Fe^{2+} ion carries two units of positive charge so the total positive charge missing = $0.07 \times 2 = 0.14$

For maintenance of electrical neutrality this much (*i.e.* 0.14) positive charge has to be compensated by the presence of Fe^{3+} ions.

If one Fe^{3+} ion replaces one Fe^{2+} ion then there is an increase of one unit positive charge. So to compensate 0.14 unit positive charge we require 0.14 Fe^{3+} ions to replace Fe^{2+} ion. Thus out of 0.93 Fe^{2+} ions present in Wustite, there are 0.14 Fe^{3+} ions.

So 100 Fe^{2+} ions have Fe^{3+} ions = $\frac{0.14}{0.93} \times 100 = 15.05\%$

53. Glauber's salt is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

Molecular weight of $\text{Na}_2\text{SO}_4 = 142$

Molecular weight of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 322$

Weight of Glauber's salt taken = 8.0575×10^{-2} kg = 80.575 g

Weight of anhydrous Na_2SO_4 in 322 g of Glauber's salt

$$= \frac{142}{322} \text{ g}$$

\therefore Weight of anhydrous Na_2SO_4 in 80.575 g of Glauber's salt

$$= \frac{142}{322} \times 80.575 = 35.53 \text{ g}$$

Hence number of moles of Na_2SO_4 per dm^3 of solution

$$= \frac{35.53}{142} = 0.25$$

So, the molarity of solution is 0.25 M

Density of solution = 1077.2 kg m^{-3}

$$= \frac{1077.2 \times 10^3}{10^6} \text{ g cm}^{-3} = 1.0772 \text{ g cm}^{-3}$$

Weight of solution = volume \times density

$$= 1000 \times 1.0772 \text{ g} = 1077.2 \text{ g}$$

Weight of water = $(1077.2 - 35.53) = 1041.67$ g

Molality of solution = $\frac{0.25}{1041.67} \times 1000 = 0.24$ m

Basic Concepts of Chemistry

13

$$\text{Number of moles of water in solution} = \frac{1041.67}{18} = 57.87$$

$$\text{Mole fraction of Na}_2\text{SO}_4 = \frac{\text{Moles of Na}_2\text{SO}_4}{\text{Total number of moles}} = \frac{0.25}{0.25 + 57.87} = 0.0043 \text{ or } 4.3 \times 10^{-3}$$

54. For $\text{Fe}_3\text{O}_4 \longrightarrow 3\text{FeO}$ 

Thus we find that valence factor for Fe_3O_4 is 2 and for FeO is 2/3.

For $\text{Fe}_2\text{O}_3 \longrightarrow 2\text{FeO}$ 

The valence factor for Fe_2O_3 is 2 and for FeO is 1.

Suppose the meq. of Fe_3O_4 and FeO in the mixture are a and b respectively.

Then, meq of Fe_3O_4 + meq of FeO = meq of I_2 liberated
= meq. of hypo used

$$\text{or } a + b = \frac{11 \times 0.5 \times 100}{20} = 27.5 \quad \dots(\text{iii})$$

Now, the Fe^{2+} ions again get oxidised to Fe^{3+} on reaction with KMnO_4 . The change can be represented as under



In this case the valence factor for Fe^{2+} is 1.

Thus, meq of Fe^{2+} (from Fe_3O_4) + meq. of Fe^{2+} (from FeO)
= meq of KMnO_4 used

If the valence factor for Fe^{2+} is 2/3 from equation (i), then meq. of Fe^{2+} (from Fe_3O_4) = a

If the valence factor for Fe^{2+} is 1 then meq. of Fe^{2+} (from Fe_3O_4) = $3a/2$

Similarly from equation (ii) meq of Fe^{2+} (from Fe_2O_3) = b

$$\therefore \frac{3a}{2} + b = 0.25 \times 5 \times 12.8 \times \frac{100}{50} = 32 \text{ or } 3a + 2b = 64 \dots(\text{iv})$$

From (iii) and (iv)

$$\text{meq. of Fe}_3\text{O}_4 = a = 9 \text{ and meq. of Fe}_2\text{O}_3 = b = 18.5$$

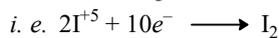
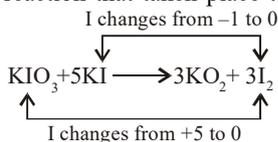
$$\text{Hence weight of Fe}_3\text{O}_4 = \frac{9 \times 232}{2 \times 1000} = 1.044 \text{ g}$$

$$\text{and weight of Fe}_2\text{O}_3 = \frac{18.5 \times 160}{2 \times 1000} = 1.48 \text{ g}$$

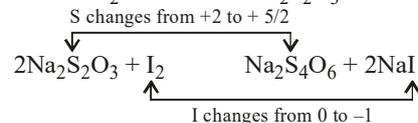
$$\therefore \% \text{ of Fe}_3\text{O}_4 = \frac{1.044 \times 100}{3} = 34.8\%$$

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

$$\% \text{ of impure substance} = 100 - (34.8 + 49.33) = 100 - 84.13 = 15.87\%$$

55. The reaction that taken place to liberate I_2 is

The liberated I_2 reacts with $\text{Na}_2\text{S}_2\text{O}_3$ as follows:



The millimole ratio of $\text{I}_2 : \text{Na}_2\text{S}_2\text{O}_3 = 1:2$

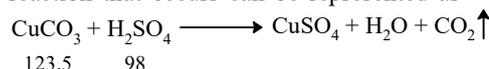
$$\therefore \text{millimoles of I}_2 \text{ liberated} = \frac{\text{millimoles of Na}_2\text{S}_2\text{O}_3 \text{ used}}{2} = \frac{45}{2} \times M \text{ (Where } M \text{ is the molarity of S}_2\text{O}_3^{2-}\text{)}$$

$$\text{Also moles of KIO}_3 = \frac{0.1}{214} \times 1000$$

Now millimole ratio of $\text{KIO}_3 : \text{I}_2 = 1 : 3$

$$\text{Thus } \frac{\frac{0.1}{214} \times 1000}{45M} = \frac{1}{3} \quad \therefore M = \frac{0.1 \times 1000 \times 3 \times 2}{214 \times 45} = 0.062$$

56. The reaction that occurs can be represented as



From the above equation we find, that

123.5 g of CuCO_3 requires $\text{H}_2\text{SO}_4 = 98$ g

$$\therefore 0.5 \text{ g CuCO}_3 \text{ will require H}_2\text{SO}_4 = \frac{98}{123.5} \times 0.5 = 0.39676 \text{ g}$$

To find the volume of H_2SO_4 solution required, use the relation

$$\text{Molarity} = \frac{\text{Weight of solute (H}_2\text{SO}_4)}{\text{Mol. wt. of solute (H}_2\text{SO}_4)} \times \frac{1000}{\text{Volume of solution}}$$

$$\therefore 0.5 = \frac{0.39676 \times 1000}{98 \times V}$$

$$\text{Or } V = \frac{0.39676 \times 1000}{98 \times 0.5} = 8.097 \text{ ml}$$

57. Since the virus is cylinder so the volume of virus = $\pi r^2 \cdot l$

$$= \frac{22}{7} \times \left(\frac{150}{2}\right)^2 \times 10^{-16} \times 5000 \times 10^{-8} = 0.884 \times 10^{-16} \text{ cm}^3$$

$$\therefore \text{Weight of one virus} = \frac{0.884 \times 10^{-16}}{0.75} \text{ g} = 1.178 \times 10^{-16}$$

$$\begin{aligned} \text{Hence gram molecular weight of virus} &= \text{Weight of one virus} \\ &\times \text{weight of } 6.023 \times 10^{23} \text{ virus} \\ &= 1.178 \times 10^{-16} \times 6.023 \times 10^{23} \text{ g} \\ &= 7.09 \times 10^7 \text{ g} \end{aligned}$$

$$\therefore \text{Molecular weight of virus} = 7.09 \times 10^7 \text{ g}$$

58. Let the molarity of KMnO_4 be M_1 . Moles of KMnO_4 in 20 ml

$$= \frac{20 \times M_1}{1000}$$

n -factor of KMnO_4 when it reacts with MnSO_4 is 3



$$\therefore \text{Equivalent of KMnO}_4 \text{ reacting with MnSO}_4 = \frac{20 \times M_1}{1000} \times 3$$

$$\therefore \text{Equivalent of MnSO}_4 \text{ reacting with KMnO}_4 = \frac{20 \times M_1}{1000} \times 3$$

Since MnSO_4 has n -factor 2, the mole of MnSO_4 reacting

$$= \frac{20 \times M_1}{1000} \times \frac{3}{2}$$

Total mole of MnO_2 produced = mole of KMnO_4 + mole of MnSO_4

$$\text{Equivalent of Na}_2\text{C}_2\text{O}_4 \text{ reacting with MnO}_2 = \frac{10 \times 0.2}{1000} \times 2$$

$$\therefore \text{Equivalent of MnO}_2 = \frac{10 \times 0.2}{1000} \times 2$$

$$\text{Mole of MnO}_2 \text{ reacting with sodium oxalate} = \frac{10 \times 0.2 \times 2}{1000 \times 2}$$

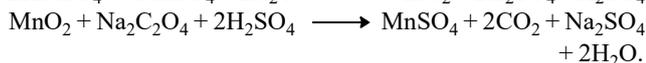
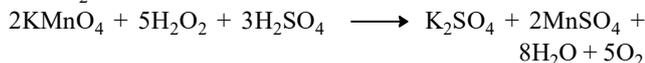
[as n -factor for MnO_2 is 2].

$$\text{Therefore, } \frac{20 \times M_1}{1000} + \left[\frac{20 \times M_1}{1000} \times \frac{3}{2} \right] = \frac{10 \times 0.2}{1000}; M_1 = 0.04$$

$$\text{Equivalent of KMnO}_4 \text{ reacting with H}_2\text{O}_2 = \frac{20 \times 0.04}{1000} \times 5 = 0.004$$

$$\text{If molarity of H}_2\text{O}_2 \text{ is } M_2, \text{ then } = \frac{20 \times M_2 \times 2}{1000} = 0.004$$

$$\therefore M_2 = 0.1 \text{ M}$$



59. 1 litre water = 1 kg

$$\text{Or } 1000 \text{ ml water} = 1 \text{ kg} \quad [\text{Given } d = 1000 \text{ kg/m}^3]$$

$$\therefore \text{Moles of water present in } 1000 \text{ ml} = 1000/18 = 55.55$$

Hence molarity of water = 55.55 M.

60. (b): In presence of methyl orange as indicator the following reaction goes to completion.



61. (b): 500 ml of 4.0 molar NaCl solution contains 2 moles of NaCl. The chlorine content of this sample will be evolved as chlorine gas.

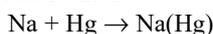
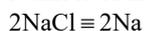
The number of moles of NaCl = Number of moles of Cl⁻

$$= 2 \text{ mole} \left(4 \times \frac{1}{2} \right)$$

\therefore Number of moles of Cl₂ gas evolved

$$= \frac{2}{2} = 1 \text{ mole } (2\text{NaCl} \rightarrow \text{Cl}_2)$$

62. (d): Number of moles of Na⁺ = 2



By electrolysis we can get a maximum of 2 moles of sodium which can combine with exactly 2 moles of mercury to give amalgam.

\therefore Maximum weight of Na amalgam (assuming equimolar Na and Hg) = 46 + 400 = 446 g

63. (d): Na⁺ + e⁻ → Na

Moles of Na⁺ discharged at cathode = 2

\therefore The number of electrons required for this purpose = 2 mole

\therefore Total charge required = 2 faraday

$$= 2 \times 96500 = 193000 \text{ coulomb}$$

64. (3): Average titre value = $\frac{25.2 + 25.25 + 25.0}{3} = 25.15$

According to rounding off rule of significant figures, if the right most digit to be removed is 5, then the preceding number is not changed, if it is even; but increased by one, if it is odd.

\therefore 25.15 can be rounded off to 25.2 and has three significant figures.

65. (7): Given, atomic weight = 108 g mol⁻¹

$$\text{Density} = 10.5 \text{ g cm}^{-3}$$

$$\text{Surface area} = 10^{-12} \text{ m}^2$$

$$\text{Volume of one silver atom} = 4/3\pi r^3$$

$$\therefore \text{Density} = \frac{\text{Mass}}{\text{Volume}} \Rightarrow \text{Volume} = \frac{\text{Mass}}{\text{Density}}$$

$$\text{or } \frac{4}{3}\pi r^3 = \frac{108}{6.023 \times 10^{23} \times 10.5}$$

$$r^3 = \frac{108 \times 3}{6.023 \times 10^{23} \times 10.5 \times 4 \times 3.14}$$

$$r^3 = 0.40 \times 10^{-23} = 4 \times 10^{-24}$$

$$\text{or } r = 1.58 \times 10^{-8} \text{ cm}$$

No. of silver atoms on a surface area of 10⁻¹² m² can be given by 10⁻¹² = πr² × n

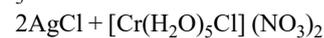
$$n = \frac{10^{-12}}{3.14 \times (1.58 \times 10^{-10})^2} = 0.127 \times 10^8$$

$$\Rightarrow n = 1.27 \times 10^7 \text{ or } x = 7$$

66. (5): 3Br₂ + 3Na₂CO₃ → 5NaBr + NaBrO₃ + 3CO₂

So, number of NaBr molecules = 5

67. (6): [Cr(H₂O)₅Cl]Cl₂ + 2AgNO₃ →



Number of ionisable chloride ions in complex [Cr(H₂O)₅Cl]Cl₂ = 2

Millimoles = Molarity × volume (ml) × 2

$$= 30 \times 0.01 \times 2 = 0.6$$

Therefore, required Ag⁺ = 0.6 millimoles

According to,

$$\text{Millimoles} = \text{Molarity} \times V_{\text{mL}}$$

$$0.6 = 0.1 \times V; V = 6 \text{ ml}$$

68. (8): 29.2% w/w of HCl

Mass of HCl = 29.2 g

Mass of solution = 100 g

$$d = 1.25 \text{ g/ml}, M_{\text{HCl}} = 36.5 \text{ g mol}^{-1}$$

$$\text{Volume of solution} = 100 \text{ g}/1.25 \text{ g ml}^{-1} = 80 \text{ ml}$$

$$\text{Molarity} = \frac{(\text{g} / \text{M.W.})}{\text{Volume of solution}} \times 1000$$

$$\text{Using } M_1V_1 = M_2V_2$$

$$10 \times V_1 = 200 \times 0.4 \Rightarrow V_1 = \frac{200 \times 0.4}{10} = 8 \text{ ml}$$

69. (4): Boltzmann constant, $k = \frac{R}{N_A}$

$$\text{or, } R = k \times N_A$$

$$= 1.380 \times 10^{-23} \times 6.023 \times 10^{23}$$

$$= 8.31174 \text{ J K}^{-1} \text{ mol}^{-1} \gg 8.312$$

Hence, no. of significant figure is 4.

70. (8): Mass of 1 L solvent = 0.4 g ml⁻¹ × 10³ ml

$$= 400 \text{ g} = 0.4 \text{ kg}$$

$$\text{So, molality } (m) = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}} = \frac{3.2}{0.4} = 8 \text{ m}$$



2

Atomic Structure

Multiple Choice Questions with ONE Correct Answer

1. Rutherford's experiment on scattering of α -particles showed for the first time that the atom has
(a) electrons (b) protons
(c) nucleus (d) neutrons. (1981)
2. Any p -orbital can accommodate upto
(a) four electrons
(b) six electrons
(c) two electrons with parallel spins
(d) two electrons with opposite spins. (1983)
3. The principal quantum number of an atom is related to the
(a) size of the orbital
(b) spin angular momentum
(c) orbital angular momentum
(d) orientation of the orbital in space. (1983)
4. Rutherford's scattering experiment is related to the size of the
(a) nucleus (b) atom
(c) electron (d) neutron. (1983)
5. The increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle (α) is
(a) e, p, n, α (b) n, p, e, α
(c) n, p, α, e (d) n, α, p, e (1984)
6. Correct set of four quantum numbers for the valence (outermost) electron of rubidium ($Z = 37$) is
(a) 5, 0, 0, +1/2 (b) 5, 1, 0, +1/2
(c) 5, 1, 1, +1/2 (d) 6, 0, 0, +1/2 (1984)
7. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon?
(a) 3s (b) 2p (c) 2s (d) 1s (1984)
8. Bohr model can explain
(a) the spectrum of hydrogen atom only
(b) spectrum of an atom or ion containing one electron only
(c) the spectrum of hydrogen molecule
(d) the solar spectrum. (1985)
9. The radius of an atomic nucleus is of the order of
(a) 10^{-10} cm (b) 10^{-13} cm (c) 10^{-15} cm (d) 10^{-8} cm (1985)
10. Electromagnetic radiation with maximum wavelength is
(a) ultraviolet (b) radiowave
(c) X-ray (d) infrared (1985)
11. Rutherford's alpha particle scattering experiment eventually led to the conclusion that
(a) mass and energy are related
(b) electrons occupy space around the nucleus
(c) neutrons are buried deep in the nucleus
(d) the point of impact with matter can be precisely determined. (1986)
12. Which one of the following sets of quantum numbers represents an impossible arrangement?
- | n | l | m_l | m_s |
|-------|-----|-------|-------|
| (a) 3 | 2 | -2 | 1/2 |
| (b) 4 | 0 | 0 | 1/2 |
| (c) 3 | 2 | -3 | 1/2 |
| (d) 5 | 3 | 0 | -1/2 |
- (1986)
13. The ratio of the energy of a photon of 2000 Å wavelength radiation to that of 4000 Å radiation is
(a) 1/4 (b) 4 (c) 1/2 (d) 2 (1986)
14. The triad of nuclei that is isotonic is
(a) ${}^{14}_6\text{C}$, ${}^{15}_7\text{N}$, ${}^{17}_9\text{F}$ (b) ${}^{12}_6\text{C}$, ${}^{14}_7\text{N}$, ${}^{19}_9\text{F}$
(c) ${}^{14}_6\text{C}$, ${}^{14}_7\text{N}$, ${}^{17}_9\text{F}$ (d) ${}^{14}_6\text{C}$, ${}^{14}_7\text{N}$, ${}^{19}_9\text{F}$ (1988)

15. The wavelength of a spectral line for an electronic transition is inversely related to
 (a) the number of electrons undergoing the transition
 (b) the nuclear charge of the atom
 (c) the difference in the energy of the energy levels involved in the transition
 (d) the velocity of the electron undergoing the transition. (1988)
16. The orbital diagram in which the Aufbau principle is violated is
- (a) $\begin{array}{cc} 2s & 2p \\ \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} \boxed{1} \boxed{} \end{array}$ (b) $\begin{array}{cc} 2s & 2p \\ \boxed{\uparrow} & \boxed{\uparrow\downarrow} \boxed{1} \boxed{1} \end{array}$
 (c) $\begin{array}{cc} 2s & 2p \\ \boxed{\uparrow\downarrow} & \boxed{1} \boxed{1} \boxed{1} \end{array}$ (d) $\begin{array}{cc} 2s & 2p \\ \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} \boxed{1} \boxed{1} \end{array}$ (1988)
17. The outermost electronic configuration of the most electronegative element is
 (a) ns^2np^3 (b) ns^2np^4 (c) ns^2np^5 (d) ns^2np^6 (1988)
18. The correct ground state electronic configuration of chromium atom is
 (a) $[\text{Ar}] 3d^5 4s^1$ (b) $[\text{Ar}] 3d^4 4s^2$
 (c) $[\text{Ar}] 3d^6 4s^0$ (d) $[\text{Ar}] 4d^5 4s^1$ (1989)
19. The correct set of quantum numbers for the unpaired electron of chlorine atom is
- | | | | | | |
|-------|-----|-----|-------|-----|-----|
| n | l | m | n | l | m |
| (a) 2 | 1 | 0 | (b) 2 | 1 | 1 |
| (c) 3 | 1 | 1 | (d) 3 | 0 | 0 |
- (1989)
20. Which of the following does not characterise X-rays?
 (a) The radiation can ionise gases.
 (b) It causes ZnS to fluoresce.
 (c) Deflected by electric and magnetic field.
 (d) Have wavelengths shorter than ultraviolet rays. (1992)
21. Which of the following relates to photons both as wave motion and as a stream of particles?
 (a) Inference (b) $E = mc^2$
 (c) Diffraction (d) $E = h\nu$ (1995)
22. A $3p$ -orbital has
 (a) two non-spherical nodes
 (b) two spherical nodes
 (c) one spherical and one non-spherical node
 (d) one spherical and two non-spherical nodes (1995)
23. The orbital angular momentum of an electron in $2s$ -orbital is
 (a) $+\frac{1}{2} \cdot \frac{h}{2\pi}$ (b) zero (c) $\frac{h}{2\pi}$ (d) $\sqrt{2} \cdot \frac{h}{2\pi}$ (1996)
24. The first use of quantum theory to explain the structure of atom was made by
 (a) Heisenberg (b) Bohr
 (c) Planck (d) Einstein (1997)
25. For a d -electron, the orbital angular momentum is
 (a) $\sqrt{6}(h/2\pi)$ (b) $\sqrt{2}(h/2\pi)$
 (c) $(h/2\pi)$ (d) $\sqrt{2}(h/2\pi)$ (1997)
26. The electrons, identified by quantum numbers n and l , (i) $n = 4, l = 1$, (ii) $n = 4, l = 0$, (iii) $n = 3, l = 2$, and (iv) $n = 3, l = 1$ can be placed in order of increasing energy, from the lowest to highest, as
 (a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)
 (c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii) (1999)
27. The number of nodal planes in a p_x -orbital is
 (a) one (b) two (c) three (d) zero (2000)
28. The electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. This represents its
 (a) excited state (b) ground state
 (c) cationic form (d) anionic form. (2000)
29. The wavelength associated with a golf ball weighing 200 g and moving at speed of 5 m/h is of the order
 (a) 10^{-10} m (b) 10^{-20} m (c) 10^{-30} m (d) 10^{-40} m (2001)
30. The quantum numbers $+1/2$ and $-1/2$ for the electron spin represent
 (a) rotation of the electron in clockwise and anticlockwise direction respectively
 (b) rotation of the electron in anticlockwise and clockwise direction respectively
 (c) magnetic moment of the electron pointing up and down respectively
 (d) two quantum mechanical spin states which have no classical analogue. (2001)
31. Rutherford's experiment, which established the nuclear model of the atom, used a beam of
 (a) β -particles, which impinged on a metal foil and got absorbed

Atomic Structure

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- (b) γ -rays, which impinged on a metal foil and ejected electrons
 (c) helium atoms, which impinged on a metal foil and got scattered
 (d) helium nuclei, which impinged on a metal foil and got scattered. (2002)
32. If the nitrogen atom has electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$, because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates
 (a) Heisenberg uncertainty principle
 (b) Hund's rule
 (c) Pauli exclusion principle
 (d) Bohr postulate of stationary orbits. (2002)
33. The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom?
 (a) He^+ ($n = 2$) (b) Li^{2+} ($n = 2$)
 (c) Li^{2+} ($n = 3$) (d) Be^{3+} ($n = 2$) (2004)
34. The number of radial nodes of $3s$ - and $2p$ -orbitals are respectively
 (a) 2, 0 (b) 0, 2 (c) 1, 2 (d) 2, 1 (2005)
35. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom [a_0 is Bohr radius]
 (a) $\frac{h^2}{4\pi^2 m a_0^2}$ (b) $\frac{h^2}{16\pi^2 m a_0^2}$
 (c) $\frac{h^2}{32\pi^2 m a_0^2}$ (d) $\frac{h^2}{64\pi^2 m a_0^2}$ (2012)
- Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer**
36. An isotone of $^{76}_{32}\text{Ge}$ is
 (a) $^{77}_{32}\text{Ge}$ (b) $^{77}_{33}\text{As}$ (c) $^{77}_{34}\text{Se}$ (d) $^{78}_{34}\text{Se}$ (1984)
37. Many elements have non-integral atomic masses because
 (a) they have isotopes
 (b) their isotopes have non-integral masses
 (c) their isotopes have different masses
 (d) the constituents, neutrons, protons and electrons, combine to give fractional masses. (1984)
38. When alpha particles are sent through a thin metal foil, most of them go straight through the foil because
 (a) alpha particles are much heavier than electrons
 (b) alpha particles are positively charged
 (c) most part of the atom is empty space
 (d) alpha particles move with high velocity (1984)
39. The sum of the number of neutrons and protons in the isotope of hydrogen is
 (a) 6 (b) 2 (c) 4 (d) 3 (1986)
40. The energy of an electron in the first Bohr orbit of H atom is -13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are)
 (a) -3.4 eV (b) -4.2 eV
 (c) -6.8 eV (d) -1.5 eV (1998)
41. Which of the following statement(s) is(are) correct?
 (a) The electronic configuration of Cr is $[\text{Ar}]3d^5 4s^1$. (Atomic number of Cr = 24)
 (b) The magnetic quantum number may have a negative value.
 (c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic number of Ag = 47)
 (d) The oxidation state of nitrogen in HN_3 is -3 . (1998)
42. Decrease in atomic number is observed during
 (a) alpha emission (b) beta emission
 (c) positron emission (d) electron capture (1998)
43. Ground state electronic configuration of nitrogen atom can be represented by
 (a) $\uparrow\downarrow\uparrow\downarrow$ $\uparrow\uparrow\uparrow$ (b) $\uparrow\downarrow\uparrow\downarrow$ $\uparrow\downarrow\uparrow$
 (c) $\uparrow\downarrow\uparrow\downarrow$ $\uparrow\downarrow\downarrow$ (d) $\uparrow\downarrow\uparrow\downarrow$ $\downarrow\downarrow\downarrow$ (1999)
- Fill in the Blanks**
44. The mass of a hydrogen atom is kg. (1982)
45. Isotopes of an element differ in the number of in their nuclei. (1982)
46. When there are two electrons in the same orbital, they have spins. (1982)

47. Elements of the same mass number but of different atomic numbers are known as (1983)
48. The uncertainty principle and the concept of wave nature of matter were proposed by and respectively. (1988)
49. The light radiations with discrete quantities of energy are called (1993)
50. Wave functions of electrons in atoms and molecules are called (1993)
51. The $2p_x$, $2p_y$ and $2p_z$ orbitals of atom have identical shapes but differ in their (1993)
52. The outermost electronic configuration of Cr is (1994)

True / False

53. The outer electronic configuration of the ground state chromium atom is $3d^4 4s^2$. (1982)
54. Gamma rays are electromagnetic radiations of wavelengths of 10^{-6} cm to 10^{-5} cm. (1983)
55. The energy of the electron in the $3d$ orbital is less than that in the $4s$ orbital in the hydrogen atom. (1983)
56. The electron density in the xy plane in $3d_{x^2-y^2}$ orbital is zero. (1986)
57. In a given electric field, β particles are deflected more than α particles in spite of α particles having larger charge. (1993)

Subjective Problems

58. Naturally occurring boron consists of two isotopes whose atomic weights are 10.01 and 11.01. The atomic weight of natural boron is 10.81. Calculate the percentage of each isotope in natural boron. (1978)
59. The energy of the electron in the second and the third Bohr's orbits of the hydrogen atom is -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from the third to the second orbit. (1981)
60. Calculate the wavelength in Angstroms of the photon that is emitted when an electron in the Bohr orbit, $n = 2$ returns to the orbit, $n = 1$ in the hydrogen atom. The

ionization potential of the ground state hydrogen atom is 2.17×10^{-11} erg per atom. (1982)

61. The electron energy in hydrogen atom is given by $E = (-21.7 \times 10^{-12})/n^2$ erg. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition? (1984)
62. Give reasons why the ground state outermost electronic configuration of silicon is
 $3s \quad 3p \quad 3s \quad 3p$
 $\boxed{\uparrow\downarrow} \quad \boxed{\uparrow} \quad \boxed{\uparrow} \quad \boxed{}$ and not $\boxed{\uparrow\downarrow} \quad \boxed{\uparrow} \quad \boxed{\downarrow} \quad \boxed{}$ (1985)
63. What is the maximum number of electrons that may be present in all the atomic orbitals with principal quantum number 3 and azimuthal quantum number 2? (1985)
64. According to Bohr's theory, the electronic energy of hydrogen atom in the n^{th} Bohr's orbit is given by $E_n = \frac{-21.76 \times 10^{-19}}{n^2}$ J. Calculate the longest wavelength of light that will be needed to remove an electron from the third Bohr orbit of the He^+ ion. (1990)
65. Estimate the difference in energy between 1st and 2nd Bohr orbit for a hydrogen atom. At what minimum atomic number, a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8}$ m? Which hydrogen atom-like species does this atomic number correspond to? (1993)
66. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum? (1993)
67. Find out the number of waves made by a Bohr electron in one complete revolution in its 3rd orbit. (1994)
68. Iodine molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (Bond energy of $\text{I}_2 = 240 \text{ kJ mol}^{-1}$) (1995)
69. A bulb emits light of wavelength = 4500 Å. The bulb is rated as 150 watt and 8% of this energy is emitted as light. How many photons are emitted by the bulb per second? (1995)

Atomic Structure

19

70. Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. (1996)

71. Consider the hydrogen atom to be a proton embedded in a cavity of radius a_0 (Bohr radius) whose charge is neutralised by the addition of an electron to the cavity in vacuum, infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralisation process. Also, if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average total energy. (1996)

72. With what velocity should an α -particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{-13} metre from the nucleus of the copper atom? (1997)

73. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 \AA . (1997)

74. Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H-H bond is 436 kJ mol^{-1} . (2000)

75. Wavelength of high energy transition of H-atoms is 91.2 nm. Calculate the corresponding wavelength of He atoms. (2003)

76. The Schrodinger wave equation for hydrogen atom is

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r_0}{a_0}\right) e^{-r_0/a_0}$$

Where a_0 is Bohr's radius. If the radial node in $2s$ be at r_0 , then find r_0 in terms of a_0 . (2004)

77. A ball of mass 100 g is moving with 100 m s^{-1} . Find its wavelength. (2004)

78. Find the velocity (ms^{-1}) of electron in first Bohr's orbit of radius a_0 . Also find the de-Broglie's wavelength (in m). Find the orbital angular momentum of $2p$ orbital of hydrogen atom in units of $h/2\pi$. (2005)

Matrix Match Type

79. According to Bohr's theory E_n = total energy, K_n = kinetic energy, V_n = potential energy, r_n = radius of n^{th} orbit

Column I

- A. $V_n/K_n = ?$
 B. If radius of n^{th} orbit μE_n^x , $x = ?$
 C. Angular momentum in lowest orbital
 D. $\frac{1}{r^n} \propto Z^y$, $y = ?$

Column II

- P. 0
 Q. -1
 R. -2
 S. 1

(2006)

80. Match the entries in Column I with the correctly related quantum number(s) in Column II.

Column I

- A. Orbital angular momentum of the electron in a hydrogen like atomic orbital
 B. A hydrogen like one-electron wave function obeying Pauli's principle
 C. Shape, size and orientation of hydrogen-like atomic orbitals
 D. Probability density of electron at the nucleus in hydrogen-like atom

Column II

- P. Principal quantum number
 Q. Azimuthal quantum number
 R. Magnetic quantum number
 S. Electron spin quantum number

(2008)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement -2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

81. **Statement-1** : Nuclide ${}_{13}^{30}\text{Al}$ is less stable than ${}_{20}^{40}\text{Ca}$.

Statement-2 : Nuclides having odd number of protons and neutrons are generally unstable. (1998)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension -1

The hydrogen-like species Li^{2+} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light the ion undergoes transition to a state S_2 . The state S_2 has one radial node and its energy is equal to the ground state energy of the hydrogen atom.

82. The state S_1 is
 (a) $1s$ (b) $2s$
 (c) $2p$ (d) $3s$
83. Energy of the state S_1 in units of the hydrogen atom ground state energy is
 (a) 0.75 (b) 1.50
 (c) 2.25 (d) 4.50
84. The orbital angular momentum quantum number of the state S_2 is
 (a) 0 (b) 1
 (c) 2 (d) 3 (2010)

Integer Answer Type

85. The maximum number of electrons that can have principal quantum number, $n = 3$, and spin quantum number, $m_s = -\frac{1}{2}$, is (2011)

86. The work function(ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is

	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
ϕ (eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

(2011)

87. The atomic masses of He and Ne are 4 and 20 a.m.u., respectively. The value of the de Broglie wavelength of He gas at -73°C is M times that of the de Broglie wavelength of Ne at 727°C . M is (2013)

88. In an atom, the total number of electrons having quantum numbers, $n = 4$, $|m_l| = 1$ and $m_s = -1/2$ is (2014)

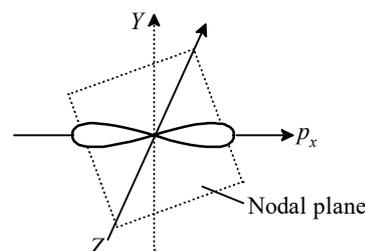
89. Not considering the electronic spin, the degeneracy of the second excited state ($n = 3$) of H atom is 9, while the degeneracy of the second excited state of H^- is (2015)

ANSWER KEY

1. (c) 2. (d) 3. (a) 4. (a) 5. (d) 6. (a)
 7. (d) 8. (b) 9. (b) 10. (b) 11. (b) 12. (c)
 13. (d) 14. (a) 15. (c) 16. (b) 17. (c) 18. (a)
 19. (c) 20. (c) 21. (d) 22. (c) 23. (b) 24. (b)
 25. (a) 26. (a) 27. (a) 28. (b) 29. (c) 30. (c)
 31. (d) 32. (c) 33. (d) 34. (a) 35. (c) 36. (b, d)
 37. (a, c) 38. (c) 39. (b, d) 40. (a, d) 41. (a, b, c) 42. (a, c, d)
 43. (a, d) 44. 1.66×10^{-27} 45. Neutrons 46. Opposite 47. Isobars
 48. Heisenberg, de-Broglie 49. Photons 50. Orbitals 51. Orientation in space
 52. $3d^5 4s^1$ 53. False 54. False 55. True 56. False 57. True
 58. 20, 80 59. 6604 Å 60. 1220 Å 61. $3.67 \times 10^{-5} \text{ cm}$ 62. Hund's rule 63. 10
 64. 2055 Å 65. He^+
 66. Transition from n_2 to n_1 in case of hydrogen atom will have the same wavelength as transition from n_4 to n_2 in case of He^+ species.
 67. 3 68. $2.165 \times 10^{-20} \text{ J}$ 69. 2.72×10^{19} 70. 27419.5 cm^{-1}
 71. (i) $\frac{-e^2}{4\pi\epsilon_0 \cdot a_0}$ (ii) $\frac{-e^2}{8\pi\epsilon_0 \cdot a_0}$ 72. $6.3 \times 10^6 \text{ m s}^{-1}$ 73. 63.3 volt
 74. 98.17 kJ 75. 22.8 nm 76. $r_0 = 2a_0$ 77. $6.626 \times 10^{-35} \text{ m}$
 78. (i) $2.18 \times 10^6 \text{ ms}^{-1}$ (ii) 3.3 \AA (iii) $\sqrt{2} \cdot \frac{h}{2\pi}$ 79. (A \rightarrow R), (B \rightarrow Q), (C \rightarrow P), (D \rightarrow S)
 80. (A \rightarrow Q), (B \rightarrow P, Q, R, S), (C \rightarrow P, Q, R), (D \rightarrow P, Q, R) 81. (c) 82. (b)
 83. (c) 84. (b) 85. (9) 86. (4) 87. (5) 88. (6)
 89. (3)

Explanations

- (c): Rutherford's scattering experiment showed for the first time that the atom has nucleus.
- (d): Any orbital can accommodate a maximum of two electrons and these two must have opposite spins (Pauli's exclusion principle).
- (a): The principal quantum number (n) of an atom is related to the size and energy of the orbital.
- (a): Rutherford's experiment was related to the size of the nucleus.
- (d): e/m for $n = 0/1 = 0$; for α -particle $= 2/4 = 0.5$; for proton $= 1/1 = 1$ and for electron $= \frac{1}{1/1837} = 1837$.
- (a): The electronic configuration of rubidium ($Z = 37$) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$, so the outermost electron is $5s^1$ and for it the values are $n = 5$, $l = 0$, $m = 0$ and $s = +1/2$ or $-1/2$.
- (d): $1s$ level is the lowest energy level. An electron in this level can absorb a photon to go to a higher energy level.
- (b): Bohr's model could successfully explain the spectrum of an atom or ion containing one electron only.
- (b): Radius of nuclei is of the order of 1.5 fermi to 6.5 fermi (1 fermi $= 10^{-13}$ cm).
- (b): In electromagnetic spectrum the radiation with maximum wavelength is radiowave. The decreasing order of wavelengths of various electromagnetic spectrum is radiowave $>$ microwave $>$ infrared wave $>$ visible wave $>$ ultraviolet wave $>$ X-rays.
- (b): From Rutherford's alpha particle scattering experiment it was concluded that electrons occupy space around the nucleus. This space is called extra nuclear space.
- (c): For $l = 2$, the possible values of m are $-2, -1, 0, +1$ and $+2$. Thus for $l = 2$, the value $m = -3$ is not possible.
- (d): $E = \frac{hc}{\lambda}$; $E_1 = \frac{hc}{2000}$; $E_2 = \frac{hc}{4000}$
 $\therefore \frac{E_1}{E_2} = \frac{hc}{2000} \times \frac{4000}{hc} = 2$
- (a): The atoms having same number of neutrons are called isotones. ${}^{14}_6\text{C}$, ${}^{15}_7\text{N}$ and ${}^{17}_9\text{F}$ have same number of neutrons. All of them have 8 neutrons ($A - Z = 8$).
- (c): The wavelength of a spectral line for an electronic transition is inversely related to the difference in the energy of the energy levels involved in the transition.
- (b): In it the electron has been assigned to $2p$ orbital which has higher energy when the $2s$ orbital of lower energy is still not completely filled. The increasing order of energy is $1s < 2s < 2p_x = 2p_y = 2p_z < 3s$
- (c): The outermost electronic configuration $2s^2 2p^5$ ($ns^2 np^5$) represents the element F which is most electronegative. Its electronegativity value is 4.
- (a): Half-filled $3d$ orbital (i.e. $3d^5 4s^1$) has lower energy (i.e. more stable) than $3d^4 4s^2$. The ground state electronic configuration of chromium ($Z = 24$) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$.
- (c): The electronic configuration of chlorine ($Z = 17$) is $1s^2 2s^2 2p^6 3s^2 3p^5$ i.e. $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$, from this we find that the quantum numbers of unpaired electron are $n = 3$, $l = 1$, $m = 1$.
- (c): X-rays are not deflected by electric and magnetic fields.
- (d): $E = h\nu$, here $h\nu$ represents packet of energy and ν represents the wave frequency.
- (c): Total number of nodes $= (n - 1)$
 For $3p$ -orbital, total nodes $= 3 - 1 = 2$
 Number of radial nodes $= n - l - 1$
 For $3p$ -orbital, radial nodes $= 3 - 1 - 1 = 1$
 Number of angular nodes $= l$
 For $3p$ -orbital number of angular nodes $= 1$
 [For $3p$ -orbital, $n = 3$, $l = 1$].
- (b): The angular momentum, $L = \sqrt{l(l+1)} \cdot \frac{h}{2\pi}$.
 For $2s$ -orbital, $l = 0$
 \therefore Angular momentum $L = 0 \times \frac{h}{2\pi} = 0$
- (b): Bohr's theory was based on some postulates of quantum theory.
- (a): The angular momentum, $L = \sqrt{l(l+1)} \cdot \frac{h}{2\pi}$.
 For d -orbital, $l = 2$.
 $\therefore L = \sqrt{2(2+1)} \cdot \frac{h}{2\pi} = \sqrt{6} \cdot \frac{h}{2\pi}$
- (a): In (i) $n + l = 5$, in (ii) $n + l = 4$, In (iii) $n + l = 5$, in (iv) $n + l = 4$.
 For orbital having same value of $(n + l)$ the one having lower value of n has lesser energy. Thus the increasing order is (iv) $<$ (ii) $<$ (iii) $<$ (i).
- (a): p_x -orbital is dumb-bell shaped consisting of two portions known as lobes. This is a plane in which the electron density is almost nil. This is known as nodal plane.



For $2p_x$ orbital, nodal plane is yz .

Similarly for $2p_y$ and $2p_z$ orbitals, the nodal planes are zx and xy respectively.

28. (b): Since $3d^54s^1$ system has lower energy (because of half-filled d orbitals) as compared to $3d^44s^2$, so $3d^54s^1$ represents the ground state of the atom.

29. (c): $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \times 3600}{200 \times 10^{-3} \times 5} = 2.38 \times 10^{-30} \text{ m.}$

30. (c): The spin angular momentum has a magnitude

$$S = [s(s+1)]^{\frac{1}{2}} h = \left(\frac{\sqrt{3}}{2}\right) h \text{ since } s = \frac{1}{2}$$

The component of S in the direction of magnetic field B can be specified by m_s , where $m_s = +\frac{1}{2}$ component has upward orientation (\uparrow) and $m_s = -\frac{1}{2}$ component has downward orientation (\downarrow). Here spinning electrons behave like tiny bar magnet.

31. (d): In Rutherford's experiment α -particles are used. α -particles are doubly positively charged helium ions *i.e.* helium nucleus.

32. (c): Pauli's exclusion principle states, "No two electrons in an atom can have all the four quantum numbers same". If they have same values for n, l, m then they must have different s values, so no orbital can accommodate more than 2 electrons.

33. (d): For an atom, $r_n = \frac{0.529 n^2}{Z} \text{ \AA}$

For hydrogen atom, $r_n = 0.529 \text{ \AA}$ ($n = 1, Z = 1$)

For Be^{3+} ($n = 2, Z = 4$), $r_n = \frac{0.529 \times 2^2}{4} \text{ \AA} = 0.529 \text{ \AA}$

So the value is same in two cases.

34. (a): Number of radial nodes = $(n - l - 1)$

For $3s$, number of radial nodes = $3 - 0 - 1 = 2$

For $2p$, number of radial nodes = $2 - 1 - 1 = 0$

35. (c): For Bohr orbit, angular momentum is

$$mvr_n = \frac{nh}{2\pi}; \quad v = \frac{nh}{2\pi mr_n} \quad \dots (i)$$

$$\text{Kinetic energy, } K.E. = \frac{1}{2}mv^2 \quad \dots (ii)$$

By putting the value of v from (i) to (ii),

$$K.E. = \frac{1}{2}m \times \frac{n^2 h^2}{4\pi^2 m^2 r_n^2} = \frac{n^2 h^2}{8\pi^2 m r_n^2}$$

For second Bohr orbit, $n = 2$

$$r_n = a_0 \times n^2 \quad (a_0 = \text{Bohr radius})$$

$$r_n = 4a_0$$

$$K.E. = \frac{(2)^2 h^2}{8\pi^2 m (4a_0)^2} \quad \text{Thus, } K.E. = \frac{h^2}{32\pi^2 m a_0^2}$$

36. (b,d): Isotones have the same number of neutrons.

Here ${}^{77}_{33}\text{As}$ and ${}^{78}_{34}\text{Se}$ have the same number of neutrons as in ${}^{76}_{32}\text{Ge}$ (*i.e.* 44 neutrons).

37. (a,c): Isotopes have same atomic number but different mass numbers. The average atomic mass is the weighed mean of their occurrence in nature. Cl^{35} and Cl^{37} occur in nature in the ratio of 3:1 so the average atomic mass of Cl is A given by

$$A = \frac{35 \times 3 + 37 \times 1}{4} = 35.5$$

38. (c): Since most part of the atoms is empty so α -particles pass through it undeflected.

39. (b,d): In tritium (an isotope of hydrogen with mass number 3 and atomic number 1). There are 2 neutrons and 1 proton *i.e.* sum = $2 + 1 = 3$. In deuterium ${}^2_1\text{D}$, $n + p = 2$. In ordinary hydrogen ${}^1_1\text{H}$, $n + p = 1$

40. (a,d): Energy in an orbit of hydrogen atom, E_n is given by

$$E_n = -\frac{2\pi^2 m e^4 Z^2}{n^2 h^2} = -\frac{\text{Constant} \times Z^2}{n^2} = -\frac{13.6 \times Z^2 \text{ eV}}{n^2}$$

$$\text{For 1st orbit, } n = 1 \text{ and } Z = 1, \text{ Hence } E_n = -\frac{13.6 \text{ eV}}{1}$$

The possible values of energies are $-13.6, -3.4, -1.5 \text{ eV} \dots$ etc. for $n = 1, 2, 3, \dots$, etc.

41. (a,b,c): (a) is the correct electronic configuration of $\text{Cr}(Z = 24)$, $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$.

(b) is correct because magnetic quantum number (m) can have values from $-l \dots 0 \dots +l$ *i.e.* it can have negative values.

(c) is correct because the electronic configuration of Ag ($Z = 47$) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^1$. From here we find 23 electrons have spin of one type and 24 electrons have spin of opposite type.

(d) is not correct because oxidation number of N in HN_3 is $-1/3$.

42. (a, c, d): ${}_Z X^A \xrightarrow{-\alpha} {}_{Z-2} Y^{A-4} + {}_2\text{He}^4$ (α -emission)

$${}_Z X^A \xrightarrow{-\beta} {}_{Z+1} Y^A + {}_{-1} e^0 \quad (\beta\text{-emission})$$

$${}_Z X^A \longrightarrow {}_{Z-1} Y^A + {}_{+1} e^0 \quad (\text{positron emission})$$

$${}_Z X^A + {}_{-1} e^0 \longrightarrow {}_{Z-1} Y^A \quad (\text{electron capture})$$

In α -emission, atomic number decreases from Z to $(Z - 2)$ *i.e.* by two units.

In β -emission, atomic number increases from Z to $(Z + 1)$ *i.e.* by one unit.

In positron emission, atomic number decreases from Z to $(Z - 1)$ *i.e.* by one unit.

In electron capture, atomic number decreases from Z to $(Z - 1)$ *i.e.* by one unit.

43. (a, d): Only these configurations follow Hund's rule.

In (b) and (c), the spin of unpaired electrons is not same and so they are not correct configurations of nitrogen atom.

44. 1.66×10^{-27} ; Mass of hydrogen atom is $1.66 \times 10^{-27} \text{ kg}$

45. Neutrons; nuclei consist of protons and neutrons. Isotopes have same number of protons.

46. Opposite; Pauli's exclusion principle

47. Isobars

Atomic Structure

23

48. Heisenberg, de-Broglie
49. Photons
50. Orbitals
51. Orientation in space
52. $3d^5 4s^1$; Cr ($Z = 24$); $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. This is due to the fact that half-filled and fully-filled orbitals are more stable.
53. **False**
The outer configuration of ground state Cr ($Z = 24$) atom is $3d^5 4s^1$.
54. **False**
The wavelength of γ -rays is of the order of 10^{-9} cm to 10^{-10} cm.
55. **True**
In case of hydrogen atom, the energy of $3d$ orbital is less than that of $4s$ orbital.
56. **False**
The orbital $d_{x^2-y^2}$ lies along x -axis and y -axis.
57. **True**
The e/m value of β -particles is quite large compared to that of α -particles. Because of this β -particles are deflected more as compared to α -particles.
58. Let the % of isotope with atomic weight 10.01 = x
 \therefore % of isotope with atomic weight 11.01 = $(100 - x)$
Now since, atomic weight = $\frac{x \times 10.01 + (100 - x) \times 11.01}{100}$
 $10.81 = \frac{x \times 10.01 + (100 - x) \times 11.01}{100}$ or, $x = 20$
Hence % of isotope with atomic weight 10.01 = 20
 \therefore % of isotope with atomic weight 11.01 = $100 - 20 = 80$.
59. Energy of electron in Bohr's second orbit
 $E_2 = -5.42 \times 10^{-12}$ erg
Energy of electrons in Bohr's third orbit
 $E_3 = -2.41 \times 10^{-12}$ erg
 $\therefore E_3 - E_2 = \Delta E = h\nu = \frac{hc}{\lambda}$
or $\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-27} \times 3 \times 10^{10}}{3.01 \times 10^{-12}} = 6.604 \times 10^{-5}$ cm
 $= 6604 \text{ \AA}$
60. $E_1 = 2.17 \times 10^{-11}$ erg; $E_2 = \frac{2.17 \times 10^{-11}}{2^2}$ erg
 $\therefore \Delta E = E_1 - E_2 = (2.17 \times 10^{-11} - \frac{2.17 \times 10^{-11}}{4})$ erg
 $= 2.17 \times 10^{-11} (1 - 1/4)$ erg
 $= 3/4 \times 2.17 \times 10^{-11}$ erg = 1.63×10^{-11} erg.
Since $E_1 - E_2 = \Delta E = \frac{hc}{\lambda}$
 $\therefore \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-27} \times 3.0 \times 10^{10}}{1.63 \times 10^{-11}}$ cm
 $= 1.22 \times 10^{-5}$ cm or 1220 \AA
Thus, the wavelength is 1220 \AA .
61. The energy of the electron in the n^{th} orbit of hydrogen, E_n is given by
 $E_n = -\frac{\text{Constant}}{n^2} = -\frac{21.7 \times 10^{-12}}{n^2}$ ergs

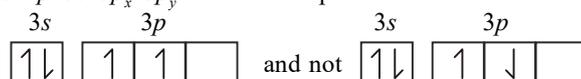
Then the energy difference (ΔE) between the energy of electrons in second Bohr's orbit and at infinity is ΔE .

$$\begin{aligned} \Delta E &= -21.7 \times 10^{-12} \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) \text{erg} \\ &= -21.7 \times 10^{-12} \times \frac{1}{4} \quad \left[\because \frac{1}{\infty^2} = 0 \right] \\ &= -5.42 \times 10^{-12} \text{ erg} \end{aligned}$$

$$\text{Since } \Delta E = h\nu = \frac{hc}{\lambda}$$

$$\text{or } \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-27} \times 3 \times 10^{10}}{5.42 \times 10^{-12}} \text{ cm} = 3.67 \times 10^{-5} \text{ cm}$$

62. Ground state electronic configuration of Si ($Z = 14$) is $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$. It can be represented as



Because in accordance with Hund's rule the unpaired electrons (*i.e.* two electrons in $3p$ orbitals) must have same spin and not opposite spins.

63. In case of $3d$ orbitals the value of $l = 2$ and so various possible values of m are $-2, -1, 0, +1,$ and $+2$ (*i.e.* a total of $2l + 1$ or $2 \times 2 + 1 = 5$ values). For each value of m there are two possible values of s *i.e.* $+1/2$ and $-1/2$.
So the maximum number of electrons in five $3d$ orbitals is $5 \times 2 = 10$.

64. For H atom, $E_n = \frac{-21.76 \times 10^{-19}}{n^2}$ Joule

$$\text{For He}^+ \text{ ion, } E_n = \frac{-21.76 \times 10^{-19}}{n^2} \times Z^2 \text{ J}$$

$$\text{For 3rd orbit of He}^+ \text{ ion, } E_3 = \frac{-21.76 \times 10^{-19}}{9} \times 4$$

[For He, $Z = 2$]

For removal of electron from third orbit of He^+ , an amount of energy equal to E_3 must be supplied. The wavelength corresponding to this energy can be calculated by using the relation $E = \frac{hc}{\lambda}$, we have

$$\begin{aligned} \lambda &= \frac{hc}{E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 9}{21.76 \times 10^{-19} \times 4} \\ &= 2055 \times 10^{-10} \text{ m or } 2055 \text{ \AA} \end{aligned}$$

65. We know $E_n = -\frac{21.76 \times 10^{-19}}{n^2}$ J

$$\therefore E_2 = -\frac{21.76 \times 10^{-19}}{4} \text{ J, and } E_1 = -21.76 \times 10^{-19} \text{ J}$$

$$\begin{aligned} \text{Hence } \Delta E &= E_2 - E_1 = 21.76 \times 10^{-19} (1 - 1/4) \text{ J} \\ &= 21.76 \times 10^{-19} \times 3/4 \text{ J} \end{aligned}$$

$$\Delta E = 16.32 \times 10^{-19} \text{ J}$$

For hydrogen like species, $n_1 = 1, n_2 = 2$

$$E_2 = -\frac{21.76 \times 10^{-19} \times Z^2}{n^2} = -\frac{21.76 \times 10^{-19} \times Z^2}{4} \text{ J}$$

$$E_1 = -\frac{21.76 \times 10^{-19} \times Z^2}{n^2} = -\frac{21.76 \times 10^{-19} \times Z^2}{1} \text{ J}$$

$$\Delta E = E_2 - E_1 = 21.76 \times 10^{-19} \left(1 - \frac{1}{4}\right) Z^2 \text{ J}$$

$$= 21.76 \times 10^{-19} \times \frac{3}{4} \times Z^2 \text{ J} = 16.32 \times 10^{-19} Z^2 \text{ J}$$

Using the relation, $\Delta E = \frac{hc}{\lambda}$, we get

$$16.32 \times 10^{-19} Z^2 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{3.0 \times 10^{-8}}$$

$$\text{or } Z^2 = \frac{6.626 \times 10^{-34} \times 10^{16}}{16.32 \times 10^{-19}}$$

$$\text{or } Z^2 = 4 \quad \text{or } Z = 2$$

Therefore, atomic number of species is 2 *i.e.* it is He^+ .

66. We know that for an atom, $\bar{\nu} = \frac{1}{\lambda} = R_H \cdot Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

$R_H = \text{Rydberg constant} = 109678 \text{ cm}^{-1}$

In case of He^+ ; $Z = 2$, $n_2 = 4$ and $n_1 = 2$

$$\therefore \bar{\nu} = R_H \times 4 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = \frac{3}{4} \times R_H$$

In case of Hydrogen: $Z = 1$

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

$$\text{or } R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{3}{4} \times R_H \quad \text{or } \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

This means $n_1 = 1$ and $n_2 = 2$

Thus the transition from n_2 to n_1 in case of hydrogen atom will have the same wavelength as transition from n_4 to n_2 in case of He^+ species.

67. Generally, the number of waves made by a Bohr electron in an orbit is equal to its quantum number.

The number of waves in any orbit could be given as

$$\text{Number of waves} = \frac{\text{Circumference of orbit}}{\text{Wavelength}} = \frac{2\pi r}{\lambda}$$

But $\lambda = \frac{h}{mv}$ [de-Broglie's relation]

$$\therefore \text{Number of waves} = 2\pi r \left(\frac{mv}{h} \right) = \frac{2\pi(mvr)}{h} \quad \dots \text{(i)}$$

$$\text{Angular momentum in Bohr's third orbit} = \frac{nh}{2\pi}$$

$$\text{for } n = 3; mvr = \frac{3h}{2\pi} \quad \dots \text{(ii)}$$

Substituting the value of mvr from (ii) into (i), we get

$$\text{Number of waves} = \frac{2\pi}{h} \times \frac{3h}{2\pi} = 3$$

Thus number of waves in Bohr's third orbit = 3.

68. Bond energy of iodine = $240 \times 10^3 \text{ J mol}^{-1}$ (given)

$$= \frac{240 \times 10^3}{6.023 \times 10^{23}} \text{ J molecule}^{-1}$$

$$= 3.984 \times 10^{-19} \text{ J molecule}^{-1}$$

$$\text{Energy absorbed} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4500 \times 10^{-10}} \text{ J}$$

$$= 4.417 \times 10^{-19} \text{ J}$$

$$\text{Thus kinetic energy} = 4.417 \times 10^{-19} \text{ J} - 3.984 \times 10^{-19} \text{ J}$$

$$= 4.33 \times 10^{-20} \text{ J}$$

$$\therefore \text{Kinetic energy of each atom} = \frac{4.33 \times 10^{-20}}{2} \text{ J}$$

$$= 2.165 \times 10^{-20} \text{ J}$$

69. According to Planck's theory, $E = \frac{nhc}{\lambda}$

Where n = number of photons.

Energy of bulb,

$$E = \frac{150 \times 8}{100} = 12 \text{ W} = 12 \text{ J s}^{-1} \quad [1 \text{ W} = 1 \text{ J s}^{-1}]$$

$$\lambda = 4500 \text{ \AA} = 4500 \times 10^{-10} \text{ m}$$

$$c = 3 \times 10^8 \text{ m s}^{-1}, \quad h = 6.626 \times 10^{-34} \text{ J s}$$

$$\text{Then } 12 = \frac{n \times (6.626 \times 10^{-34}) \times (3 \times 10^8)}{4500 \times 10^{-10}}$$

$$\text{or } n = \frac{12 \times 4500 \times 10^{-10}}{6.626 \times 10^{-34} \times 3 \times 10^8} = 2.72 \times 10^{19} \text{ s}^{-1}$$

$$\therefore \text{Number of photons emitted per second} = 2.72 \times 10^{19}$$

70. We know, $\bar{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

For the wavelength to be shortest the wave number must

be maximum because $\bar{\nu} = \frac{1}{\lambda}$

For this n_2 must be highest *i.e.* $n_2 = \infty$

Thus we find that shortest wavelength transition in the Balmer series will correspond to the transition from $n \rightarrow 2$ to $n \rightarrow \infty$, Hence

$$\bar{\nu} = 109678 \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) \text{ cm}^{-1} \quad [\because R_H = 109678 \text{ cm}^{-1}]$$

$$= 109678 \times 1/4 = 27419.5 \text{ cm}^{-1}$$

71. Work obtained in neutralisation process is given by:

$$W = - \frac{e^2}{4\pi \epsilon_0 \cdot a_0}$$

This work is called potential energy. According to given problem, this work done is equal to the total energy possessed by the electron in its ground state in an atom of hydrogen. At this stage, the electron is not moving and possesses no kinetic energy therefore the total energy is equal to potential energy.

Total energy = Potential energy + Kinetic energy

$$= \text{Potential energy} + 0 = - \frac{e^2}{4\pi \epsilon_0 \cdot a_0}$$

In order the electron to be captured by the proton to form a ground state hydrogen atom, it should also attain kinetic energy $\frac{e^2}{8\pi \epsilon_0 a_0}$ (as it is half of the potential energy according

to the given question). Thus,

Total energy = Potential energy + Kinetic energy

$$= - \frac{e^2}{4\pi \epsilon_0 \cdot a_0} + \frac{e^2}{8\pi \epsilon_0 a_0} = - \frac{e^2}{8\pi \epsilon_0 a_0}$$

Atomic Structure

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72. Since the α -particle travelling with velocity u comes to a stop at a distance 10^{-13} m, so its *K.E.* becomes zero.

$$\therefore \frac{1}{2} mu^2 = \frac{1}{4\pi\epsilon_0} \times \frac{2Ze^2}{r} \quad \text{or} \quad u^2 = \frac{Ze^2}{\pi\epsilon_0 m.r}$$

For copper atom, $Z = 29$

$$\therefore u^2 = \frac{29 \times (1.6 \times 10^{-19})^2}{3.14 \times 8.85 \times 10^{-12} \times (4 \times 1.672 \times 10^{-27}) \times 10^{-13}}$$

[Here m = mass of α -particle and r = radius of nucleus]

or $u = 6.3 \times 10^6 \text{ m s}^{-1}$

73. For an electron, $\frac{1}{2} mv^2 = eV$ and $\lambda = \frac{h}{mv}$

$$\text{Thus, } \frac{1}{2} \times m \frac{h^2}{m^2 \lambda^2} = eV$$

$$\text{or } V = \frac{1}{2} \times \frac{h^2}{m \lambda^2 \cdot e}$$

$$= \frac{1 \times (6.62 \times 10^{-34})^2}{2 \times 9.108 \times 10^{-31} \times (1.54 \times 10^{-10})^2 \times 1.602 \times 10^{-19}}$$

$$= 63.3 \text{ volt}$$

74. Using gas equation, $PV = nRT$, we have

Number of moles of hydrogen gas, $n = PV/RT$

$$= \frac{1 \times 1}{0.082 \times 298} = 0.0409$$

The reaction can be represented as



Thus, the energy required to convert 0.0409 moles of hydrogen gas into atomic state = $436 \times 0.0409 \text{ kJ} = 17.83 \text{ kJ}$

Number of hydrogen atoms in 0.0409 moles of H_2 :

$$1 \text{ mole of } \text{H}_2 = 6.02 \times 10^{23} \text{ molecules of } \text{H}_2$$

$$= 2 \times 6.02 \times 10^{23} \text{ atoms of } \text{H}_2$$

$$[1 \text{ molecule} = 2 \text{ atoms of } \text{H}_2]$$

$$\therefore 0.0409 \text{ moles of } \text{H}_2 = 0.0409 \times 2 \times 6.02 \times 10^{23} \text{ atoms}$$

$$= 4.92 \times 10^{22} \text{ atoms}$$

Energy required for exciting an electron from ground state to the next excited state

$$= 13.6 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ eV} = 13.6 \left(\frac{1}{1} - \frac{1}{4} \right)$$

$$= 13.6 \times 3/4 \text{ eV} = 10.2 \text{ eV}$$

$$= 1.632 \times 10^{-21} \text{ kJ} [1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}]$$

Therefore, energy required to excite 4.92×10^{22} electrons

$$= 1.632 \times 10^{-21} \times 4.92 \times 10^{22} \text{ kJ} = 80.3 \text{ kJ}$$

Therefore, the total energy required = $17.83 + 80.3$

$$= 98.17 \text{ kJ}$$

75. For maximum energy, $n_1 = 1$ and $n_2 = \infty$

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

or $\frac{1}{\lambda} \propto Z^2$ [$\because R_H$ is constant and transition remains same]

$$\therefore \frac{\lambda_{\text{He}}}{\lambda_{\text{H}}} = \frac{Z_{\text{H}}^2}{Z_{\text{He}}^2} = \frac{1^2}{2^2} = \frac{1}{4} \quad (\text{For He, } Z = 2)$$

$$\text{Hence } \lambda_{\text{He}} = \frac{1}{4} \times 91.2 \text{ nm} = 22.8 \text{ nm}$$

76. The probability of finding of $2s$ electron at a point,

$$\psi_{2s}^2 = \frac{1}{32\pi} \left(\frac{1}{a_0} \right)^3 \left(2 - \frac{r}{a_0} \right)^2 e^{-\frac{2r}{a_0}}$$

Node is the point at which probability of finding an electron is zero. It means the value of ψ_{2s}^2 is zero when $r = r_0$.

$$\frac{1}{32\pi} \left(\frac{1}{a_0} \right)^3 \left(2 - \frac{r_0}{a_0} \right)^2 e^{-\frac{2r_0}{a_0}} = 0 \Rightarrow 2 - \frac{r_0}{a_0} = 0 \therefore r_0 = 2a_0$$

77. $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{0.1 \times 100}$ or $\lambda = 6.626 \times 10^{-35} \text{ m}$

78. For hydrogen atom, $Z = 1, n = 1$

$$v = 2.18 \times 10^6 \times \frac{Z}{n} \text{ m s}^{-1} = 2.18 \times 10^6 \text{ m s}^{-1}$$

de-Broglie's wavelength, $\lambda = \frac{h}{mv}$

$$= \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.18 \times 10^6} = 3.34 \times 10^{-10} \text{ m or } 3.3 \text{ \AA}$$

$$\therefore \text{Orbital angular momentum} = \sqrt{l(l+1)} \cdot \frac{h}{2\pi}$$

$$= \sqrt{l(l+1)} \cdot \frac{h}{2\pi} \quad [\because \text{For } 2p \text{ orbital, } l = 1]$$

$$= \sqrt{2} \cdot \frac{h}{2\pi}$$

79. According to Bohr's theory

$$\text{Potential energy } (V_n) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

$$\text{Kinetic energy } (K_n) = \frac{1}{8\pi\epsilon_0} \frac{Ze^2}{r}$$

$$\text{Radius of } n^{\text{th}} \text{ orbit } (r_n) = \frac{n^2 h^2 \epsilon_0}{\pi m Z e^2};$$

$$\text{Potential energy } (E_n) = -\frac{me^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n^2} \right)$$

$$\frac{V_n}{K_n} = \frac{-\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}}{\frac{1}{8\pi\epsilon_0} \frac{Ze^2}{r}} = -2 \quad (\text{A} \rightarrow \text{R});$$

$$E_n \propto \frac{1}{n^2} \propto \frac{1}{r_n}$$

$$r^n \rightarrow E_n^x \quad \therefore x = -1. \quad (\text{B} \rightarrow \text{Q})$$

l , the orbital quantum number, is connected to the total angular momentum of the electron. This quantum number is an integer less than n , and the total angular momentum of the electron can be calculated using:

Total angular momentum,

$$L = [l(l+1)]^{1/2} \frac{h}{2\pi} \quad (l = 0, 1, 2, \dots, n-1)$$

The lowest energy orbital in the hydrogen atom is the $1s$ orbital, which corresponds with $n = 1, l = 0$ and $m = 0$.

Hence total angular momentum in lowest orbital = 0.

(C → P)

$$\frac{1}{r^n} \propto Z^y \quad \text{as} \quad r_n \propto \frac{1}{Z}$$

∴ $y = 1$. (D → S)

80. (A → Q), (B → P, Q, R, S), (C → P, Q, R), (D → P, Q, R)

Principal quantum number represents the shape, size and energy of the shell to which the electron belongs.

Azimuthal quantum number describes the spatial distribution of electron cloud and angular momentum. It gives the name of the subshell associated with the main shell.

Pauli's exclusion principle states that an orbital accommodates two electrons with opposite spin. These two electrons have same values of principal, azimuthal and magnetic quantum number but the fourth *i.e.*, spin quantum number will be different.

Magnetic quantum number describes the orientation or distribution of electron cloud.

81. (c) : The statement-2 is not correct because nuclides having even number of protons and even number of neutrons have maximum stability. The statement-1 is correct because $^{40}_{20}\text{Ca}$ has even number of protons (*i.e.* 20) and even number of neutrons (*i.e.* $40 - 20 = 20$) whereas $^{30}_{13}\text{Al}$ has odd number of protons (*i.e.* 13) and odd number of neutrons (*i.e.* $30 - 13 = 17$). Thus the nuclide $^{30}_{13}\text{Al}$ is less stable. Thus we can say that nuclides having odd number of protons and neutrons are generally less stable not unstable.

82. (b) : It is given that the state S_1 has one radial node; or $(n - l - 1) = 1$.

It is possible only when state S_1 is $2s$ with $n = 2$ and $l = 0$ (since S_1 is spherically symmetrical).

83. (c) : For S_1 state of Li^{2+} , $n = 2$ and $Z = 3$.

∴ Energy of state S_1 in the units of hydrogen atom ground state energy is

$$E = E_H \times \frac{Z^2}{n^2} = E_H \times \frac{3^2}{2^2} = \frac{9}{4} E_H = 2.25 \times E_H$$

84. (b) : The state S_2 has one radial node and its energy is equal to the ground state energy of the hydrogen atom. This is possible only for $3p$ orbital.

$3p$ orbital has one radial node,

$$n = 3, l = 1 \Rightarrow 3 - 1 - 1 = 1$$

$$E = E_H \times \frac{Z^2}{n^2} = E_H \times \frac{3^2}{3^2} = E_H$$

85. (9) : For principal quantum number ($n = 3$)

Number of orbitals = $n^2 = 9$

So, number of electrons with $m_s = -\frac{1}{2}$ will be 9.

86. (4) : The energy associated with incident photon

$$\Rightarrow E = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9}}$$

$$E \text{ in eV} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9} \times 1.6 \times 10^{-19}} = 4.141 \text{ eV} \approx 4$$

Photoelectric effect can take place only if $E_{\text{photon}} \geq \phi$

Thus, Li, Na, K and Mg can show photoelectric effect. So the answer is 4.

87. (5) : $\lambda = \frac{h}{\sqrt{2m \times K.E.}}$

$$\frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \frac{\sqrt{m_{\text{Ne}} \times K.E._{\text{Ne}}}}{\sqrt{m_{\text{He}} \times K.E._{\text{He}}}}$$

$$\frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \frac{\sqrt{m_{\text{Ne}} \times T_{\text{Ne}}}}{\sqrt{m_{\text{He}} \times T_{\text{He}}}} \quad [\because K.E. \propto T]$$

$$= \sqrt{\frac{20 \times 1000}{4 \times 200}}$$

$$\frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \sqrt{\frac{20000}{800}} = 5$$

$$\lambda_{\text{He}} = 5\lambda_{\text{Ne}}$$

88. (6) : $n = 4, l = 0, 1, 2, 3$

$m_l = 1$ (only in p, d and f -orbitals)

2 electrons on each orbital have $m_s = -1/2$

Hence, total no. of electrons is 6.

89. (3) : In case of H-atom, the energies of the orbitals are in the order :

$1s < 2s < 2p < 3s < 3p < 3d < 4s < 4p < 4d < 4f < \dots$

For multielectronic system, *i.e.*, H^- ion, the order is $1s < 2s < 2p \dots$ [follow $(n + l)$ rule]

For H-atom, $Z = 1$, $1s^1$, the second excited state ($n = 3$) is

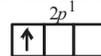
$$3s = 3p = 3d$$

Degenerate orbitals 1 3 5

∴ Degeneracy = $1 + 3 + 5 = 9$

For H^- ion, $Z = 1$, $1s^2$, the first excited state would be $1s^1, 2s^1$.

And the second excited state would be $1s^1, 2s^0, 2p^1$



$P_x \quad P_y \quad P_z$

(3 degenerate orbitals)

∴ degeneracy = 3



3

Chemical Bonding

Multiple Choice Questions with ONE Correct Answer

- The compound which contains both ionic and covalent bonds is
(a) CH_4 (b) H_2
(c) KCN (d) KCl (1979)
- Which of the following compounds is covalent?
(a) H_2 (b) CaO
(c) KCl (d) Na_2S (1980)
- Element X is strongly electropositive and element Y is strongly electronegative. Both are univalent. The compound formed would be
(a) X^+Y^- (b) X^-X^+
(c) $X - Y$ (d) $X \rightarrow Y$ (1980)
- The total number of electrons that take part in forming the bond in N_2 is
(a) 2 (b) 4
(c) 6 (d) 10 (1980)
- If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atomic number < 21) are
(a) pure p (b) sp hybrid
(c) sp^2 hybrid (d) sp^3 hybrid. (1981)
- The ion that is isoelectronic with CO is
(a) CN^- (b) O_2^+
(c) O_2^- (d) N_2^+ (1982)
- Among the following, the molecule that is linear is
(a) CO_2 (b) NO_2
(c) SO_2 (d) ClO_2 (1982)
- The compound with no dipole moment is
(a) methyl chloride (b) carbon tetrachloride
(c) methylene chloride (d) chloroform. (1982)
- Carbon tetrachloride has no net dipole moment because of
(a) its planar structure
(b) its regular tetrahedral structure
(c) similar sizes of carbon and chlorine
(d) similar electron affinities of carbon and chlorine. (1983)
- Which one among the following does not have the hydrogen bond?
(a) Phenol (b) Liquid NH_3
(c) Water (d) Liquid HCl (1983)
- The types of bonds present in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are only
(a) electrovalent and covalent
(b) electrovalent and coordinate covalent
(c) electrovalent, covalent and coordinate covalent
(d) covalent and coordinate covalent. (1983)
- On hybridization of one s and one p orbital we get
(a) two mutually perpendicular orbitals
(b) two orbitals at 180°
(c) four orbitals directed tetrahedrally
(d) three orbitals in a plane. (1984)
- The molecule having one unpaired electron is
(a) NO (b) CO
(c) CN^- (d) O_2 (1985)
- The bond between two identical non-metal atoms has a pair of electrons
(a) unequally shared between the two
(b) transferred fully from one atom to another
(c) with identical spins
(d) equally shared between them. (1986)
- The hydrogen bond is strongest in
(a) $\text{O} - \text{H} \cdots \cdots \text{S}$ (b) $\text{S} - \text{H} \cdots \cdots \text{O}$
(c) $\text{F} - \text{H} \cdots \cdots \text{F}$ (d) $\text{F} - \text{H} \cdots \cdots \text{O}$ (1986)
- The hybridisation of sulphur in sulphur dioxide is
(a) sp (b) sp^3
(c) sp^2 (d) dsp^2 (1986)
- Hydrogen bonding is maximum in
(a) ethanol (b) diethyl ether
(c) ethyl chloride (d) triethyl amine. (1987)

18. The species in which the central atom uses sp^2 hybrid orbitals in its bonding is
 (a) PH_3 (b) NH_3
 (c) CH_3^+ (d) SbH_3 (1988)
19. The molecule which has zero dipole moment is
 (a) CH_2Cl_2 (b) BF_3
 (c) NF_3 (d) ClO_2 (1989)
20. The molecule which has pyramidal shape is
 (a) PCl_3 (b) SO_3
 (c) CO_3^{2-} (d) NO_3^- (1989)
21. The compound in which C uses its sp^3 hybrid orbitals for bond formation is
 (a) HCOOH^* (b) $(\text{H}_2\text{N}_2)^*$
 (c) $(\text{CH}_3)_3\text{COH}^*$ (d) CH_3CHO^* (1989)
22. The type of hybrid orbitals used by the chlorine atom in ClO_2^- is
 (a) sp^3 (b) sp^2
 (c) sp (d) none of these (1992)
23. The maximum possible number of hydrogen bonds, a water molecule can form is
 (a) 2 (b) 4
 (c) 3 (d) 1 (1992)
24. Which one is most ionic?
 (a) P_2O_5 (b) CrO_3
 (c) MnO (d) Mn_2O_7 (1995)
25. Number of paired electrons in O_2 molecule is
 (a) 7 (b) 8
 (c) 16 (d) 14 (1995)
26. Among the following species, identify the isostructural pairs
 $\text{NF}_3, \text{NO}_3^-, \text{BF}_3, \text{H}_3\text{O}^+, \text{HN}_3$
 (a) $[\text{NF}_3, \text{NO}_3^-]$ and $[\text{BF}_3, \text{H}_3\text{O}^+]$
 (b) $[\text{NF}_3, \text{HN}_3]$ and $[\text{NO}_3^-, \text{BF}_3]$
 (c) $[\text{NF}_3, \text{H}_3\text{O}^+]$ and $[\text{NO}_3^-, \text{BF}_3]$
 (d) $[\text{NF}_3, \text{H}_3\text{O}^+]$ and $[\text{HN}_3, \text{BF}_3]$ (1996)
27. The number and type of bonds between two carbon atoms in CaC_2 are
 (a) one sigma (σ) and one pi (π) bonds
 (b) one sigma (σ) and two pi (π) bonds
 (c) one sigma (σ) and one and a half pi (π) bonds
 (d) one sigma (σ) bond. (1996)
28. Among $\text{KO}_2, \text{AlO}_2^-, \text{BaO}_2$ and NO_2^+ , unpaired electron is present in
 (a) NO_2^+ and BaO_2 (b) KO_2 and AlO_2^-
 (c) KO_2 only (d) BaO_2 only. (1997)
29. Among the following compounds the one that is polar and has the central atom with sp^2 hybridisation is
 (a) H_2CO_3 (b) SiF_4
 (c) BF_3 (d) HClO_2 (1997)
30. The critical temperature of water is higher than that of O_2 because the H_2O molecule has
 (a) fewer electrons than O_2
 (b) two covalent bonds
 (c) V-shape
 (d) dipole moment. (1997)
31. Which one of the following compounds has sp^2 hybridisation?
 (a) CO_2 (b) SO_2 (c) N_2O (d) CO (1997)
32. The correct order of increasing C—O bond length of $\text{CO}, \text{CO}_3^{2-}, \text{CO}_2$ is
 (a) $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$ (b) $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$
 (c) $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$ (d) $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$ (1999)
33. The geometry of H_2S and its dipole moment are
 (a) angular and non-zero (b) angular and zero
 (c) linear and non-zero (d) linear and zero. (1999)
34. Molecular shapes of SF_4, CF_4 and XeF_4 are
 (a) the same, with 2, 0 and 1 lone pairs of electrons respectively
 (b) the same, with 1, 1 and 2 lone pairs of electrons respectively
 (c) different, with 0, 1 and 2 lone pairs of electrons respectively
 (d) different, with 1, 0 and 2 lone pairs of electrons respectively. (2000)
35. The hybridisation of atomic orbitals of nitrogen in $\text{NO}_2^+, \text{NO}_3^-$ and NH_4^+ are
 (a) sp, sp^3 and sp^2 respectively
 (b) sp, sp^2 and sp^3 respectively
 (c) sp^2, sp and sp^3 respectively
 (d) sp^2, sp^3 and sp respectively. (2000)
36. The common features among the species CN^-, CO and NO^+ are
 (a) bond order three and isoelectronic
 (b) bond order three and weak field ligands
 (c) bond order two and π -acceptors
 (d) isoelectronic and weak field ligands. (2001)

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37. The correct order of hybridisation of the central atom in the following species NH_3 , $[\text{PtCl}_4]^{2-}$, PCl_5 and BCl_3 is
 (a) dsp^2 , dsp^3 , sp^2 and sp^3 (b) sp^3 , dsp^2 , dsp^3 , sp^2
 (c) dsp^2 , sp^2 , sp^3 , dsp^3 (d) dsp^2 , sp^3 , sp^2 , dsp^3 (2001)
38. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3
 (a) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3
 (b) N : pyramidal, sp^3 ; B : pyramidal, sp^3
 (c) N : pyramidal, sp^3 ; B : planar, sp^2
 (d) N : pyramidal, sp^3 ; B : tetrahedral, sp^3 (2002)
39. Identify the least stable ion amongst the following
 (a) Li^- (b) Be^-
 (c) B^- (d) C^- (2002)
40. Which of the following molecular species has unpaired electron(s)?
 (a) N_2 (b) F_2
 (c) O_2^- (d) O_2^{2-} (2002)
41. Which of the following are isoelectronic and isostructural?
 NO_3^- , CO_3^{2-} , ClO_3^- , SO_3
 (a) NO_3^- , CO_3^{2-} (b) SO_3 , NO_3^-
 (c) ClO_3^- , CO_3^{2-} (d) CO_3^{2-} , SO_3 (2003)
42. According to molecular orbital theory which of the following statement about the magnetic character and bond order is correct regarding O_2^+ ?
 (a) Paramagnetic and Bond order $< \text{O}_2$
 (b) Paramagnetic and Bond order $> \text{O}_2$
 (c) Diamagnetic and Bond order $< \text{O}_2$
 (d) Diamagnetic and Bond order $> \text{O}_2$ (2004)
43. Which species has the maximum number of lone pair of electrons on the central atom?
 (a) $[\text{ClO}_3]^-$ (b) XeF_4
 (c) SF_4 (d) $[\text{I}_3]^-$ (2005)
44. (I) 1,2-dihydroxybenzene
 (II) 1,3-dihydroxybenzene
 (III) 1,4-dihydroxybenzene
 (IV) Hydroxybenzene.
 The increasing order of boiling points of above mentioned alcohols is
 (a) $\text{I} < \text{II} < \text{III} < \text{IV}$ (b) $\text{I} < \text{II} < \text{IV} < \text{III}$
 (c) $\text{IV} < \text{I} < \text{II} < \text{III}$ (d) $\text{IV} < \text{II} < \text{I} < \text{III}$. (2006)
45. The species having bond order different from that in CO is
 (a) NO^- (b) NO^+
 (c) CN^- (d) N_2 . (2007)
46. Among the following, the paramagnetic compound is
 (a) Na_2O_2 (b) O_3
 (c) N_2O (d) KO_2 . (2007)
47. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is
 (a) 1 and diamagnetic (b) 0 and diamagnetic
 (c) 1 and paramagnetic (d) 0 and paramagnetic. (2010)
48. The species having pyramidal shape is
 (a) SO_3 (b) BrF_3
 (c) SiO_3^{2-} (d) OSF_2 (2010)
49. The shape of XeO_2F_2 molecule is
 (a) trigonal bipyramidal (b) square planar
 (c) tetrahedral (d) see-saw (2012)
50. Assuming $2s-2p$ mixing is not operative, the paramagnetic species among the following is
 (a) Be_2 (b) B_2
 (c) C_2 (d) N_2 (2014)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

51. CO_2 is isostructural with
 (a) HgCl_2 (b) SnCl_2
 (c) C_2H_2 (d) NO_2 (1986)
52. The linear structure is assumed by
 (a) SnCl_2 (b) NCO^-
 (c) CS_2 (d) NO_2^+ (1991)
53. Which of the following have identical bond order?
 (a) CN^- (b) O_2^-
 (c) NO^+ (d) CN^+ (1992)
54. The molecules that will have dipole moment are
 (a) 2,2-dimethylpropane
 (b) *trans*-2-pentene
 (c) *cis*-3-hexene
 (d) 2,2,3,3-tetramethylbutane. (1992)
55. Pick out the isoelectronic structures from the following
 I. CH_3^+ II. H_3O^+ III. NH_3 IV. CH_3^-
 (a) I and II (b) III and IV
 (c) I and III (d) II, III and IV (1993)

56. The geometry and the type of hybrid orbital present about the central atom in BF_3 is
 (a) linear, sp (b) trigonal planar, sp^2
 (c) tetrahedral, sp^3 (d) pyramidal, sp^3 (1998)
57. If the bond length of CO bond in carbon monoxide is 1.128 Å, then what is the value of CO bond length in $\text{Fe}(\text{CO})_5$?
 (a) 1.15 Å (b) 1.128 Å
 (c) 1.72 Å (d) 1.118 Å (2006)
58. Hydrogen bonding plays a central role in the following phenomena
 (a) ice floats in water
 (b) higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
 (c) formic acid is more acidic than acetic acid
 (d) dimerisation of acetic acid in benzene (2014)
59. The pair(s) of reagents that yield paramagnetic species is/are
 (a) Na and excess of NH_3
 (b) K and excess of O_2
 (c) Cu and dilute HNO_3
 (d) O_2 and 2-ethylanthraquinol. (2014)
60. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2 . The TRUE statement(s) regarding this adsorption is(are)
 (a) O_2 is physisorbed
 (b) heat is released
 (c) occupancy of π_{2p}^* of O_2 is increased
 (d) bond length of O_2 is increased. (2015)

Fill in the Blanks

61. The angle between two covalent bonds is maximum in (CH_4 , H_2O , CO_2) (1981)
62. Pair of molecules which forms strongest intermolecular hydrogen bond is
 (SiH_4 and SiF_4 , $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ and CHCl_3 , $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$
 and $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$) (1981)
63. There are π bonds in a nitrogen molecule. (1982)
64. hybrid orbitals of nitrogen atom are involved in the formation of ammonium ion. (1982)
65. The shape of $[\text{CH}_3]^+$ is (1990)

66. The two types of bonds present in B_2H_6 are covalent and (1994)
67. When N_2 goes to N_2^+ the N—N bond distance and when O_2 goes to O_2^+ the O—O bond distance (1996)
68. Among N_2O , SO_2 , I_2^+ and I_3^- the linear species are and (1997)

True / False

69. Linear overlap of two atomic p -orbitals leads to a sigma bond. (1983)
70. All molecules with polar bonds have dipole moment. (1985)
71. SnCl_2 is a non-linear molecule. (1985)
72. In benzene, carbon uses all the three p -orbitals for hybridisation. (1987)
73. sp^2 hybrid orbitals have equal s and p character. (1987)
74. The presence of polar bonds in a poly-atomic molecule suggests that the molecule has non-zero dipole moment. (1990)
75. The dipole moment of CH_3F is greater than that of CH_3Cl . (1993)

Subjective Problems

76. State four major physical properties that can be used to distinguish between covalent and ionic compounds. Mention the distinguishing features in each case. (1978)
77. Write the Lewis dot structural formula for each of the following. Give also, the formula of a neutral molecule, which has the same geometry and the same arrangement of the bonding electrons as in each of the following. An example is given below in the case of H_3O^+
- | | |
|---|--|
| $\left[\begin{array}{c} \text{H} \\ \\ \text{H} : \ddot{\text{O}} : \text{H} \\ \\ \text{H} \end{array} \right]^+$ Lewis dot structure | $\left[\begin{array}{c} \text{H} \\ \\ \text{H} : \ddot{\text{N}} : \text{H} \\ \\ \text{H} \end{array} \right]$ Neutral molecule |
|---|--|
- (i) O_2^{2-} (ii) CO_3^{2-}
 (iii) CN^- (iv) NCS^- (1983)
78. How many sigma bonds and how many pi-bonds are present in a benzene molecule? (1985)
79. Write the Lewis dot structure of the following
 O_3 , COCl_2 (1986)

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- 80.** Arrange the following
- (i) $N_2, O_2, F_2, Cl_2 \Rightarrow$ in increasing order of bond dissociation energy. (1988)
- (ii) Increasing strength of hydrogen bonding ($X-H-X$):
O, S, F, Cl, N (1991)
- (iii) In the decreasing order of the O–O bond length present in them O_2, KO_2 and $O_2[AsF_4]$. (2004)
- 81.** Write the resonance structures of N_2O that satisfy octet rule. (1990)
- 82.** The dipole moment of KCl is 3.336×10^{-29} Coulomb meters which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl. (1993)
- 83.** Using the VSEPR theory, identify the type of hybridisation and draw the structure of OF_2 . What are the oxidation states of O and F? (1994)
- 84.** The experimentally determined N–F bond length in NF_3 is greater than the sum of the single covalent radius of N and F. Explain. (1995)
- 85.** A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound. (1997)
- 86.** Interpret the non-linear shape of H_2S molecule and non-planar shape of PCl_3 using valence shell electron pair repulsion (VSEPR) theory. (Atomic numbers : H = 1, P = 15, S = 16, Cl = 17) (1998)
- 87.** Explain why *o*-hydroxybenzaldehyde is liquid at room temperature while *p*-hydroxybenzaldehyde is a high melting solid. (1999)
- 88.** In the equation $A + 2B + H_2O \longrightarrow C + 2D$ [$A = HNO_2, B = H_2SO_3, C = NH_2OH$], identify *D*. Draw the structures of *A, B, C, D*. (1999)
- 89.** Write the M.O. electron distribution of O_2 . Specify its bond order and magnetic property. (2000)
- 90.** Using VSEPR theory, draw the shape of PCl_5 and BrF_5 . (2003)
- 91.** Draw the structure of XeF_4 and OSF_4 according to VSEPR theory, clearly indicating the state of hybridisation of the central atom and lone pair of electrons (if any) on the central atom. (2004)

Matrix Match Type

- 92.** Match each of the diatomic molecules in column I with its property/properties in column II.

Column I	Column II
(A) B_2	(p) Paramagnetic
(B) N_2	(q) Undergoes oxidation
(C) O_2^-	(r) Undergoes reduction
(D) O_2	(s) Bond order ≥ 2
	(t) Mixing of <i>s</i> and <i>p</i> orbitals

(2009)

- 93.** Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists.

List I	List II
(P) 	1. <i>p</i> - <i>d</i> π antibonding
(Q) 	2. <i>d</i> - <i>d</i> σ bonding
(R) 	3. <i>p</i> - <i>d</i> π bonding
(S) 	4. <i>d</i> - <i>d</i> σ antibonding

Code :

P	Q	R	S
(a) 2	1	3	4
(b) 4	3	1	2
(c) 2	3	1	4
(d) 4	1	3	2

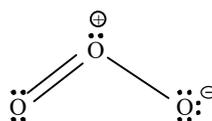
(2014)

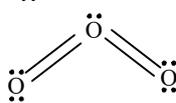
Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
- (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
- (c) Statement-1 is true, statement-2 is false.
- (d) Statement-1 is false, statement-2 is true.

- 94. Statement-1:** The electronic structure of O_3 is



Statement-2:  structure is not allowed because octet around O cannot be expanded. (1998)

95. Statement-1: LiCl is predominantly a covalent compound.
Statement-2: Electronegativity difference between Li and Cl is too small. (1998)

96. Statement-1 : *p*-Hydroxybenzoic acid has a lower boiling point than *o*-hydroxybenzoic acid.

Statement-2: *o*-Hydroxybenzoic acid has intramolecular hydrogen bonding. (2007)

97. Statement-1: Band gap in germanium is small.

Statement-2: The energy spread of each germanium atomic energy level is infinitesimally small. (2007)

Integer Answer Type

98. Based on VSEPR theory, the number of 90 degree F-Br-F angles in BrF₅ is (2010)

99. A list of species having the formula XZ₄ is given below. XeF₄, SF₄, SiF₄, BF₄⁻, BrF₄⁻, [Cu(NH₃)₄]²⁺, [FeCl₄]²⁻, [CoCl₄]²⁻ and [PtCl₄]²⁻.

Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is (2014)

100. The total number of lone pairs of electrons in N₂O₃ is (2015)

101. Among the triatomic molecules/ions, BeCl₂, N₃⁻, N₂O, NO₂⁺, O₃, SCl₂, ICl₂⁻, I₃⁻ and XeF₂, the total number of linear molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the *d*-orbital(s) is

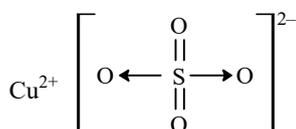
[Atomic number : S = 16, Cl = 17, I = 53 and Xe = 54] (2015)

ANSWER KEY

- | | | | | | |
|--|------------------------------------|--|---------------------|---------------|--|
| 1. (c) | 2. (a) | 3. (a) | 4. (c) | 5. (c) | 6. (a) |
| 7. (a) | 8. (b) | 9. (b) | 10. (d) | 11. (c) | 12. (b) |
| 13. (a) | 14. (d) | 15. (c) | 16. (c) | 17. (a) | 18. (c) |
| 19. (b) | 20. (a) | 21. (c) | 22. (a) | 23. (b) | 24. (c) |
| 25. (d) | 26. (c) | 27. (b) | 28. (c) | 29. (a) | 30. (d) |
| 31. (b) | 32. (d) | 33. (a) | 34. (d) | 35. (b) | 36. (a) |
| 37. (b) | 38. (a) | 39. (b) | 40. (c) | 41. (a) | 42. (b) |
| 43. (d) | 44. (c) | 45. (a) | 46. (d) | 47. (a) | 48. (d) |
| 49. (d) | 50. (c) | 51. (a, c) | 52. (b, c, d) | 53. (a, c) | 54. (b, c), |
| 55. (b, d) | 56. (b) | 57. (a) | 58. (a, b, d) | 59. (a, b, c) | 60. (b, c, d) |
| 61. CO ₂ | 62. HCOOH and CH ₃ COOH | 63. 2 | 64. sp ³ | 65. Planar | 66. Banana bonds |
| 66. Banana bonds | 67. Increases, Decreases | 68. N ₂ O and I ₃ ⁻ | 69. True | 70. False | 71. True |
| 71. True | 72. False | 73. False | 74. False | 75. False | 92. A - (p, r, t); B - (s, t); C - (p, q); D - (p, q, s) |
| 92. A - (p, r, t); B - (s, t); C - (p, q); D - (p, q, s) | 93. (c) | 94. (a) | 95. (c) | 96. (d) | 97. (b) |
| 96. (d) | 97. (b) | 98. (8) | 99. (4) | 100. (8) | 101. (4) |

Explanations

- (c): $K^+[C\equiv N]^-$
- (a): Rest all are ionic compounds.
- (a): They will form ionic bonding due to the difference in electronegativity.
- (c): $N\equiv N$, total no. of electrons = $2 \times 3 = 6$.
- (c): For resultant dipole moment for a molecule MX_3 , the molecule must be trigonal *i.e.* sp^2 hybridised orbital should be used by M .
- (a): Both CO and CN^- have 14 electrons.
- (a): CO_2 is a linear molecule, in CO_2 , C is sp hybridised.
- (b): The resultant dipole moment of CCl_4 is zero. It has a symmetrical tetrahedral structure.
- (b): It has zero dipole moment because of its regular tetrahedral structure.
- (d): In liquid HCl hydrogen bonds are not present because the electronegativity of Cl is not enough to form H-bonds, H-bonds are formed when the H-atom is linked to O, F or N.
- (c): Cu^{2+} and SO_4^{2-} have an ionic bond. In SO_4^{2-} the oxygen atoms are attached to sulphur atom by covalent and coordinate bonds.



- (b): We get sp hybrid orbitals which are at 180° .
- (a): The electronic configurations are:
 $NO: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1$
 $CO: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$
 $CN^-: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$
 $O_2: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$
 Thus we find that NO has one unpaired electron.
 CO and CN^- have no unpaired electron.
 O_2 has two unpaired electrons.
- (d): In case of two identical non-metals the pair of electrons is equally shared between them.
- (c): F — H ... F bonding is strongest because of maximum electronegativity and smallest size of fluorine atom.
- (c): SO_2 has a trigonal planar structure so it involves sp^2 hybridisation of S-atom.

- (a): In ethanol, $C_2H_5O - H$, the hydrogen is bonded to most electronegative O-atom and so it has maximum H-bonding.
- (c): Only CH_3^+ is sp^2 hybridised, all others are sp^3 hybridised.
- (b): BF_3 has a symmetrical trigonal planar structure, hence it has zero dipole moment.
- (a): In PCl_3 , there are three bond pairs and one lone pair on P atom so it is sp^3 hybridised and thus has pyramidal shape.
- (c): In $(CH_3)_3COH$, C^{*} is bound to four σ -bonds and so it is sp^3 hybridised.
- (a): We can calculate the number of orbitals involved in hybridisation by using the relation:

Number of orbital involved in hybridisation

$$= \frac{1}{2} (V + M - C + A)$$

Where V = Number of valence electrons

M = Number of monovalent atoms surrounding the atom

C = Charge on cation, A = Charge on anion

\therefore Number of orbitals involved in hybridisation

$$= \frac{1}{2} [7 + 0 + 0 + 1] = 4$$

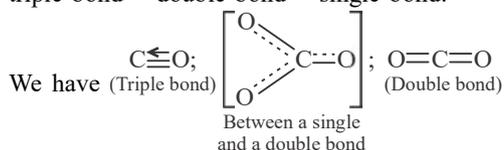
Since 4 orbitals are involved in hybridisation so it is sp^3 hybridised.

- (b): The water (H_2O) molecules are tetrahedrally oriented with respect to each other. In this arrangement each oxygen atom is surrounded tetrahedrally by four hydrogen atoms. Therefore one water molecule is capable of forming 4 hydrogen bonds.
- (c): P_2O_5 is a non-metallic oxide and so it must be more covalent than others which are metallic oxides. Moreover the metallic oxide with metal in higher oxidation state is more covalent so Mn_2O_7 (Mn = +7 state) is most covalent and MnO (Mn = +2 state) is most ionic amongst Mn_2O_7 , MnO and CrO_3 (Cr = +6 state).
- (d): $O_2: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$
 $\pi^* 2p_y^1$
 In it we find 7 pairs of electrons *i.e.* there are 14 paired electrons.
- (c): Isostructural compounds have same type of hybridisation.
 In NF_3 , N is sp^3 hybridised (3 *b.p.* + 1 *l.p.*)
 In NO_3^- ; N is sp^2 hybridised.
 In BF_3 ; B is sp^2 hybridised.
 In H_3O^+ ; O is sp^3 hybridised.

In HN_3 ; central nitrogen is sp hybridised.

From this we find that NF_3 and H_3O^+ are isostructural and BF_3 and NO_3^- are isostructural.

27. (b): In CaC_2 we have Ca^{2+} and C_2^{2-} which are held together by ionic bonds. The structure of C_2^{2-} is $[\text{C}\equiv\text{C}]^{2-}$, thus it contains one σ - and two π -bonds between two carbon atoms.
28. (c): In KO_2 we have O_2^- ion, which has one unpaired electron.
29. (a): From amongst the given compounds only H_2CO_3 and BF_3 are sp^2 hybridised, out of these H_2CO_3 is polar whereas BF_3 has zero dipole moment (*i.e.* non-polar).
30. (d): The resultant dipole moment of water is due to its V-shape.
31. (b): $\text{SO}_2: H = \frac{1}{2} [6 + 0 + 0 + 0] = 3$ *i.e.* sp^2 hybridisation.
32. (d): In general the bond length follows the order triple bond < double bond < single bond.



33. (a): H_2S has non-zero dipole moment (*i.e.* it has resultant dipole moment) and it has an angular geometry. It is V-shaped.
34. (d): Making calculations of hybridisation involved in various species, we find
- $\text{SF}_4: H = \frac{1}{2} [6 + 4 - 0 + 0] = 5$ *i.e.* sp^3d
- $\text{CF}_4: H = \frac{1}{2} [4 + 4 - 0 + 0] = 4$ *i.e.* sp^3
- $\text{XeF}_4: H = \frac{1}{2} [8 + 4 + 0 - 0] = 6$ *i.e.* sp^3d^2
- i.e.* they have different shapes.
- In SF_4 we have five hybrid orbitals but only four are used by F atoms so it has one lone pair.
- In CF_4 , C has four hybrid orbitals and all of these are used by F so it has no or zero lone pair of electron.
- In XeF_4 , there are six hybrid orbitals and only four are used by F atoms. Thus there are two lone pairs around Xe.

35. (b): $\text{NO}_2^+: H = \frac{1}{2} [5 + 0 - 1 + 0] = 2$ *i.e.* sp
- $\text{NO}_3^-: H = \frac{1}{2} [5 + 0 - 0 + 1] = 3$ *i.e.* sp^2
- $\text{NH}_4^+: H = \frac{1}{2} [5 + 4 - 1 + 0] = 4$ *i.e.* sp^3
36. (a): Each of these have 14 electrons and have same bond order of 3. In each case we have $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$.
37. (b): In NH_3 , N is sp^3 hybridised.
- In $[\text{PtCl}_4]^{2-}$, Pt is dsp^2 hybridised.
- In PCl_5 , P is dsp^3 hybridised.
- In BCl_3 , B is sp^2 hybridised.

38. (a): In $\text{H}_3\text{N} \rightarrow \text{BF}_3$ complex, both N and B have tetrahedral geometry.

39. (b): The electronic configuration of Be^- is $1s^2 2s^2 2p^1$. So it will lose an electron to get stability.

40. (c): $\text{O}_2^-: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$.

Thus it has one unpaired electron. All other species have paired electrons only.

41. (a): Both CO_3^{2-} and NO_3^- have same number of electrons (*i.e.* isoelectronic). They both have 32 electrons. Both of these involve same type of hybridisation so they are isostructural. Both have sp^2 hybridisation and so are planar.

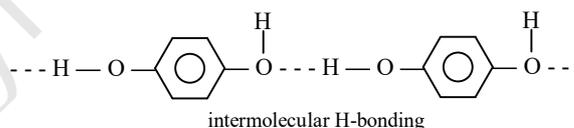
42. (b): O_2^+ has one unpaired electron and O_2 has two unpaired electrons. Thus O_2 is more paramagnetic or O_2^+ is less paramagnetic.

The bond order of O_2^+ is 2.5 and that of O_2 is 2. Thus O_2^+ is paramagnetic and its bond order is greater than that of O_2 .

43. (d): The number of lone pairs is

$$\text{ClO}_3^- = 1; \text{XeF}_4 = 2, \text{SF}_4 = 1 \text{ and } \text{I}_3^- = 3$$

44. (c): 1,4-dihydroxybenzene shows the highest boiling point among given compounds because it forms strong intermolecular hydrogen bond.



Order of H-bonding in *o*, *m* and *p*-isomers of a compound is given below:

Intermolecular H-bonding $o < m < p$ -isomers

Hydroxy benzene do not form a chain of H-bonding. Hence, the stability of 1,4-dihydroxy benzene is highest. Hence, its boiling point is highest. The increasing order of the boiling points of the given compounds is

$$\text{IV} < \text{I} < \text{II} < \text{III}.$$

45. (a): Molecular electronic configuration of

$$\text{CO}: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$$

$$\text{Therefore, bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

$$\text{NO}^+: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$$

$$\text{Bond order} = \frac{10 - 4}{2} = 3$$

$$\text{CN}^-: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$$

$$\text{Bond order} = \frac{10 - 4}{2} = 3$$

$$\text{N}_2: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$$

$$\text{Bond order} = \frac{10 - 4}{2} = 3$$

$$\text{NO}^-: \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$$

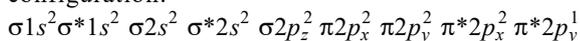
$$\text{Bond order} = \frac{10 - 6}{2} = 2$$

\therefore NO^- has different bond order from that of CO.

Chemical Bonding

35

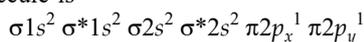
46. (d) : Superoxide ion, O_2^- has molecular orbital electronic configuration:



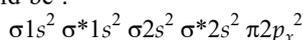
O_2^- has one unpaired electron and hence paramagnetic in nature. The paramagnetic content is measured with magnetic moment,

$$\mu = \sqrt{n(n+2)} = \sqrt{3} = 1.732 \text{ B.M.}$$

47. (a) : The molecular orbital electronic configuration of B_2 molecule is



If however, the Hund's rule is violated, then the configuration would be :

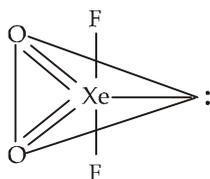


$$\therefore \text{B.O.} = \frac{6-4}{2} = 1$$

Since all the electrons are paired up, the molecule is diamagnetic.

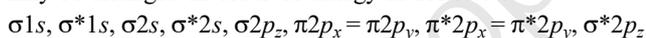
48. (d) : SO_3 is trigonal planar; BrF_3 is bent T shaped;
 SiO_3^{2-} is tetrahedral; OSF_2 is pyramidal.

49. (d) : Xe is in sp^3d hybrid state in XeO_2F_2 with 1 lone pair of electrons.



Geometry : Trigonal bipyramidal
Shape : See-saw

50. (c) : If $2s-2p$ mixing is not operative, then molecular orbitals may be arranged in order of energy as follows :



Applying this configuration, Be_2 , B_2 and N_2 will be diamagnetic, but C_2 will be paramagnetic.

51. (a,c) : $HgCl_2$ and C_2H_2 are linear molecules like CO_2 . In all of them we find sp -hybridisation.

$SnCl_2$ is trigonal (sp^2 - hybridisation)

and NO_2 is V-shaped (sp^2 - hybridisation)

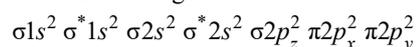
52. (b,c,d) : CS_2 like CO_2 is linear molecule ($S=C=S$)

It involves sp hybridisation.

$[O=N=O]^+$; $[N\equiv C-O]^-$ are also linear like CS_2 .

$SnCl_2$ is trigonal (sp^2 - hybridisation).

53. (a,c) : Both CN^- and NO^+ each have 14 electrons and their electronic configuration are same.



and so their bond order is same i.e. 3.

The number of electrons in CN^+ is 12 and in O_2^- is 17.

54. (b,c) : 2, 2-dimethylpropane and 2, 2, 3, 3 - tetramethylbutane are symmetrical molecules so their net dipole moment is zero.

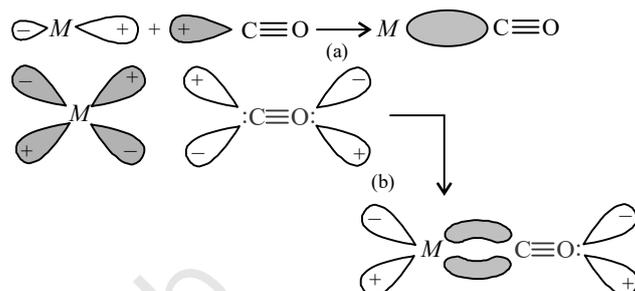
(b) and (c) have resultant dipole moment.

55. (b,d) : H_3O^+ , NH_3 and $^-CH_3$ each have 10 electrons and so are isoelectronic.

56. (b) : For BF_3 , $H = \frac{1}{2} [3+3-0+0] = 3$

i.e. sp^2 hybridisation and thus trigonal shape.

57. (a) : The bond length in CO itself is 1.128 Å, while the bond lengths in metal carbonyl molecules are ~ 1.15 Å, a shift in the proper direction but of little quantitative significance owing to its small magnitude and the uncertainties (~ 0.01 Å) in the individual distances.

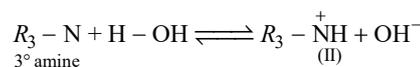
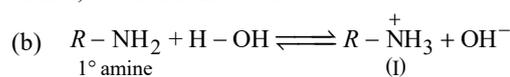


(a) The formation of the metal ← carbon σ -bond using an unshared pair of the C atom. (b) The formation of the metal → carbon π -bond.

This bonding mechanism is synergic, since the drift of metal electrons, referred to as back-bonding, into CO orbitals, will tend to make the CO as a whole negative, hence to increase its basicity via the s -orbital of carbon; at the same time the drift of electrons to the metal in the σ -bond tends to make the CO positive, thus enhancing the acceptor strength of the p -orbitals. Thus up to a point, the effect of σ -bond formation strengthen the π -bonding, and vice versa.

Thus this synergic effect results in the contraction of CO bond length.

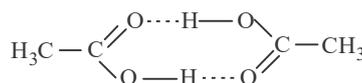
58. (a, b, d) : (a) Density of ice is less than water due to cage-like structure, in which each water molecule is surrounded by four other water molecules tetrahedrally through H-bonding. Hence, ice floats in water.



The cation (I) is more stabilised through hydrogen bonding than cation (II). So, $R-NH_2$ is stronger base than R_3N in aqueous solution.

(c) $HCOOH$ is stronger acid than CH_3COOH due to inductive effect and not due to hydrogen bonding.

(d) Acetic acid dimerises in benzene through intermolecular hydrogen bonding.



59. (a, b, c) : (a) $Na + (x+y)NH_3 \xrightarrow{\text{excess}}$
 $[Na(NH_3)_x]^+ + e^- (NH_3)_y \leftarrow$
 solvated e^-
 (Paramagnetic)

Chemical Bonding

37

In oxygen there are two unused pairs of electron on each oxygen atom ($\ddot{\text{O}}=\ddot{\text{O}}$) in this case there is less repulsion as compared to F_2 or Cl_2 .

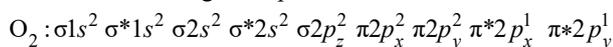
In nitrogen ($\text{:}\ddot{\text{N}}\equiv\ddot{\text{N}}\text{:}$) there is only one unused pair of electron on each atom and the repulsion is less than O_2 .

(ii) The strength of hydrogen bonding depends upon the size and electronegativity of the atom that is covalently bonded to the H-atom. Higher the value of electronegativity and smaller the size of the covalently bonded atom to the H-atom, stronger is the hydrogen bonding.

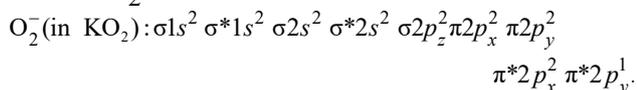
Out of the given atoms Cl (being larger in size) does not show the tendency of hydrogen bond formation.

The strength of H-bonds is $\text{Cl} < \text{S} < \text{N} < \text{O} < \text{F}$.

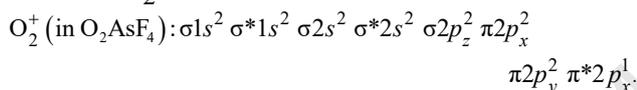
(iii) Since bond strength \propto bond order, so we calculate the bond order in the given species.



$$\therefore \text{B.O.} = \frac{10-6}{2} = 2$$



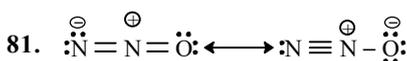
$$\therefore \text{B.O.} = \frac{10-7}{2} = 1.5$$



$$\therefore \text{B.O.} = \frac{10-5}{2} = 2.5$$

The B.O. of three species follows the order is $\text{O}_2^+ > \text{O}_2 > \text{O}_2^-$.

\therefore Bond strength in decreasing order is $\text{O}_2^+ > \text{O}_2 > \text{O}_2^-$.



82. Dipole moment (μ) = $e \times d$ Coulombs metre (C m)

For KCl, $d = 2.6 \times 10^{-10}$ m

In case of complete separation of charge (i.e. one unit charge or one electron i.e. 1.602×10^{-19} C)

$$\mu = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29} \text{ C m}$$

But $\mu_{\text{KCl}} = 3.336 \times 10^{-29}$ C m (given)

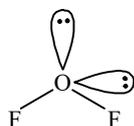
$$\therefore \text{Ionic character of KCl} = \frac{3.336 \times 10^{-29}}{4.1652 \times 10^{-29}} \times 100 = 80\%$$

83. The hybridisation of O atom in OF_2 is:

Hybridisation (H) = $\frac{1}{2}$ [Number of valence electron on O + Number of monovalent F atoms attached - Charge on cation + Charge on anion]

$$= \frac{1}{2} [6 + 2 - 0 + 0] = 4$$

i.e. it is sp^3 hybridised and since it involves sp^3 hybridisation so its shape is tetrahedral.



Oxidation number of fluorine (F) = -1

Oxidation number of oxygen (O) = +2

84. Both N and F atoms are small in size and their electron density is high. Both N and F repel the bond pair and as a result N-F bond length is larger than the sum of the atomic radii of N and F atoms.

85. We know that $\mu = \sqrt{n(n+2)}$ BM

Where, n = number of unpaired electrons

Given: $\mu = 1.73$ BM for vanadium ion

$$\therefore 1.73 = \sqrt{n(n+2)}$$

$$\text{or } 1.73 \times 1.73 = n(n+2)$$

$$3.0 = n^2 + 2n$$

$$\text{or } n^2 + 2n - 3 = 0$$

$$\text{or } n = \frac{-2 \pm \sqrt{4+4 \times 3}}{2} = \frac{-2 \pm 4}{2} \text{ i.e. } -3 \text{ or } +1$$

Since negative value is not valid, $\therefore n = +1$

It shows that number of unpaired electrons in vanadium ion is 1.

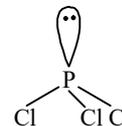
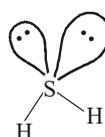
The electronic configuration of vanadium ($Z = 23$) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$.

It will have one unpaired electron if it loses 2 electrons from 4s and 2 electrons from 3d, i.e. in +4 state as V^{4+} .

86. Hybridisation of S-atom in $\text{H}_2\text{S} = \frac{1}{2} [6 + 2 - 0 + 0] = 4$ i.e. sp^3

Hybridisation of P-atom in $\text{PCl}_3 = \frac{1}{2} [5 + 3 - 0 + 0] = 4$ i.e. sp^3

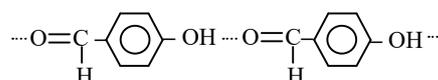
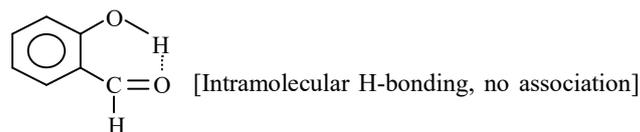
The shapes are:



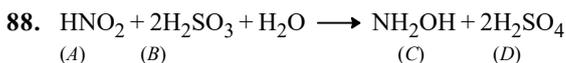
In H_2S , the sulphur atom has two shared pairs and two lone pairs and so it is non-linear or bent in shape.

In PCl_3 , phosphorus atom has three shared pairs and one lone pair and so the molecule is non-planar (or pyramidal) in shape.

87. Intramolecular hydrogen bonding is present in *ortho*-hydroxybenzaldehyde and it exists as a single molecule. In case of *para*-hydroxybenzaldehyde there is association in the molecule because of intermolecular hydrogen bonding. Due to this association, the molecules get aggregated which results in a high melting solid. Since there is no association in *ortho*-hydroxybenzaldehyde so it is liquid at room temperature.

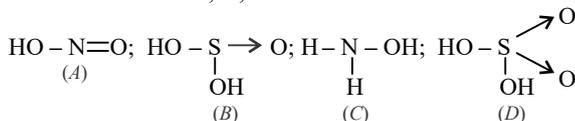


[Intermolecular hydrogen bonding, association occurs]

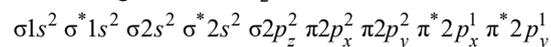


The compound (D) is H_2SO_4

The structures of A, B, C and D are

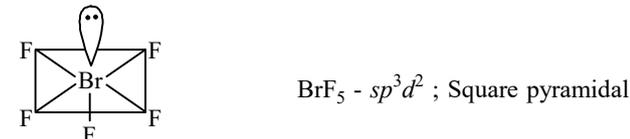
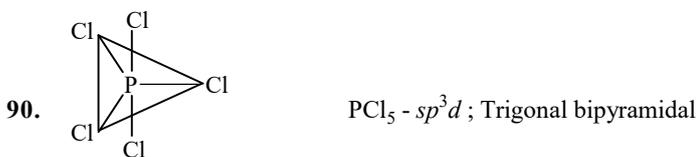


89. M.O configuration of O_2 :

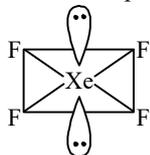


$\therefore \text{B.O.} = \frac{10-6}{2} = 2.$

In O_2 molecule there are two unpaired electrons so it is paramagnetic.

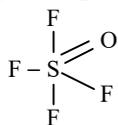


91. In XeF_4 , total number of electron pairs around Xe = $\frac{8+4}{2} = 6$
 Thus in XeF_4 , Xe is sp^3d^2 hybridised. It is an octahedral molecule. Its shape is square planar with two lone pairs.

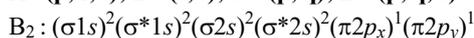


In OSF_4 , the number of electron pairs around the central atom is $\frac{6+4}{2} = 5$

Thus the central atom(s) is sp^3d hybridised. So its structure is trigonal bipyramidal with no lone pair of electrons.

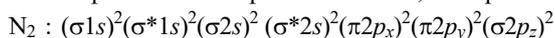


92. A - (p, r, t); B - (s, t); C - (p, q); D - (p, q, s):



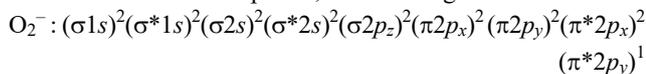
$\text{B.O.} = \frac{6-4}{2} = 1$

Due to presence of unpaired electrons, it is paramagnetic.



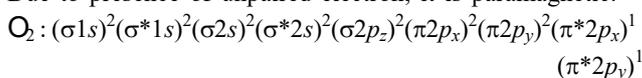
$\text{B.O.} = \frac{10-4}{2} = 3$

Due to all electron are paired, it is deamagnetic.



$\text{B.O.} = \frac{10-7}{2} = 1.5$

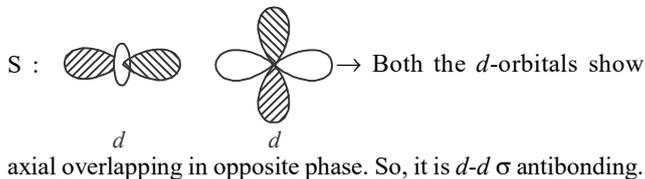
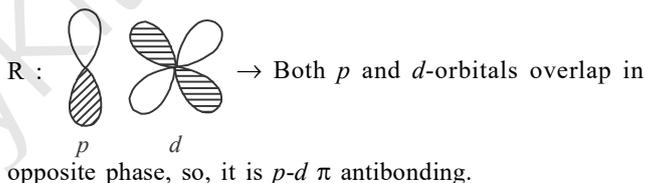
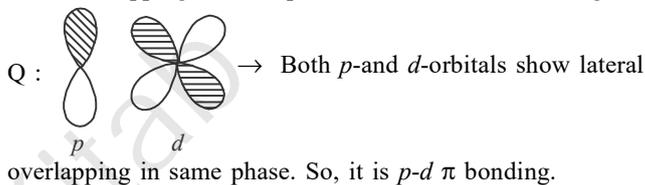
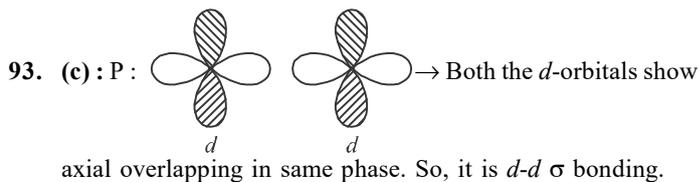
Due to presence of unpaired electron, it is paramagnetic.



$\text{B.O.} = \frac{10-6}{2} = 2$

Due to presence of unpaired electrons, it is paramagnetic.

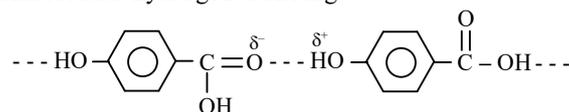
If loss of electron increases the bond order oxidation will be feasible and if the gain of electron increases bond order reduction will be feasible.



94. (a) : Both statement-1 and statement-2 are correct and statement-2 explains statement-1 because the central atom (O-atom) cannot have more than 8 electrons.

95. (c) : statement-1 is correct but statement-2 is not correct. According to Fajan's rule, the smaller the size of cation and the larger the size of anion, greater is the polarising power and hence greater is the covalent character of ionic bond.

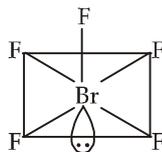
96. (d) : p-Hydroxybenzoic acid has higher boiling point than o-hydroxybenzoic acid, because para isomer has intermolecular hydrogen bonding.



97. (b) : Germanium is a semiconductor, where the energy gap between adjacent bands is sufficiently small for thermal energy to be able to promote a small number of electrons from the full valence band to the empty conduction band. This leaves both bands partially filled, so the material can conduct electricity.

Chemical Bonding

98. (8) : BrF_5 is square pyramidal in shape.



The observed bond angles are 87° , which is close to the theoretical 90° . This slight distortion is caused due to presence of one lone pair.

99. (4) : XeF_4 – Square planar

SF_4 – See-saw, SiF_4 – Tetrahedral

BF_4^- – Tetrahedral

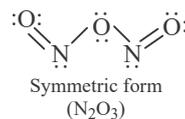
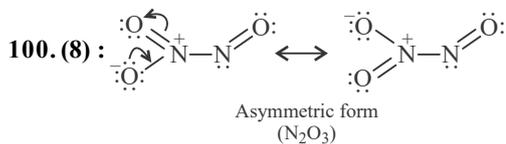
BrF_4^- – Square planar

$[\text{Cu}(\text{NH}_3)_4]^{2+}$ – Square planar

$[\text{FeCl}_4]^{2-}$ – Tetrahedral

$[\text{CoCl}_4]^{2-}$ – Tetrahedral

$[\text{PtCl}_4]^{2-}$ – Square planar



It has 8 lone pairs of electrons.

101. (4) :

Molecule/ion	Hybridisation	Shape
BeCl_2	sp	linear
N_3^-	sp	linear
N_2O	sp	linear
NO_2^+	sp	linear
O_3	sp^2	bent
SCl_2	sp^3	bent
ICl_2^-	sp^3d	linear
I_3^-	sp^3d	linear
XeF_2	sp^3d	linear

Thus, there are total four linear molecules/ions where the hybridisation of the central atom does not have contribution from the d -orbitals.

4

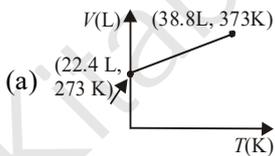
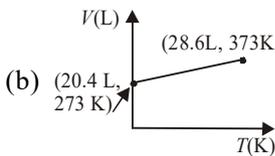
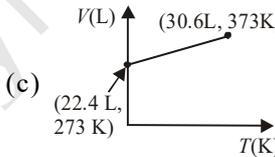
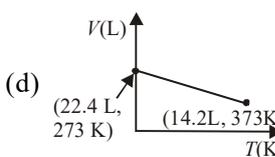
Gaseous and Liquid States

Multiple Choice Questions with ONE Correct Answer

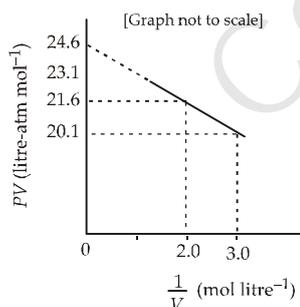
- Equal weights of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is
(a) $\frac{1}{3}$ (b) $\frac{1}{2}$ (c) $\frac{2}{3}$ (d) $\frac{1}{3} \times \frac{273}{298}$ (1981)
- The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is
(a) critical temperature (b) boyle temperature
(c) inversion temperature (d) reduced temperature. (1981)
- The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is
(a) 1.086 : 1 (b) 1 : 1.086
(c) 2 : 1.086 (d) 1.086 : 2 (1981)
- Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is
(a) two times that of a hydrogen molecule
(b) same as that of a hydrogen molecule
(c) four times that of a hydrogen molecule
(d) half that of a hydrogen molecule. (1982)
- Equal weights of methane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is
(a) $\frac{1}{2}$ (b) $\frac{8}{9}$ (c) $\frac{1}{9}$ (d) $\frac{16}{17}$ (1984)
- Rate of diffusion of a gas is
(a) directly proportional to its density
(b) directly proportional to its molecular weight
(c) directly proportional to the square root of its molecular weight
(d) inversely proportional to the square root of its molecular weight. (1985)
- The average velocity of an ideal gas molecule at 27°C is 0.3 m/sec. The average velocity at 927°C will be
(a) 0.6 m/sec (b) 0.3 m/sec
(c) 0.9 m/sec (d) 3.0 m/sec (1986)
- 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
(c) $\left(P + \frac{a}{V^2}\right)$ (d) $(RT)^{-1}$ (1988)
- A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends, the white ammonium chloride ring first formed will be
(a) at the centre of the tube
(b) near the hydrogen chloride bottle
(c) near the ammonia bottle
(d) throughout the length of the tube. (1988)
- The values of van der Waals constant a for the gases O₂, N₂, NH₃ and CH₄ are 1.360, 1.390, 4.170 and 2.253 L² atm mol⁻² respectively. The gas which can most easily be liquefied is
(a) O₂ (b) N₂ (c) NH₃ (d) CH₄ (1989)
- The density of neon will be highest at
(a) S.T.P. (b) 0°C, 2 atm
(c) 273°C, 1 atm (d) 273°C, 2 atm (1990)
- The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecular weight of X is
(a) 64.0 (b) 32.0 (c) 4.0 (d) 8.0 (1990)
- According to kinetic theory of gases, for a diatomic molecule
(a) the pressure exerted by the gas is proportional to mean velocity of the molecule
(b) the pressure exerted by the gas is proportional to the root mean velocity of the molecule
(c) the root mean square velocity of the molecule is inversely proportional to the temperature
(d) the mean translational kinetic energy of the molecule is proportional to the absolute temperature. (1991)

Gaseous and Liquid States

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14. At constant volume, for a fixed number of moles of a gas the pressure of the gas increases with rise in temperature due to
 (a) increase in average molecular speed
 (b) increased rate of collisions amongst molecules
 (c) increase in molecular attraction
 (d) decrease in mean free path. (1992)
15. Longest mean free path stands for
 (a) H_2 (b) N_2 (c) O_2 (d) Cl_2 (1995)
16. Arrange the van der Waals constant a for the gases:
 I $C_6H_6(g)$ A 0.217
 II $C_6H_5.CH_3(g)$ B 5.464
 III $Ne(g)$ C 18.000
 IV $H_2O(g)$ D 24.060
 (a) I - A, II - D, III - C, IV - B
 (b) I - D, II - A, III - B, IV - C
 (c) I - C, II - D, III - A, IV - B
 (d) I - B, II - C, III - A, IV - D (1995)
17. The ratio between the root mean square speed of H_2 at 50 K and that of O_2 at 800 K is
 (a) 4 (b) 2 (c) 1 (d) 1/4 (1996)
18. X ml of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is
 (a) 10 seconds : He (b) 20 seconds : O_2
 (c) 25 seconds : CO (d) 55 seconds : CO_2 (1996)
19. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is
 (a) 1.2 atm (b) 2.4 atm (c) 2.0 atm (d) 1.0 atm (1996)
20. The compressibility factor for an ideal gas is
 (a) 1.5 (b) 1.0 (c) 2.0 (d) ∞ (1997)
21. A gas will approach ideal behaviour at
 (a) low temperature and low pressure
 (b) low temperature and high pressure
 (c) high temperature and low pressure
 (d) high temperature and high pressure. (1999)
22. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is the temperature of the gas, then
 (a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$
 (c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7} T(N_2)$ (2000)
23. The compressibility of a gas is less than unity at STP. Therefore,
 (a) $V_m > 22.4$ litres (b) $V_m < 22.4$ litres
 (c) $V_m = 22.4$ litres (d) $V_m = 44.8$ litres (2000)
24. At $100^\circ C$ and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3} , then the volume occupied by water molecules in 1 litre of steam at that temperature is
 (a) 6 cm^3 (b) 60 cm^3 (c) 0.6 cm^3 (d) 0.06 cm^3 (2000)
25. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as
 (a) d^2 (b) d (c) \sqrt{d} (d) $1/\sqrt{d}$ (2001)
26. Which of the following volume (V)-temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?
 (a)  (b) 
 (c)  (d)  (2002)
27. When the temperature is increased, surface tension of water
 (a) increases
 (b) decreases
 (c) remains constant
 (d) shows irregular behaviour. (2002)
28. Positive deviation from ideal behaviour takes place because of
 (a) molecular interaction between atoms and $PV/nRT > 1$
 (b) molecular interaction between atoms and $PV/nRT < 1$
 (c) finite size of atoms and $PV/nRT > 1$
 (d) finite size of atoms and $PV/nRT < 1$ (2003)
29. The root mean square velocity of one mole of a monoatomic gas having molar mass M is $u_{r.m.s.}$. The relation between the average kinetic energy (E) of the gas and $u_{r.m.s.}$ is
 (a) $u_{r.m.s.} = \sqrt{\frac{3E}{2M}}$ (b) $u_{r.m.s.} = \sqrt{\frac{2E}{3M}}$
 (c) $u_{r.m.s.} = \sqrt{\frac{2E}{M}}$ (d) $u_{r.m.s.} = \sqrt{\frac{E}{3M}}$ (2004)

30. The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be
 (a) 4 (b) 2
 (c) 1 (d) 0.5 (2005)
31. When one mole of monoatomic ideal gas at T K undergoes adiabatic change under a constant external pressure of 1 atm changes volume from 1 litre to 2 litre, the final temperature in Kelvin would be
 (a) $\frac{T}{2^{(2/3)}}$ (b) $T + \frac{2}{3} \times 0.0821$
 (c) T (d) $T - \frac{2}{3} \times 0.0821$ (2005)
32. The heat capacity of liquid water at constant pressure, C_p is 18 cal deg⁻¹ mol⁻¹. The value of heat capacity of water at constant volume C_v is approximately
 (a) 18 cal deg⁻¹ mol⁻¹ (b) 16 cal deg⁻¹ mol⁻¹
 (c) 10.8 cal deg⁻¹ mol⁻¹ (d) cannot be predicted. (2006)
33. The term that corrects for the attractive forces present in a real gas in the van der Waals equation is
 (a) nb (b) $\frac{an^2}{V^2}$ (c) $-\frac{an^2}{V^2}$ (d) $-nb$. (2009)
34. For one mole of a van der Waals gas when $b = 0$ and $T = 300$ K, the PV vs $1/V$ plot is shown below. The value of the van der Waals constant a (atm litre² mol⁻²) is

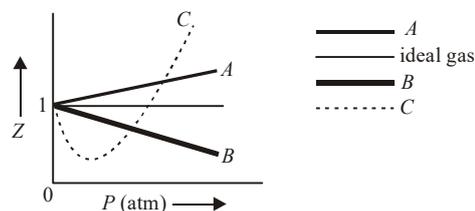


- (a) 1.0 (b) 4.5 (c) 1.5 (d) 3.0 (2012)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

35. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules
 (a) are above the inversion temperature
 (b) exert no attractive forces on each other
 (c) do work equal to loss in kinetic energy
 (d) collide without loss of energy. (1984)

36. If a gas is expanded at constant temperature
 (a) the pressure decreases
 (b) the kinetic energy of the molecules remains the same
 (c) the kinetic energy of the molecules decreases
 (d) the number of molecules of the gas increases. (1986)
37. Equal weights of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is
 (a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16 (1993)
38. According to Graham's law, at a given temperature the ratio of the rates of diffusion $\frac{A}{B}$ of gases A and B is given by
 (a) $(P_A/P_B) (M_A/M_B)^{1/2}$ (b) $(M_A/M_B) (P_A/P_B)^{1/2}$
 (c) $(P_A/P_B) (M_B/M_A)^{1/2}$ (d) $(M_A/M_B) (P_B/P_A)^{1/2}$
 (Where P and M are pressure and molecular weights of gases A and B respectively). (1998)
39. The given graph represents the variation of Z (compressibility factor = $\frac{PV}{nRT}$) versus P , for three real gases A , B and C . Identify the only incorrect statement.



- (a) For the gas A , $a = 0$ and its dependence on P is linear at all pressures.
 (b) For the gas B , $b = 0$ and its dependence on P is linear at all pressures.
 (c) For the gas C , which is typical real gas for which neither a nor $b = 0$. By knowing the minima and the point of intersection, with $Z = 1$, a and b can be calculated.
 (d) At high pressure, the slope is positive for all real gases. (2006)
40. A gas described by van der Waals equation
 (a) behaves similar to an ideal gas in the limit of large molar volumes
 (b) behaves similar to an ideal gas in the limit of large pressures
 (c) is characterised by van der Waals coefficients that are dependent on identity of the gas but are independent of temperature

Gaseous and Liquid States

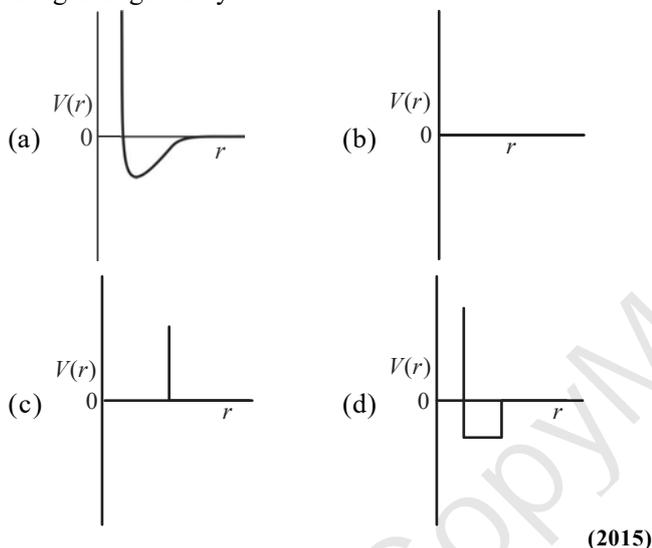
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(d) has the pressure that is lower than the pressure exerted by the same behaving ideally. (2008)

41. According to kinetic theory of gases

- (a) collisions are always elastic
 (b) heavier molecules transfer more momentum to the walls of the container
 (c) only a small number of molecules have very high velocity
 (d) between collisions, the molecules move in straight lines with constant velocities. (2011)

42. One mole of a monoatomic real gas satisfies the equation $p(V - b) = RT$ where b is a constant. The relationship of interatomic potential $V(r)$ and interatomic distance r for the gas is given by



Fill in the Blanks

43. The total energy of one mole of an ideal monoatomic gas at 27°C is calories. (1984)
 44. $C_p - C_v$ for an ideal gas is..... . (1984)
 45. The rate of diffusion of gas is proportional to square root of both and molecular mass. (1986)
 46. The value of PV for 5.6 litres of an ideal gas is RT , at N.T.P. (1987)
 47. 8 gram each of oxygen and hydrogen at 27°C will have the total kinetic energy in the ratio of (1989)
 48. The absolute temperature of an ideal gas is to/ than the average kinetic energy of the gas molecules. (1997)

True / False

49. Kinetic energy of a molecule is zero at 0°C . (1985)
 50. A gas in a closed container will exert much higher pressure due to gravity at the bottom than at the top. (1985)
 51. In the van der Waals equation, $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$, the constant a reflects the actual volume of the gas molecules. (1993)
 52. A mixture of ideal gases is cooled upto liquid helium temperature (4.22 K) to form an ideal solution. (1996)

Subjective Problems

53. Calculate the density of NH_3 at 30°C and 5 atm pressure. (1978)
 54. 3.7 g of a gas at 25°C occupied the same volume as 0.184 g of hydrogen at 17°C and at the same pressure. What is the molecular weight of the gas? (1979)
 55. 4.215 g of a metallic carbonate was heated in a hard glass tube and the CO_2 evolved was found to measure 1336 ml at 27°C and 700 mm pressure. What is the equivalent weight of the metal? (1979)
 56. A hydrocarbon contains 10.5 g of carbon per gram of hydrogen. 1 litre of the vapour of the hydrocarbon at 127°C and 1 atmosphere pressure weighs 2.8 g. Find the molecular formula of the hydrocarbon. (1980)
 57. A straight glass tube has two inlets X and Y at the two ends. The length of the tube is 200 cm. HCl gas through inlet X and NH_3 gas through inlet Y are allowed to enter the tube at the same time. White fumes appear at a point P inside the tube. Find the distance of P from X . (1980)
 58. The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 minutes. (1981)
 59. At room temperature, ammonia gas at 1 atm pressure and hydrogen chloride gas at P atm pressure are allowed to effuse through identical pin holes from opposite ends of a glass tube of one metre length and of uniform cross-section. Ammonium chloride is first formed at a distance of 60 cm from the end through which HCl gas is sent in. What is the value of P ? (1982)

60. Calculate the average of kinetic energy, in Joules of the molecules in 8.0 g of methane at 27°C. (1982)
61. Oxygen is present in 1 litre flask at a pressure of 7.6×10^{-10} mm of Hg. Calculate the number of oxygen molecules in the flask at 0°C. (1983)
62. When 2 g of a gas *A* is introduced into an evacuated flask kept at 25°C, the pressure is found to be one atmosphere. If 3 g of another gas *B* is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights $M_A : M_B$. (1983)
63. 'Equal volumes of gases contain equal number of atoms', is true at what conditions? (1984)
64. Calculate the root mean square velocity of ozone kept in a closed vessel at 20°C and 82 cm mercury pressure. (1985)
65. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at N.T.P. from a cylinder containing the gas at 20 atmospheres at 27°C. If the cylinder can hold 2.82 litres of water, calculate the number of balloons that can be filled up. (1987)
66. The average velocity at T_1 K, and the most probable at T_2 K of CO_2 gas is 9.0×10^4 cm sec⁻¹. Calculate the value of T_1 and T_2 . (1990)
67. Calculate the volume occupied by 5.0 g of acetylene gas at 50°C and 740 mm pressure. (1991)
68. At 27°C, hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of H_2 is leaked through the same hole for 20 minutes. After the effusion of the gases the mixture exerts a pressure of 6 atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litres, what is the molecular weight of the unknown gas? (1992)
69. At room temperature the following reactions proceed nearly to completion:

$$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$$
The dimer, N_2O_4 , solidifies at 262 K. A 250 ml flask and a 100 ml flask are separated by a stopcock. At 300 K, the nitric oxide in the larger flask exerts a pressure of 1.053 atm, and the smaller one contains oxygen at 0.789 atm. The gases are mixed by opening the stopcock and after the end of the reaction the flasks are cooled at 220 K. Neglecting the vapour pressure of the dimer, find out the pressure and composition of the gas remaining at 220 K. (Assume the gases to behave ideally). (1992)
70. A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of 7.57×10^3 Nm⁻². Calculate the root mean square (r.m.s) speed and the temperature of the gas molecules. If the ratio of the most probable speed to the root mean square speed is 0.82, calculate the most probable speed for these molecules at this temperature. (1993)
71. A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. What is the composition of the mixture effusing out initially? (1994)
72. An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the weight of the full cylinder reduces to 23.2 kg. Find out the volume of the gas in cubic meters used up at the normal usage conditions, find the final pressure inside the cylinder. Assume LPG to be *n*-butane with normal boiling point of 0°C. (1994)
73. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 litres at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O . Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture. (1995)
74. The composition of the equilibrium mixture ($\text{Cl}_2 \rightleftharpoons 2\text{Cl}$), which is attained at 1200°C, is determined by measuring the rate of effusion through a pin-hole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of the chlorine molecules dissociated into atoms. (Relative atomic mass of Kr = 84.) (1995)
75. A 20.0 cm³ mixture of CO , CH_4 and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13.0 cm³. A further contraction of 14.0 cm³ occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage. (1995)
76. One litre of a mixture of O_2 and O_3 at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 ml of *M*/10 sodium thiosulphate solution for titration. What is the weight percent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture? (1997)

Gaseous and Liquid States

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77. One way of writing the equation of state for real gases is

$$PV = RT \left[1 + \frac{B}{V} + \dots \right]$$

where B is a constant. Derive an approximate expression for B in terms of the van der Waals constant a and b .

(1997)

78. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g ml⁻¹ and, 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molar mass of the gas.

(1998)

79. The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$. Assuming ideal behaviour of all gases, calculate the density of equilibrium mixture at 400 K and 1.0 atmosphere. (Relative atomic mass of P = 31.0 and Cl = 35.5).

(1998)

80. Using van der Waals equation, calculate the constant, a when two moles of a gas confined in a four litre flask exerts a pressure of 11.0 atmospheres at a temperature of 300 K. The value of b is 0.05 L mol⁻¹.

(1998)

81. For the reaction, $\text{N}_2\text{O}_{5(g)} = 2\text{NO}_{2(g)} + 0.5 \text{O}_{2(g)}$, calculate the mole fraction of $\text{N}_2\text{O}_{5(g)}$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

(1998)

82. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound.

(1998)

83. The pressure exerted by 12 g of an ideal gas at temperature $t^\circ\text{C}$ in a vessel of volume V litre is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V . (Molecular weight of the gas = 120).

(1999)

84. Calculate the pressure exerted by one mole of CO_2 gas at 273 K if the van der Waals constant $a = 3.592 \text{ dm}^6 \text{ atm mol}^{-2}$. Assume that the volume occupied by CO_2 molecules is negligible.

(2000)

85. The compression factor (compressibility factor) for one mole of a van der Waals gas at 0°C and 100 atmospheric pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals constant a .

(2001)

86. The density of the vapours of a substance at 1 atm pressure and 500 K is 0.36 kg m⁻³. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

(a) Determine

(i) molecular weight,

(ii) molar volume,

(iii) compression factor (Z) of the vapour and

(iv) which forces among the gas molecules are dominating, the attractive or the repulsive?

(b) If the vapour behaves ideally at 1000 K, determine the average translational kinetic energy of a molecule.

(2002)

87. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature.

(2003)

88. A graph is plotted between PV_m along Y -axis and P along X -axis, where V_m is the molar volume of a real gas. Find the intercept along Y -axis.

(2004)

Matrix Match Type

89. Match gases under specified conditions listed in Column I with their properties/laws in Column II.

Column I

Column II

- | | |
|--|--|
| (A) hydrogen gas
($P = 200 \text{ atm}$,
$T = 273 \text{ K}$) | (p) compressibility
factor $\neq 1$ |
| (B) hydrogen gas
($P \approx 0$, $T = 273 \text{ K}$) | (q) attractive forces are
dominant |
| (C) CO_2 ($P = 1 \text{ atm}$,
$T = 273 \text{ K}$) | (r) $PV = nRT$ |
| (D) real gas with very
large molar volume | (s) $P(V - nb) = nRT$ |

(2007)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

90. **Statement-1** : The value of van der Waals constant a is larger for ammonia than for nitrogen.

Statement-2 : Hydrogen bonding is present in ammonia.

(1998)

91. Statement-1 : The pressure of a fixed amount of an ideal gas is proportional to its temperature.

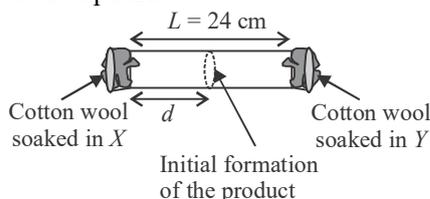
Statement-2 : Frequency of collisions and their impact both increase in proportion to the square root of temperature. (2000)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension-1

X and Y are two volatile liquids with molar weights of 10 g mol^{-1} and 40 g mol^{-1} respectively. Two cotton plugs, one soaked in X and the other soaked in Y , are simultaneously placed at the ends of a tube of length $L = 24 \text{ cm}$, as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K. Vapours of X and Y react to form a product which is first observed at a distance $d \text{ cm}$ from the plug soaked in X . Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.



92. The value of d in cm (shown in the figure), as estimated from Graham's law, is

- (a) 8 (b) 12 (c) 16 (d) 20

93. The experimental value of d is found to be smaller than the estimate obtained using Graham's law. This is due to

(a) larger mean free path of X as compared to that of Y
 (b) larger mean free path for Y as compared to that of X
 (c) increased collision frequency of Y with the inert gas as compared to that of X with the inert gas
 (d) increased collision frequency of X with the inert gas as compared to that of Y with the inert gas. (2014)

Integer Answer Type

94. At 400 K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is (2009)

95. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm. at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to (2011)

ANSWER KEY

- | | | | | | |
|---|--|--|---|------------------------------|----------------------------|
| 1. (a) | 2. (b) | 3. (a) | 4. (b) | 5. (b) | 6. (d) |
| 7. (a) | 8. (c) | 9. (b) | 10. (c) | 11. (b) | 12. (a) |
| 13. (d) | 14. (a) | 15. (a) | 16. (c) | 17. (c) | 18. (b) |
| 19. (b) | 20. (b) | 21. (c) | 22. (c) | 23. (b) | 24. (c) |
| 25. (d) | 26. (c) | 27. (b) | 28. (a) | 29. (c) | 30. (b) |
| 31. (a) | 32. (b) | 33. (b) | 34. (c) | 35. (b) | 36. (a, b) |
| 37. (d) | 38. (c) | 39. (b) | 40. (a, c) | 41. (a, b, d) | 42. (c) |
| 43. 900 | 44. R | 45. Inversely, density | 46. 0.25 | 47. 1 : 16 | |
| 48. Less | 49. False | 50. False | 51. False | 52. False | 53. 3.42 g/litre |
| 54. 41.32 | 55. 12.16 | 56. C_7H_8 | 57. 81.13 cm | 58. 1.236 : 1 | 59. 2.198 atm |
| 60. $6.21 \times 10^{-21} \text{ J}$ | 61. 2.69×10^{10} | 62. 1 : 3 | 63. Under similar conditions of temperature and pressure. | 67. 5.23 L | 68. 1033 |
| 64. $3.9 \times 10^4 \text{ cm sec}^{-1}$ | 65. 10 | 66. 1682.5 K | 67. 5.23 L | 70. 405.2 m s^{-1} | 71. 8 : 1 |
| 69. 350 ml is occupied by NO that has been left unreacted., 0.221 atm | 72. 1.48 atm, 2.460 m^3 | 73. ethane = 66.25, ethene = 33.75 | 74. 0.137 | 77. $B = \frac{b - a/RT}{V}$ | |
| 75. CO = 50%, CH_4 = 20%, He = 30% | 76. 6.66%, 1.2×10^{21} | | | 81. 0.4 | 82. XeF_6 |
| 78. 123.0 | 79. 4.54 g/lit | 80. $6.46 \text{ atm L}^2 \text{ mol}^{-2}$ | | | |
| 83. 0.821 L | 84. 0.9922 atm | 85. $1.253 \text{ atm L}^2 \text{ mol}^{-2}$ | | | |
| 86. 18.09, 50.25 L, 1.225, repulsive force dominates, $2.07 \times 10^{-20} \text{ J}$ per molecule | | | | | 87. 434 m s^{-1} |
| 88. RT | 89. (A) \rightarrow p, s, (B) \rightarrow r, (C) \rightarrow p, q, (D) \rightarrow r | | | 90. (a) | 91. (b) |
| 92. (c) | 93. (d) | 94. (4) | 95. (7) | | |

Explanations

1. (a): Pressure exerted by $O_2 \propto$ mole fraction of O_2

$$\text{Mole fraction of } O_2 = \frac{W/32}{W/16 + W/32} = \frac{1}{3}$$

2. (b): The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle temperature or Boyle point.

3. (a): $U_{rms} : U_{av} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} = \sqrt{3} : \sqrt{\frac{8}{\pi}} = 1.086:1$

4. (b): K.E. $\propto T$, kinetic energy depends on temperature of the gas and is independent of the nature of the gas. Thus at 298 K, K.E. of both H and He is same *i.e.* same as that of H_2 .

5. (b): Pressure exerted by hydrogen \propto mole fraction of H_2

$$\text{Mole fraction of } H_2 = \frac{W/2}{W/16 + W/2} = \frac{8}{9}$$

6. (d): According to Graham's law of diffusion,

$$r \propto \frac{1}{\sqrt{d}} \text{ or } r \propto \frac{1}{\sqrt{M}}; \quad \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

7. (a): $U_{av} = \sqrt{\frac{8RT}{\pi M}}$

$$\text{or } \frac{U_{av_1}}{U_{av_2}} = \sqrt{\frac{T_1}{T_2}} \text{ or } \frac{0.3}{U_{av_2}} = \sqrt{\frac{300}{1200}} = \sqrt{\frac{1}{4}} = \frac{1}{2}$$

$$\text{or } U_{av_2} = 0.3 \times 2 = 0.6 \text{ m/s}$$

8. (c): According to van der Waals equation,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ (for one mole of real gas).}$$

In this equation $\left(P + \frac{a}{V^2}\right)$ accounts for intermolecular forces.

9. (b): Rate of diffusion, $r \propto \sqrt{\frac{1}{\text{Molar mass}}}$

$$\text{Molar mass of HCl} = 1 + 35.5 = 36.5$$

$$\text{Molar mass of } NH_3 = 14 + 3 \times 1 = 17$$

$$\therefore \text{Molar mass of HCl} > \text{Molar mass of } NH_3$$

Thus rate of diffusion of NH_3 will be more and so the white NH_4Cl ring will be formed near the hydrogen chloride bottle.

10. (c): a refers to the force of attraction between the gas molecules. Greater the value of a more easily the gas gets liquefied.

11. (b): $V_m \propto \frac{nT}{P}$, so lower the temperature and higher the pressure, lower is the molar volume and hence higher is the density.

12. (a): $\frac{r_{CH_4}}{r_X} = \sqrt{\frac{M_X}{M_{CH_4}}}$ or, $2 = \sqrt{\frac{M_X}{16}}$ or $M_X = 4 \times 16 = 64$

13. (d): Average K.E. = $\frac{3}{2} kT$ or K.E. $\propto T$.

14. (a): With increase of temperature, K.E. increases *i.e.* the average molecular speed increases. The molecules now strike the walls of the container with greater velocity and it increases the pressure. Because more number of collisions occur on walls of container.

15. (a): The mean free path $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N}$

$$\text{or } \lambda \propto \frac{1}{\sigma^2} \text{ [}\sigma \text{ is molecular diameter]}$$

Thus the path is largest for smallest s . Here the s is smallest for H_2 .

16. (c): a (*i.e.* the magnitude of attractive forces) increases with the size of the molecules. Thus inert gases will have minimum value followed by H_2O , C_6H_6 and $C_6H_5CH_3$.

17. (c): $U_{rms} = \sqrt{\frac{3RT}{M}}$

$$\therefore \frac{U_{H_2}}{U_{O_2}} = \left[\frac{3R \times 50}{2} \bigg/ \frac{3R \times 800}{32} \right]^{\frac{1}{2}} = 1$$

18. (b): Under similar conditions of temperature and pressure

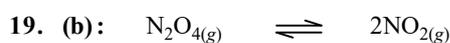
$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \text{ and } \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}} \text{ [}\therefore t \propto \frac{1}{r}\text{]}$$

$$\text{For He, } t_2 = 5 \times \sqrt{\frac{4}{2}} = 5 \times \sqrt{2} \neq 10 \text{ sec.}$$

$$\text{For } O_2, t_2 = 5 \times \sqrt{\frac{32}{2}} = 5 \times 4 = 20 \text{ sec.}$$

$$\text{For CO, } t_2 = 5 \times \sqrt{\frac{28}{2}} = 5 \times \sqrt{14} \neq 25 \text{ sec.}$$

$$\text{For } CO_2, t_2 = 5 \times \sqrt{\frac{44}{2}} = 5 \times \sqrt{22} \neq 55 \text{ sec.}$$



$$\text{Initial } 1 \text{ mol} \qquad \qquad \qquad 0$$

$$\text{At eq. } \frac{80}{92} = 0.86 \text{ mol} \qquad \qquad \qquad \frac{20}{46} = 0.43 \text{ mol}$$

According to ideal gas equation, at two conditions.

$$\text{At } 300 \text{ K} \quad P_0 V = n_0 R T_0$$

$$1 \times V = 1 \times R \times 300 \qquad \qquad \qquad \dots(i)$$

$$\text{At } 600 \text{ K} \quad P_1 V = n_1 R T_1$$

$$P_1 \times V = (0.86 + 0.43) \times R \times 600 \\ = 1.29 \times R \times 600 \qquad \qquad \qquad \dots(ii)$$

Dividing (ii) by (i), we get

$$\frac{P_1}{1} = \frac{1.29 \times 600}{1 \times 300} \text{ or } P_1 = 2.58 \text{ atm}$$

20. (b): Compressibility factor, $Z = \frac{PV}{RT}$
In case of an ideal gas $PV = RT$ (for 1 mole)
Hence, $Z = 1$
21. (c): For ideal behaviour, the gaseous molecules should be far apart. This is favoured by high temperature and low pressure.
22. (c): $\sqrt{\frac{3RT}{2}}$ for $H_2 = \sqrt{7} \times \sqrt{\frac{3RT}{28}}$ for $N_2 \therefore T_{H_2} < T_{N_2}$

$$\left[T_{N_2} \text{ or } T_{H_2} = \frac{1}{2} T_{N_2} \right]$$
23. (b): $Z = \frac{PV}{nRT}$ for ideal gas.
As, $Z < 1$, $\therefore \frac{PV}{nRT} < 1$ or $PV < nRT$
or, $1 \text{ atm} \times V < 1 \text{ mole} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}$
or, $V < 0.0821 \times 273 \text{ L}$ or, $V < 22.4 \text{ L}$
24. (c): Mass of 1 L of water vapour = 0.6 g
 $\therefore V = \frac{\text{mass}}{\text{density}} = \frac{0.6}{1.0} = 0.6 \text{ cm}^3$
25. (d): $U_{rms} = \sqrt{\frac{3RT}{M}}$, $PV = nRT$ [Ideal gas Eqn.]
or $\frac{RT}{M} = \frac{PV}{M}$ [$\because RT = PV$]
or $\frac{RT}{M} = \frac{P}{d}$ [$\because \frac{V}{M} = \frac{1}{d}$]
 $\therefore U_{rms} = \sqrt{\frac{3P}{d}}$
Hence, at constant pressure $U_{rms} \propto \frac{1}{\sqrt{d}}$
26. (c): $PV = RT$ (For 1 mole of gas)
or $V = \frac{RT}{P} = \frac{0.082 \times 373}{1} = 30.58 \text{ L}$
27. (b): The internal energy increases with increase of temperature and it causes decrease in other molecular forces of attraction and so the surface tension decreases.
28. (a): The extent of deviation of a real gas from an ideal behaviour is expressed in terms of compressibility factor.
For ideal gas, $Z = \frac{PV}{nRT}$
For positive deviation $Z > 1$ i.e. $\frac{PV}{nRT} > 1$
29. (c): Average K.E., $E = \frac{1}{2} MU_{rms}^2$
 $\therefore U_{rms}^2 = \frac{2E}{M}$ or $U_{rms} = \sqrt{\frac{2E}{M}}$
30. (b): $\frac{r_{He}}{r_{CH_4}} = \sqrt{\frac{M_{CH_4}}{M_{He}}} = \sqrt{\frac{16}{4}} = 2$
31. (a): $TV^{\gamma-1} = \text{constant}$ or $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$
In case of a monoatomic gas $\gamma = \frac{5}{3}$, thus $\gamma - 1 = \frac{2}{3}$
So, $T_1 V_1^{2/3} = T_2 V_2^{2/3}$
or $T_1 (1)^{2/3} = T_2 (2)^{2/3}$ or $T_2 = \frac{T_1}{2^{2/3}}$
32. (b): $C_p - C_v = 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$
 $C_v = C_p - 2 = 18 - 2 = 16 \text{ cal deg}^{-1} \text{ mol}^{-1}$.
33. (b): The gas equation, $PV = nRT$, is followed by ideal gases, however no gas is ideal or perfect, so the behaviour of real gases is governed by the van der Waals gas equation.
The pressure correction term $\frac{n^2 a}{V^2}$ corresponds to the attractive forces among the molecules (in the van der Waals equation).
 \therefore The equation is $\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$.
34. (c): van der Waal's equation is $\left(P + \frac{a}{V^2} \right) (V - b) = RT$
As given that $b = 0$
 $PV + \frac{a}{V} = RT$ or $PV = RT - \frac{a}{V}$
Comparing with $y = mx + c$
Intercept (c) = RT
Slope (m) = $-a$
Slope = $\frac{y_2 - y_1}{x_2 - x_1} = \frac{20.1 - 21.6}{3 - 2} = -1.5$
Thus, $a = +1.5$
35. (b): In case of ideal gases, there exists no forces of attraction between the molecules.
36. (a,b): At constant temperature, the kinetic energy remains same ($\therefore K.E. \propto T$) i.e. (b) is correct and (c) is incorrect.
At constant temperature
 $PV = \text{Constant}$ [Boyle's law]
If a gas expands i.e. V increases then P decreases i.e. (a) is correct (d) is incorrect because there is no change in number of molecules of gas.
37. (d): Pressure exerted by hydrogen \propto mole fraction of hydrogen
Mole fraction of hydrogen = $\frac{W/2}{W/2 + W/30} = \frac{W/2}{16W/30}$
 $= \frac{30}{2 \times 16} = \frac{15}{16}$ i.e. 15 : 16
38. (c): $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$
At constant temperature $r \propto P \times \sqrt{\frac{1}{M}}$

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$$\therefore r_A \propto P_A \times \sqrt{\frac{1}{M_A}} \text{ and } r_B \propto P_B \times \sqrt{\frac{1}{M_B}}$$

$$\text{or } \frac{r_A}{r_B} = \frac{P_A}{P_B} \times \sqrt{\frac{M_B}{M_A}} \text{ or } \frac{P_A}{P_B} \times \left(\frac{M_B}{M_A}\right)^{\frac{1}{2}}$$

39. (b) : From the graph it is clear that the value of Z decreases with increase of pressure. We can explain it as follows:
At high pressure, when P is large, V will be small and one cannot ignore b in comparison to V_m . However, the term $\frac{a}{V_m^2}$ may be considered negligible in comparison to P in van der Waals equation.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT, \quad P(V_m - b) = RT$$

$$\text{or, } Z = 1 + \frac{Pb}{RT}$$

Here Z is greater than 1 and it increases linearly with pressure.

Hence statement (b) is false.

40. (a, c) : van der Waals equation is given as

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

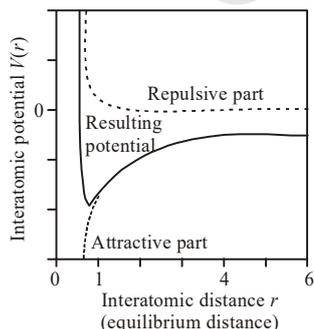
The term $\left(P + \frac{n^2 a}{V^2}\right)$ represents the pressure exerted by real gases. Whereas P is the pressure exerted by ideal gases.

$$P + \frac{a}{V_m^2} \approx P \text{ and } V_m - b = V_m$$

and van der Waals coefficient a and b are independent of temperature.

41. (a, b, d)

42. (c) : The interatomic potential $V(r)$ and interatomic distance (r) are related as

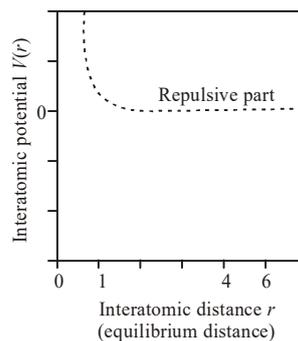


Now, for one mole of a monoatomic real gas which satisfies the equation,

$$p(V - b) = RT$$

the attractive forces are negligible because $a = 0$. Thus, only repulsive forces are present.

The repulsive forces tend to increase the energy of the system and contribute only at very close distance.



43. 900; For one mole of an ideal gas, $E = \frac{3}{2} RT$
 $= \frac{3}{2} \times 2 \times 300 = 900$ calories
44. R ; The specific heat constants for constant pressure and constant volume processes are related to the gas constant for a given gas.
45. Inversely, density; According to Graham's law of diffusion
 $\left[\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}\right]$
46. 0.25; Use $PV = nRT$ [5.6 L = 0.25 mole of gas]
47. 1:16; $\frac{K.E_{O_2}}{K.E_{H_2}} = \frac{\frac{3}{2} n_{O_2} \cdot RT}{\frac{3}{2} n_{H_2} \cdot RT} = \frac{n_{O_2}}{n_{H_2}} = \frac{8/32}{8/2} = \frac{1}{16}$ or 1 : 16.
48. Less; Average kinetic energy $K.E. = \frac{3}{2} RT$ or $E > T$.
49. False
 $K.E. = \frac{3}{2} RT$, $0^\circ C = 0 + 273$ or 273 K
 and at this temperature, $K.E. = \frac{3}{2} \times R \times 273$
50. False
 The gas pressure is due to collision of gaseous molecules on the walls of the container.
51. False
 In van der Waals equation 'a' refers to the intermolecular force of attraction between the gaseous molecules.
52. False
 It is not possible to liquefy an ideal gas because in an ideal gas no intermolecular forces of attraction exist.
53. From the ideal gas equation, $PV = nRT$
 $PV = \frac{m}{M} RT \Rightarrow P = \frac{m}{V} \times \frac{RT}{M} = d \frac{RT}{M} \therefore d = \frac{MP}{RT}$
 Substituting the values, we get
 $d = \frac{17 \times 5}{0.082 \times 303} = 3.42$ g/litre
54. Number of moles (n_1) of hydrogen = $\frac{0.184}{2} = 0.092$.
 Let M be the molecular weight of the gas. Then, number of moles (n_2) of gas = $\frac{3.7}{M}$.
 Using general gas equation for hydrogen

$$P_1V_1 = n_1RT_1 \quad \dots(i)$$

$$\text{and for gas } P_1V_1 = n_2RT_2 \quad \dots(ii)$$

(Note : Pressure and volume of hydrogen and gas are same)

$$\therefore \frac{P_1V_1}{P_1V_1} = \frac{n_1RT_1}{n_2RT_2} \text{ or } 1 = \frac{0.092 \times 290}{n_2 \times 298} \text{ or } n_2 = \frac{0.092 \times 290}{298}$$

$$\text{or } \frac{3.7}{M} = \frac{0.092 \times 290}{298} \text{ or } M = \frac{3.7 \times 298}{290 \times 0.092} = 41.32$$

The molecular weight of the gas is 41.32

55. $P_1 = 700 \text{ mm}, P_2 = 760 \text{ mm}$

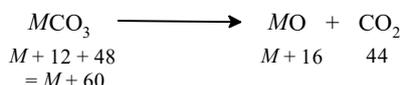
$$V_1 = 1336 \text{ ml}, V_2 = ?, T_1 = 300 \text{ K}, T_2 = 273 \text{ K}$$

$$\text{Since } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore V_2 = \frac{700 \times 1336 \times 273}{300 \times 760} = 1.1198 \text{ L at N.T.P.}$$

1.1198 L CO_2 is given by carbonate = 4.215 g

$$22.4 \text{ L } \text{CO}_2 \text{ is given by carbonate} = \frac{4.215}{1.1198} \times 22.4 \text{ g} = 84.315$$



Thus molecular weight of carbonate = 84.315

$$\therefore \text{Atomic weight of } M = 84.315 - 60 = 24.315$$

$$\therefore \text{Equivalent weight of } M = \frac{1}{2} \times 24.315 = 12.157 = 12.16$$

56. Since $PV = nRT \Rightarrow \therefore n = \frac{PV}{RT}$

$$n = \frac{1 \times 1}{0.082 \times 400}$$

$$\text{Number of moles } (n) = \frac{\text{weight}}{\text{molecular weight}}$$

$$\therefore \text{molecular weight} = \frac{\text{weight}}{n}$$

$$\therefore \text{molecular weight of hydrocarbon} = \frac{2.8 \times 400 \times 0.082}{1} = 91.84$$

Element	Weight of element	Relative number of atoms	Ratio of atoms	Whole number of atoms
Carbon	10.5	$10.5 \div 12 = 0.875$	1	7
Hydrogen	1.0	$1.0 \div 1 = 1.000$	1.1428	8

Thus empirical formula is C_7H_8

$$\text{Empirical formula weight} = (7 \times 12) + (1 \times 8) = 84 + 8 = 92$$

$$n = \frac{\text{molecular weight}}{\text{empirical formula weight}} = \frac{91.84}{92}$$

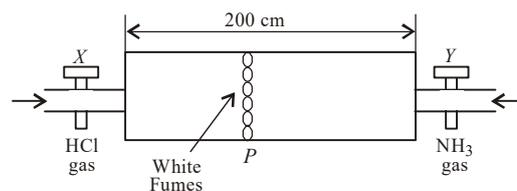
$$= 1 \text{ (nearest whole number)}$$

\therefore Empirical formula is the molecular formula.

Thus the molecular formula i.e. C_7H_8 .

57. Let ammonia diffuses through = $x \text{ cm}$.

and HCl diffuses through = $y \text{ cm}$.



Molecular weight of $\text{NH}_3 = 17$

Molecular weight of HCl = $35.5 + 1 = 36.5$

According to the Graham's law of diffusion

$$\frac{x}{y} = \sqrt{\frac{36.5}{17}} = \sqrt{2.147} = 1.465$$

$$\therefore \frac{x}{y} = 1.465 \text{ or } x = 1.465 y$$

$$x + y = 200 \text{ cm}$$

$$1.465 y + y = 200 \text{ or } y(1.465 + 1) = 200 \text{ cm}$$

$$\therefore y = \frac{200}{2.465} = 81.13 \text{ cm}$$

Distance between P and X = 81.13 cm

58. In the evacuated bulb we have a mixture of oxygen and another gas in 1 : 1 ratio and the total pressure due to both is 4000 mm.

Since they are in equal molar ratio, so the pressure of each gas is 2000 mm.

$$\begin{aligned} \text{Change in pressure} &= (2000 - 1500) \text{ mm of mercury} \\ &= 500 \text{ mm of mercury} \end{aligned}$$

$$\begin{aligned} \text{After 74 minutes, pressure of oxygen} &= 2000 - \frac{500 \times 74}{47} \\ &= (2000 - 787.2) \text{ mm} \\ &= 1212.8 \text{ mm} \end{aligned}$$

Since the rate of diffusion of a gas is inversely proportional to the square root of the molar mass of the gas, therefore

$$\frac{\text{Rate of diffusion of unknown gas}}{\text{Rate of diffusion of } \text{O}_2} = \sqrt{\frac{32}{79}}$$

$$\text{Now, at constant } T, \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$$

$$\therefore \text{Pressure drop of the other gas will be} = \sqrt{\frac{(787.2)^2 \times 32}{79}}$$

$$= 501.01 \text{ mm.}$$

$$\begin{aligned} \text{Thus pressure of the other gas} &= (2000 - 501.01) \text{ mm} \\ &= 1498.99 \text{ mm} \end{aligned}$$

$$\text{Hence molar ratio} = \frac{1498.99}{1212.8} = 1.236$$

i.e. the ratio is 1.236 : 1

59. At constant temperature, $\frac{r_1}{r_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}}$

When d distance is travelled by gas molecules in time t , then

$$r = \frac{d}{t} \text{ or } \frac{d_1}{t_1} \times \frac{t_2}{d_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}}$$

when $t_1 = t_2$

$$\frac{d_1}{d_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}} \text{ or, } \frac{40}{60} = \frac{1}{P_2} \times \sqrt{\frac{36.5}{17}}$$

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$$\text{or, } P_2 = \sqrt{\frac{36.5}{17}} \times \frac{60}{40} = 2.198 \text{ atm}$$

60. We know kinetic energy = $\frac{3}{2} RT$ [For 1 mole]

$$\text{Thus for } n \text{ moles the } K.E. \text{ will be} = n \times \frac{3}{2} RT$$

$$\text{Here } n = \frac{8}{16} = 0.5 \text{ [Mol. wt. of } \text{CH}_4 = 16]$$

$$R = 8.314 \text{ J/K/mole, } T = 27 + 273 = 300 \text{ K}$$

Substituting these values, we get

$$\text{Total } K.E. = 0.5 \times \frac{3}{2} \times 8.314 \times 300 = 1870.65 \text{ J}$$

$$\text{Hence average } K.E. \text{ per molecule} = \frac{1870.65}{0.5 \times 6.023 \times 10^{23}} = 6.21 \times 10^{-21} \text{ J}$$

61. Volume of the flask, $V = 1$ Litre

$$\text{Pressure in the flask, } P = 7.6 \times 10^{-10} \text{ mm of Hg}$$

$$= \frac{7.6 \times 10^{-10}}{760} \text{ atm} = 10^{-12} \text{ atm}$$

$$R = 0.082 \text{ atm litre } K^{-1} \text{ mol}^{-1}$$

$$T = 0 + 273 = 273 \text{ K.}$$

Using the gas equation,

$$PV = nRT, \text{ we get}$$

$$n \text{ (number of moles of gas)} = \frac{PV}{RT} = \frac{10^{-12} \times 1}{0.082 \times 273}$$

$$\therefore \text{Number of molecules of gas} = \frac{10^{-12} \times 1 \times 6.023 \times 10^{23}}{0.082 \times 273} = 2.69 \times 10^{10}$$

62. Given, weight of gas $A = 2$ g

$$\text{Pressure of } A = 1 \text{ atm, } T = 298 \text{ K}$$

Now another gas is introduced

$$\text{Weight of gas } B = 3 \text{ g}$$

$$\text{Pressure of mixture} = 1.5 \text{ atm}$$

From Dalton's law of partial pressure

$$P_M = P'_A + P'_B; \quad 1.5 = 1.0 + P'_B \text{ or } P'_B = 0.5 \text{ atm}$$

$$\text{For } A = P'_A \times V = \frac{2}{M_A} \times RT$$

$$\text{For } B = P'_B \times V = \frac{3}{M_B} \times RT$$

$$\therefore \frac{P'_A}{P'_B} = \frac{2}{3} \times \frac{M_B}{M_A} \quad \therefore \frac{M_A}{M_B} = \frac{2}{3} \times \frac{P'_B}{P'_A} = \frac{2}{3} \times \frac{0.5}{1.0} = \frac{1}{3}$$

i.e. 1 : 3

63. This is true under similar conditions of temperature and pressure. (According to Avogadro's law)

$$64. U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 293}{48}} = 3.9 \times 10^4 \text{ cm sec}^{-1}$$

$$65. \begin{array}{ll} V_1 = 2.82 \text{ L} & V_2 = ? \\ P_1 = 20 \text{ atm} & P_2 = 1 \text{ atm} \\ T_1 = 27 + 273 & T_2 = 273 \text{ K} \\ = 300 & \end{array}$$

$$\therefore V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{20 \times 2.82}{300} \times \frac{273}{1} \text{ L} = 51.324 \text{ L or } 51324 \text{ ml}$$

$$\text{Capacity of the balloon} = 2.82 \text{ L or } 2820 \text{ ml}$$

$$\text{Hence volume of hydrogen available for filling} = (51324 - 2820) \text{ ml} = 48504 \text{ ml}$$

Number of balloons to be filled up

$$\text{Radius of balloon} = \frac{21}{2} = 10.5 \text{ cm}$$

$$\therefore \text{Volume of balloon} = \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10.5)^3 = 4851 \text{ cm}^3 \text{ or } 4851 \text{ ml}$$

$$\therefore \text{Number of balloons to be filled} = \frac{48504}{4851} = 10$$

$$66. \text{ We know } U_{Av} = \sqrt{\frac{8RT}{\pi M}} = 9.0 \times 10^4 \text{ cm sec}^{-1} \text{ at } T_1$$

$$\text{Most probable velocity} = \sqrt{\frac{2RT}{M}} = 9.0 \times 10^4 \text{ cm sec}^{-1} \text{ at } T_2$$

$$\text{Now average velocity at } T_1 = \sqrt{\frac{8 \times 8.314 \times T_1}{3.14 \times 44 \times 10^{-3}}}$$

$$\text{Most probable velocity at } T_2 = \sqrt{\frac{2 \times 8.314 \times T_2}{44 \times 10^{-3}}}$$

$$\text{Since average velocity at } T_2 = \text{Most probable velocity at } T_2 = 9.0 \times 10^2 \text{ ms}^{-1}$$

$$\therefore \sqrt{\frac{8 \times 8.314 \times T_1}{3.14 \times 44 \times 10^{-3}}} = \sqrt{\frac{2 \times 8.314 \times T_2}{44 \times 10^{-3}}} = 9.0 \times 10^2$$

$$\text{or } \sqrt{\frac{4 T_1}{3.14}} = \sqrt{T_2}$$

$$\text{or } \frac{4 T_1}{3.14} = T_2 \text{ or } T_1 = \frac{3.14}{4} T_2 = 0.785 T_2$$

$$\text{Also } \sqrt{\frac{2 \times 8.314 \times T_2}{44 \times 10^{-3}}} = 9.0 \times 10^2$$

$$\text{or } \frac{2 \times 8.314 \times T_2}{44 \times 10^{-3}} = 81.0 \times 10^4$$

$$\text{or } T_2 = \frac{81.0 \times 10^4 \times 44 \times 10^{-3}}{2 \times 8.314} = 2143.4 \text{ K}$$

$$\therefore T_1 = 0.785 T_2 = 2143.4 \times 0.785 = 1682.5 \text{ K}$$

67. Using the gas equation, $PV = nRT$

$$\text{or } PV = \frac{m}{M} RT \text{ or } V = \frac{m}{M} \times \frac{RT}{P}$$

$$\text{Here } M = \text{Molecular weight of acetylene (C}_2\text{H}_2) = 24 + 2 = 26$$

$$P = 740 \text{ mm} = \frac{740}{760} \text{ atm}$$

$$T = 50 + 273 = 323 \text{ K}$$

$$\therefore V = \frac{mRT}{MP} = \frac{5 \times 0.082 \times 323 \times 760}{26 \times 740} = 5.23 \text{ L}$$

$$68. \text{ Total number of moles in gaseous mixture, } n = \frac{PV}{RT} = \frac{6 \times 3}{0.082 \times 300} = 0.7308 \text{ mol}$$

∴ Number of moles of unknown gas in the mixture
 = (0.7308 - 0.7) mol = 0.0308 mol

$$\text{since } \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

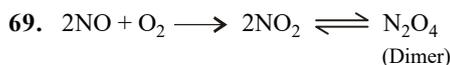
$$\text{or } \sqrt{M_2} = \frac{r_1}{r_2} \times \sqrt{M_1} \quad \text{or } M_2 = \left(\frac{r_1}{r_2}\right)^2 \times M_1$$

$$\text{Also } \frac{r_1}{r_2} = \frac{\text{Amount of hydrogen gas}}{\text{Amount of unknown gas}} = \frac{0.7}{0.0308}$$

$$\therefore M_2 = \left(\frac{0.7}{0.0308}\right)^2 \times 2 \quad [\because \text{Mol. wt. of H}_2 = 2]$$

$$\text{or } M_2 = 1033$$

∴ Molecular weight of unknown gas = 1033



$$\text{Now, } PV = nRT \quad \text{or } n = \frac{PV}{RT}$$

$$\text{Moles of NO in the larger flask} = \frac{1.053 \times 0.25}{0.082 \times 300} = 0.0107 \text{ moles}$$

$$\text{Moles of O}_2 \text{ in the smaller flask} = \frac{0.789 \times 0.1}{0.082 \times 300} = 0.0032 \text{ moles}$$

Therefore, moles of NO reacting completely with 0.0032 moles of O₂ = 2 × 0.0032 = 0.0064 moles

$$\text{Hence, moles of NO left unreacted} = 0.0107 - 0.0064 = 0.0043 \text{ moles}$$

Oxygen will be completely converted into NO₂ and NO₂ will then be completely converted into N₂O₄ (dimer) which becomes solid at 262 K; hence at 220 K, N₂O₄ is in solid state and only NO is present in gaseous state. Thus the whole volume (250 + 100 = 350 ml) of 350 ml is occupied by NO that has been left unreacted.

$$\begin{aligned} \text{Therefore the pressure, } P \text{ of NO gas} &= \frac{nRT}{V} \\ &= \frac{0.0043 \times 0.082 \times 220}{0.350} = 0.221 \text{ atm} \end{aligned}$$

70. $U_{rms} = \sqrt{\frac{3P}{d}}$

$$\text{Here, } P = 7.57 \times 10^3 \text{ Nm}^{-2} = 7.57 \times 10^3 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$\text{Density of gas, } d = \frac{\text{Mass of } 2 \times 10^{21} \text{ molecules of N}_2}{\text{Volume of } 2 \times 10^{21} \text{ molecules of N}_2}$$

$$\begin{aligned} \text{Mass of } 2 \times 10^{21} \text{ molecules of N}_2 &= \frac{28 \times 2 \times 10^{21}}{6.023 \times 10^{23}} = \frac{56}{602.3} = 0.093 \text{ g} \end{aligned}$$

$$\therefore \text{Density} = \frac{0.093 \times 10^{-3}}{10^{-3}} = 0.093 \text{ kg/m}^3$$

Substituting these values of P and d , we get

$$U_{rms} = \sqrt{\frac{3 \times 7.57 \times 10^3}{0.093}} \text{ ms}^{-1} = 494.16 \text{ ms}^{-1}$$

$$\text{Now, } PV = nRT$$

$$\text{Here } n = \frac{2.0 \times 10^{21}}{6.023 \times 10^{23}} = 3.32 \times 10^{-3} \text{ mol}$$

$$V = 1 \text{ L} = 10^{-3} \text{ m}^3 \therefore T = \frac{PV}{nR} = \frac{7.57 \times 10^3 \times 10^{-3}}{3.32 \times 10^{-3} \times 8.34} \text{ K} = 273.39 \text{ K}$$

Since most probable velocity = $0.82 \times U_{rms}$

$$\therefore \text{Most probable velocity} = 0.82 \times 494.16 \text{ ms}^{-1} = 405.2 \text{ ms}^{-1}$$

71. Molar ratio of He : CH₄ = 4 : 1

$$\therefore \text{Mole fraction of He} = \frac{4}{5} \text{ or } 0.80$$

$$\text{Mole fraction of CH}_4 = \frac{1}{5} \text{ or } 0.20$$

Total pressure of gaseous mixture = 20 bar

$$\begin{aligned} \text{Partial pressure of He} &= \text{Total pressure} \times \text{Mole fraction of He} \\ &= (20 \times 0.80) \text{ bar} = 16 \text{ bar} \end{aligned}$$

$$\text{Partial pressure of CH}_4 = (20 \times 0.20) \text{ bar} = 4 \text{ bar}$$

According to Graham's law of diffusion as applicable to effusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2} \quad \text{or, } \frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$$

$$\text{or } \frac{n_1}{n_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2} \quad [\text{when } t_1 = t_2]$$

$$\therefore \frac{n_{\text{He}}}{n_{\text{CH}_4}} = \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} \times \frac{P_{\text{He}}}{P_{\text{CH}_4}} = \sqrt{\frac{16}{4}} \times \frac{16}{4} = 8 \text{ or } \frac{8}{1}$$

∴ Molar ratio of mixture (composition of the mixture) effusing out initially (He : CH₄) = 8 : 1

72. Weight of cylinder with gas = 29.0 kg

$$\text{Weight of empty cylinder} = 14.8 \text{ kg}$$

$$\text{Weight of gas in the cylinder} = (29.0 - 14.8) \text{ kg} = 14.2 \text{ kg}$$

$$\text{Pressure in cylinder} = 2.5 \text{ atm}$$

Number of moles (n) in 14.2 kg (14.2 × 10³ g) of butane

$$= \frac{\text{Weight of butane}}{\text{Molecular wt. of butane}}$$

$$\text{or } n = \frac{14.2 \times 10^3}{58} = 244.83 \text{ mol}$$

Using the gas equation,

$$PV = nRT$$

$$\text{we have, } V = \frac{nRT}{P} = \frac{244.83 \times 0.082 \times 300}{2.5}$$

$$= 2409.13 \text{ L}$$

To calculate final pressure inside the cylinder :

Mass of LPG before use *i.e.* initially = 14.2 kg

Mass of LPG used = (29.0 - 23.2) = 5.8 kg

Mass of LPG left in the cylinder = (14.2 - 5.8) kg = 8.4 kg

Using gas equation, $PV = nRT$

$$P = \frac{8.4 \times 10^3 \times 0.082 \times 300}{58 \times 2409.13} = 1.48 \text{ atm}$$

Gaseous and Liquid States

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To calculate volume of used gas :

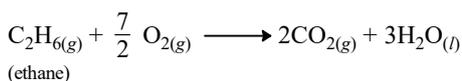
Mass of gas used = 5.8 kg or 5800 g

Number of moles of butane used = $\frac{5800}{58}$ or 100 mol

Normal pressure = 1 atm

Normal temperature = $27 + 273 = 300$ KApplying gas equation, $PV = nRT$ We have $V = 2460$ L or 2.460 m³73. Let the volume of ethane in mixture = x LThen volume of ethene in mixture = $(40 - x)$ L

The combustion reactions are as follows :

From these equations of combustion, we find volume of O₂required for combustion of ethane = $\frac{7x}{2}$ and volume of O₂ required for combustion of ethene = $(40 - x) \times 3$ ∴ Total volume of O₂ required for combustion

$$= \frac{7x}{2} + (40 - x) \times 3 = \frac{7x}{2} - 3x + 120 = \frac{x}{2} + 120$$

To calculate the number of moles of O₂ : $P = 1$ atm, $V = \frac{x}{2} + 120$, $T = 400$ K, $R = 0.082$

$$\therefore n = \frac{PV}{RT} = \frac{1 \times \left(\frac{x}{2} + 120\right)}{0.082 \times 400}$$

$$\text{or } n = \frac{x + 240}{2 \times 0.082 \times 400} \text{ moles}$$

$$\text{or mass of } n \text{ moles of O}_2 = \frac{x + 240}{2 \times 0.082 \times 400} \times 32$$

$$\therefore 130 = \frac{(x + 240) \times 32}{2 \times 0.082 \times 400}$$

$$\text{or } 130 = \frac{32x + 7680}{2 \times 0.082 \times 400}$$

$$\text{or } 130 \times 2 \times 0.082 \times 400 = 32x + 7680$$

$$\text{or } 32x = (130 \times 2 \times 0.082 \times 400) - 7680$$

$$\text{or } x = \frac{(130 \times 2 \times 0.082 \times 400) - (7680)}{32} \\ = \frac{8528 - 7680}{32} \text{ or } \frac{848}{32} = 26.5$$

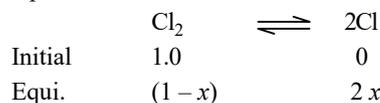
Hence mole fraction (%) of ethane = $\frac{26.5}{40} \times 100$ or 66.25and mole fraction (%) of ethene = $100 - 66.25 = 33.75$

74. Graham's law of diffusion is applicable to effusion, so we have

$$\frac{r_{\text{mix}}}{r_{\text{Kr}}} = \sqrt{\frac{M_{\text{Kr}}}{M_{\text{mix}}}}$$

$$\text{or } 1.16 = \sqrt{\frac{84}{M_{\text{mix}}}} \text{ or } 1.16 \times 1.16 = \frac{84}{M_{\text{mix}}}$$

$$\text{or } M_{\text{mix}} = \frac{84}{1.16 \times 1.16} \text{ or } 62.43 \text{ amu}$$

Determination of composition of mixture at equilibrium:Let the fraction of Cl₂ molecules dissociated at equilibrium = x Total number of moles = $(1 + 2x - x) = 1 + x$

$$\therefore M_{\text{mix}} = \frac{2x \times M_{\text{Cl}} + (1-x) M_{\text{Cl}_2}}{(1+x)}$$

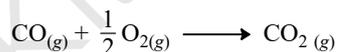
$$\text{or } 62.43 = \frac{2x \times 35.5 + (1-x) 71}{1+x} \\ = \frac{71x + 71 - 71x}{1+x} = \frac{71}{1+x}$$

$$\text{or } (62.43)(1+x) = 71$$

$$\text{or } 1+x = \frac{71}{62.43} = 1.137 \text{ or } x = 0.137.$$

75. Under given conditions CO_(g) and CH_{4(g)} react with oxygen to form CO_{2(g)} and H₂O_(l) but helium remains unaffected.

The reactions can be represented as:

Let the volume of CO_(g) and CH_{4(g)} in the gaseous mixture be x and y ml respectively. Then volume of He in the gaseous mixture = $[20 - (x + y)]$ mlAfter the reaction, the mixture consists of CO_{2(g)} formed by the action of O₂ on CO and CH₄ and helium (He) that remains as such.

Volume of left hand side in the above reactions – 13

= Volume of right hand side

$$\text{or } [20 - (x + y)] + \left(x + \frac{1}{2}x\right) + (y + 2y) - 13 \\ = [20 - (x + 2y) + x + y]$$

[∴ For gases, volume ∝ number of moles]

$$\text{or } \frac{1}{2}x + 2y = 13 \text{ or } x + 4y = 26 \quad \dots (i)$$

The volume of CO_{2(g)} formed in the above reaction is x ml from x ml of CO_(g) and y ml from y ml of CH_{4(g)} i.e. total volume of CO_{2(g)} formed is $(x + y)$ ml∴ $x + y = 14$ ml ... (ii) [KOH absorbs CO₂ when gaseous mixture is passed through it to form K₂CO₃ and H₂O]

From (i) and (ii),

$$3y = 12 \text{ or } y = 4 \text{ ml and } x = 14 - 4 = 10 \text{ ml}$$

∴ Volume of CO in mixture = 10 ml

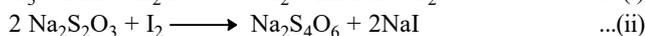
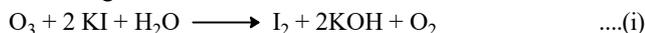
Volume of CH₄ in mixture = 4 mlVolume of He in mixture = $20 - (10 + 4) = 6$ ml

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

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

$$\% \text{ of He} = \frac{6}{20} \times 100 = 30\%$$

76. Following reactions occur:



From equation (i) we find

Millimoles of O_3 = millimoles of I_2

From equation (ii) we find

$$\text{Millimoles of I}_2 = \frac{1}{2} \text{ millimoles of Na}_2\text{S}_2\text{O}_3$$

$$\therefore \text{ Millimoles of O}_3 = \text{ millimoles of I}_2 = \frac{1}{2} \times 40 \times \frac{1}{10} = 2 \text{ millimoles}$$

$$\therefore \text{ Moles of O}_3 \text{ in mixture} = 0.002 \text{ moles}$$

To calculate total number of moles of O_2 and O_3 :

According to ideal gas equation, $PV = nRT$

$$\therefore 1 \times 1 = n \times 0.082 \times 273 \quad (0^\circ\text{C} = 273 \text{ K})$$

$$\text{or } n = \frac{1}{0.082 \times 273} = 0.044 \text{ mole}$$

Hence moles of oxygen = $0.044 - 0.002 = 0.042$ moles

$$\text{Weight of oxygen} = 0.042 \times 32 \quad [\because \text{mol. wt. of O}_2 = 32] = 1.344 \text{ g}$$

$$\text{Weight of ozone} = 0.002 \times 48 \quad [\because \text{mol. wt. of O}_3 = 48] = 0.096 \text{ g}$$

$$[\text{Total weight} = 1.344 + 0.096 = 1.44 \text{ g}]$$

$$\text{Thus weight \% of O}_3 = \frac{0.096}{1.44} \times 100 = 6.66 \%$$

Number of photons or number of O_3 molecules

$$= \frac{0.096 \times 6.023 \times 10^{23}}{48} = 1.2 \times 10^{21}$$

77. van der Waals equation is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad (\text{for 1 mole})$$

$$\text{or } \left(P + \frac{a}{V^2}\right) = \frac{RT}{(V - b)} \quad \text{or } P = \frac{RT}{(V - b)} - \frac{a}{V^2}$$

$$\text{or } P = \frac{RT}{V\left(1 - \frac{b}{V}\right)} - \frac{a}{V^2}$$

$$\text{or } PV = RT\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V}$$

$$\text{or } PV = RT\left[1 + \frac{b}{V} + \frac{b^2}{V^2} + \dots\right] - \frac{a}{V}$$

$$\therefore \left(1 - \frac{b}{V}\right)^{-1} = 1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2$$

$$\text{or } PV = RT\left(1 + \frac{b}{V} + \frac{b^2}{V^2} + \dots - \frac{a}{VRT}\right)$$

$$\text{or, } PV = RT\left[1 + \left(b - \frac{a}{RT}\right) \cdot \frac{1}{V} + \frac{b^2}{V^2} + \dots\right]$$

Comparing the above equation with the given equation *i.e.*

$$PV = RT\left[1 + \frac{B}{V} + \dots\right]$$

$$\text{We get, } B = \frac{b - a/RT}{V}$$

78. From the given data, we have,

$$\text{Weight of the liquid} = (148 - 50 \text{ g}) = 98 \text{ g}$$

$$\text{Volume of the liquid} = \frac{98}{0.98} = 100 \text{ ml} = \text{Volume of vessel}$$

\therefore The vessel of 100 ml contains ideal gas at 760 mm of Hg and 300 K.

$$\text{Now weight of the gas} = (50.5 - 50) = 0.5 \text{ g}$$

Using ideal gas equation, $PV = nRT$, we get

$$\frac{760}{760} \times \frac{100}{1000} = \frac{0.5}{M} \times 0.082 \times 300$$

or M (Molecular weight of gas)

$$= \frac{0.5 \times 0.082 \times 300 \times 10}{1} = 123.0$$

79. Given degree of dissociation, $\alpha = 0.4$

Now, van't Hoff factor,

$$i = \frac{\text{Normal molecular weight of PCl}_5}{\text{Experimental molecular weight of PCl}_5} = 1 + \alpha$$

$$\text{or } 1 + 0.4 = \frac{208.5}{M_{\text{exp}}} \quad \text{or, } M_{\text{exp}} = \frac{208.5}{1.4}$$

Now, according to ideal gas equation

$$PV = nRT$$

$$\text{or, } PV = \frac{W}{M} RT \quad \text{or, } PM = \frac{W}{V} RT \quad \text{or } PM = \rho RT$$

$$\text{or } \rho = \frac{PM}{RT} = \frac{1 \times 208.5}{1.4 \times 0.082 \times 400} = 4.54 \text{ g/lit}$$

80. From the given data, we have

$$n = 2 \text{ mol; } V = 4 \text{ L } P = 11.0 \text{ atm}$$

$$b = 0.05 \text{ L mol}^{-1} \quad T = 300 \text{ K; } R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

Using van der Waals equation,

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (\text{For } n \text{ moles})$$

We get

$$\left(11 + \frac{a \times 4}{16}\right)(4 - 2 \times 0.05) = 2 \times 0.082 \times 300$$

$$\text{or } \left(\frac{176 + 4a}{16}\right)(3.9) = 49.2$$

$$\text{or } 4a = \frac{49.2 \times 16}{3.9} - 176 = 201.85 - 176 = 25.85$$

$$\therefore a = \frac{25.85}{4} \text{ or } 6.46 \text{ atm L}^2 \text{ mol}^{-2}.$$

81. $\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$

$$\text{Initial } P; \quad 600 \quad 0 \quad 0$$

$$\text{Equi. } P; \quad (600 - P) \quad 2P \quad P/2$$

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Where moles equivalent to pressure P are decomposed ($P \propto$ moles when V and T are constant)

$$\text{Thus } 600 - P + 2P + P/2 = 960$$

$$\therefore \frac{3}{2}P = 960 - 600 = 360$$

$$\text{or } P = \frac{360 \times 2}{3} = 240 \text{ mm of Hg}$$

$$\text{Thus moles of } \text{N}_2\text{O}_5 \text{ decomposed} = \frac{240}{600} = 0.4$$

$$82. \text{ We know, } \frac{r_1}{r_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}}$$

$$\text{or } \frac{n_1}{t_1} \times \frac{t_2}{n_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}}$$

$$\text{or } \frac{1}{38} \times \frac{57}{1} = \frac{0.8}{1.6} \times \sqrt{\frac{M_2}{28}}$$

$$\text{or } M_2 = \frac{57 \times 57}{38 \times 38} \times \frac{1.6 \times 1.6}{0.8 \times 0.8} \times 28 = 252$$

Thus we have $\text{XeF}_n = 252$

$$\text{or } 131 + 19n = 252$$

$$\text{or } 19n = 252 - 131$$

$$\text{or } 19n = 121$$

$$\text{or } n = 6.3 \text{ i.e. } \approx 6$$

i.e. It is XeF_6 .

$$83. \text{ Number of moles of gas} = \frac{12}{120} = 0.1 \text{ mol}$$

$$P = 1 \text{ atm; } T = (t + 273) \text{ K;}$$

Using gas equation, $PV = nRT$, we get

$$1 \times V = 0.1 \times R \times (273 + t) \quad \dots(i)$$

Under new condition

$$1.1V = 0.1 \times R \times (273 + 10 + t)$$

$$\text{or } 1.1V = 0.1 \times R \times (283 + t) \quad \dots(ii)$$

Dividing (ii) by (i), we get

$$\frac{1.1V}{1V} = \frac{0.1 \times R \times (283 + t)}{0.1 \times R \times (273 + t)}$$

$$\text{or } 1.1 = \frac{283 + t}{273 + t}$$

$$1.1t + 1.1 \times 273 = t + 283$$

$$\text{or } 0.1t = 283 - 300.3 \quad \text{or } 0.1t = -17.3$$

$$\text{or } t = -\frac{17.3}{0.1} \quad \text{or } 173^\circ\text{C} \quad \text{or } (-173 + 273) = 100 \text{ K}$$

Substituting this value of t in equation (i),

$$1 \times V = 0.1 \times 0.082 \times (273 - 173)$$

$$\text{or } V = 0.1 \times 0.082 \times 100 = 0.821 \text{ L}$$

84. For one mole of real gas, we have

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad [\text{van der Waals Eqn.}]$$

Since the volume occupied by CO_2 molecules is negligible

$b = 0$, hence the above equation can be written as

$$\left(P + \frac{a}{V^2}\right)V = RT \quad \text{or } P = \frac{RT}{V} - \frac{a}{V^2}$$

Substituting the given values

$$P = \frac{0.082 \times 273}{22.4} - \frac{3.592}{(22.4)^2} \quad [1 \text{ mole} = 22.4 \text{ L at NTP}]$$

$$\text{or } P = 0.9993 - 0.0071 = 0.9922 \text{ atm}$$

$$85. \left(P + \frac{a}{V^2}\right)(V - b) = RT \quad (\text{for 1 mole})$$

Since the actual volume of gas molecules is negligible so we can write

$$\left(P + \frac{a}{V^2}\right)V = RT \quad \dots(i)$$

$$\text{The compressibility factor, } Z = \frac{PV}{RT} \quad \text{or } V = \frac{Z \cdot RT}{P}$$

Substituting the value of V in (i), we get

$$\left[P + \frac{a \times P^2}{Z^2 R^2 T^2}\right] \left[\frac{ZRT}{P}\right] = RT$$

$$\text{or } Z \left[1 + \frac{aP}{Z^2 R^2 T^2}\right] = 1$$

Now from given data, we have

$$T = 0 + 273 = 273 \text{ K; } P = 100 \text{ atm; } Z = 0.5$$

Substituting these values, we get

$$0.5 \left[1 + \frac{a \times 100}{(0.5)^2 (0.082)^2 (273)^2}\right] = 1$$

$$\text{or } = \frac{a \times 100}{0.5 \times 0.082 \times 0.082 \times 273 \times 273} = 1 - 0.5 = 0.5$$

$$\text{or } a = \frac{0.5 \times 0.5 \times 0.082 \times 0.082 \times 273 \times 273}{100} = 1.253 \text{ atm L}^2 \text{ mol}^{-2}$$

86. (a) $d = 0.36 \text{ kg m}^{-3} = 0.36 \text{ g/L}$

(i) From Graham's law of diffusion

$$\frac{r_v}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_v}} \quad \text{or } 1.33 = \sqrt{\frac{32}{M_v}}$$

$$\text{or } M_v = \frac{32}{1.33 \times 1.33} = 18.09$$

[Where M_v = Mol. wt. of vapour]

$$(ii) 0.36 \text{ g} = \frac{0.36}{18.09} \text{ mol}$$

$$\text{Since } \frac{0.36}{18.09} \text{ mol occupies volume} = 1 \text{ L}$$

$$\therefore \text{Volume occupied by 1 mol} = \frac{18.09}{0.36} \text{ L or } 50.25 \text{ L}$$

So the molar volume of vapour = 50.25 L

(iii) If we assume ideal behaviour of vapour, we have

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or } V_2 = 22.4 \times \frac{500}{273} = 41.025 \text{ L}$$

$$\text{Compressibility factor } (Z) = \frac{(PV)_{\text{obs}}}{(PV)_{\text{ideal}}} = \frac{1 \times 50.25}{1 \times 41.025} = 1.225$$

(iv) Since $Z > 1$, hence repulsive force dominates.

$$\begin{aligned} \text{(b) We know, } E &= \frac{3}{2} kT = \frac{3}{2} \frac{R}{N} T \\ &= \frac{3}{2} \times \frac{8.31}{6.023 \times 10^{23}} \times 1000 \\ &= 2.07 \times 10^{-20} \text{ J per molecule.} \end{aligned}$$

$$87. U_{rms} = \sqrt{\frac{3RT}{M}} \text{ and } U_{Av} = \sqrt{\frac{8RT}{\pi M}}$$

$$\therefore \frac{U_{rms}}{U_{Av}} = \sqrt{\frac{3RT}{M}} \times \sqrt{\frac{\pi M}{8RT}} = \sqrt{\frac{3\pi}{8}} = 1.085$$

$$\text{or } U_{rms} = 1.085 \times U_{Av} = 1.085 \times 400 = 434 \text{ ms}^{-1}.$$

88. For real gases, van der Waals' equation for one mole is :

$$\left[P + \frac{a}{V_m^2} \right] [V_m - b] = RT$$

$$\text{or } PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT \quad \dots(i)$$

For intercept of PV_m vs P graph at y -axis, $P = 0$ and thus,

$$V_m \rightarrow \infty. \text{ Thus neglecting } \frac{a}{V_m} \text{ and } \frac{ab}{V_m^2} \text{ terms in equation (i)}$$

$$\text{or } PV_m = Pb + RT \quad \dots(ii)$$

Thus, a graph between PV_m vs. P will lead to an intercept RT as equation (ii) represents a straight line equation ($y = mx + c$).

89. (A) \rightarrow p, s, (B) \rightarrow r, (C) \rightarrow p, q, (D) \rightarrow r

(A) For H_2 gas, the value of a is negligible.

$$\therefore P(V - nb) = nRT$$

$$\text{or, } \frac{PV}{nRT} = Z = 1 + \frac{Pb}{RT}$$

Therefore compressibility factor of H_2 is always greater than 1.

(B) At extremely low pressure, real gas (H_2) behaves almost ideally, hence for H_2 gas at 0 atm, $PV = nRT$.

(C) CO_2 at room temperature, behaves ideally and van der Waal's force of attraction dominates.

Since P is 1 atm, Z will be less than 1.

$$\text{(D) } \left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

If V is very high, $PV = nRT$.

90. (a): a refers to the magnitude of attractive forces among the gas molecules which increases in ammonia because of H-bonding.

91. (b): According to Gay - Lussac's law, at constant volume, the pressure of a given mass of a gas is directly proportional to the absolute temperature of the gas. $P \propto T$ or $P = KT$

92. (c): According to Graham's law, $r \propto \frac{1}{\sqrt{M}}$

As all conditions are identical for X and Y ,

$$\frac{r_X}{r_Y} = \sqrt{\frac{M_Y}{M_X}} \Rightarrow \frac{d}{24-d} = \sqrt{\frac{40}{10}} = 2$$

$$d = 48 - 2d \Rightarrow 3d = 48$$

$$d = 16 \text{ cm}$$

93. (d): As the collision frequency increases, molecular speed decreases.

94. (4): Given, $T_1 = 400 \text{ K}$, $T_2 = 60 \text{ K}$

Molecular weight of X , $M_1 = 40$,

Molecular weight of Y , $M_2 = ?$

$$v_{rms(X)} = \sqrt{\frac{3RT_1}{M_1}}, v_{mp(Y)} = \sqrt{\frac{2RT_2}{M_2}}$$

$$\text{given, } v_{rms(X)} = v_{mp(Y)}$$

$$\therefore \sqrt{\frac{3R \times 400}{40}} = \sqrt{\frac{2R \times 60}{M_2}}$$

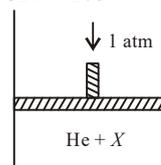
$$30 = \frac{120}{M_2} \Rightarrow M_2 = 4.$$

95. (7): For any ideal gas, $PV = nRT$

$$P = 1 - 0.68$$

$$\text{He} = 0.32 \text{ atm}$$

$$0.32 \times V = 0.1 \times 0.0821 \times 273 \Rightarrow V = 7 \text{ litre}$$



For He, $n = 0.1$, $P = 0.32 \text{ atm}$, $V = ?$, $T = 273 \text{ K}$
(unknown compound X will not follow ideal gas equation)

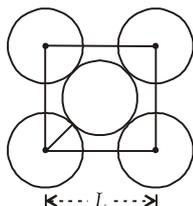


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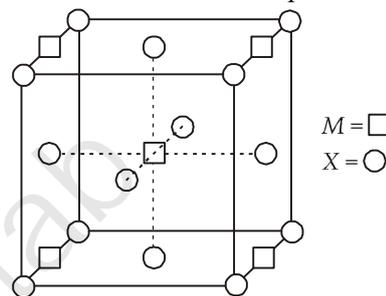
Multiple Choice Questions with ONE Correct Answer

1. CsBr has *bcc* structure with edge length 4.3. The shortest interionic distance in between Cs^+ and Br^- is
(a) 3.72 (b) 1.86 (c) 7.44 (d) 4.3 (1995)
2. The coordination number of a metal crystallizing in a hexagonal close-packed structure is
(a) 12 (b) 4 (c) 8 (d) 6 (1999)
3. In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is
(a) AB_2 (b) A_2B (c) A_4B_3 (d) A_3B_4 (2001)
4. A substance A_xB_y crystallizes in a face centred cubic *fcc* lattice in which atoms A occupy each corner of the cube and atoms B occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y .
(a) AB_3 (b) A_4B_3
(c) A_3B
(d) Composition cannot be specified. (2002)
5. In which of the following crystals alternate tetrahedral voids are occupied?
(a) NaCl (b) ZnS (c) CaF_2 (d) Na_2O (2005)
6. The packing efficiency of the two-dimensional square unit cell shown below is

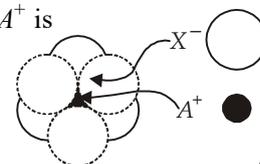


- (a) 39.27% (b) 68.02% (c) 74.05% (d) 78.54% (2010)

7. A compound M_pX_q has cubic close packing (*ccp*) arrangement of X . Its unit cell structure shown below. The empirical formula of the compound is



- (a) MX (b) MX_2 (c) M_2X (d) M_5X_{14} (2012)
8. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is
(a) 104 pm
(b) 125 pm
(c) 183 pm
(d) 57 pm (2013)



Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

9. Which of the following statement(s) is(are) correct?
(a) The coordination number of each type of ion in CsCl crystal is 8.
(b) A metal that crystallizes in *bcc* structure has a coordination number of 12.
(c) A unit cell of an ionic crystal shares some of its ions with other unit cells.
(d) The length of the unit cell in NaCl is 552 pm. ($r_{\text{Na}^+} = 95$ pm; $r_{\text{Cl}^-} = 181$ pm). (1998)
10. The correct statement(s) regarding defects in solids is(are)
(a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion
(b) Frenkel defect is a dislocation defect
(c) Trapping of an electron in the lattice leads to the formation of F-center
(d) Schottky defects have no effect on the physical properties of solids. (2009)

11. If the unit cell of a mineral has cubic close packed (*ccp*) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions, m and n , respectively, are

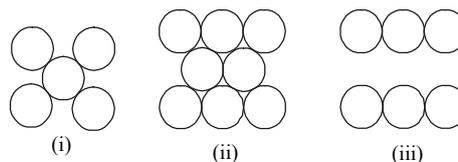
(a) $\frac{1}{2}, \frac{1}{8}$ (b) $1, \frac{1}{4}$ (c) $\frac{1}{2}, \frac{1}{2}$ (d) $\frac{1}{4}, \frac{1}{8}$
(2015)

Fill in the Blanks

12. In the sodium chloride structure, each Na^+ ion is surrounded by 6 Cl^- ions nearest neighbours and Na^+ ion next nearest neighbours. (1997)

Subjective Problems

13. The density of mercury is 13.6 g/ml. Calculate approximately the diameter of an atom of mercury assuming that each atom is occupying a cube of edge length equal to the diameter of the mercury atom. (1983)
14. Sodium metal crystallizes in body centred cubic lattice with the cell edge, $a = 4.29 \text{ \AA}$. What is the radius of sodium atom? (1994)
15. A metallic element crystallizes into a lattice containing a sequence of layers of *ABABAB*....., any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space? (1996)
16. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride? (1997)
17. Chromium metal crystallizes with a body centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3 ? (1997)
18. A metal crystallizes into two cubic phases, face centred cubic (*fcc*) and body centred cubic (*bcc*), whose unit cell lengths are 3.5 and 3.0 \AA , respectively. Calculate the ratio of densities of *fcc* and *bcc*. (1999)
19. The figures given below show the location of atoms in three crystallographic planes in *fcc* lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram.



(2000)

20. A compound *AB* has rock salt type structure. The formula weight of *AB* is 6.023 Y amu, and the closest $A - B$ distance is $Y^{1/3}$ nm, where Y is an arbitrary number.
(a) Find the density of lattice.
(b) If the density of lattice is found to be 20 kg m^{-3} , then predict the type of defect. (2004)
21. In face centred cubic (*fcc*) crystal lattice, edge length is 400 pm. Find the diameter of greatest sphere which can fit into the interstitial void without distortion of lattice. (2005)
22. 20% of surface sites are occupied by N_2 molecules. The density of surface site is $6.023 \times 10^{14} \text{ cm}^{-2}$ and total surface area is 1000 cm^2 . The catalyst is heated to 300 K while N_2 is completely desorbed into a pressure of 0.001 atm and volume of 2.46 cm^3 . Find the number of active sites occupied by each N_2 molecule. (2005)
23. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 \AA which crystallises in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ($N_A = 6 \times 10^{23}$). Give the answer in pm. (2006)

Matrix Match Type

24. Match the crystal system/unit cells mentioned in Column I with their characteristic features mentioned in Column II.

Column I	Column II
(A) simple cubic and face-centred cubic	(p) have these cell parameters $a = b = c$ and $\alpha = \beta = \gamma$
(B) cubic and rhombohedral	(q) are two crystal systems
(C) cubic and tetragonal	(r) have only two crystallographic angles of 90°
(D) hexagonal and monoclinic	(s) belong to same crystal system

(2007)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.

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- (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

25. Statement-1 : In any ionic solid $[MX]$ with Schottky defects, the number of positive and negative ions are same.

Statement-2 : Equal number of cation and anion vacancies are present. (2001)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension - 1

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they

touch each other and represent the second layer. Each one of these spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be ' r '.

26. The number of atoms in this HCP unit cell is

- (a) 4 (b) 6 (c) 12 (d) 17

27. The volume of this HCP unit cell is

- (a) $24\sqrt{2}r^3$ (b) $16\sqrt{2}r^3$ (c) $12\sqrt{2}r^3$ (d) $\frac{64}{3\sqrt{3}}r^3$

28. The empty space in this HCP unit cell is

- (a) 74% (b) 47.6% (c) 32% (d) 26%

(2008)

Integer Answer Type

29. The coordination number of Al in the crystalline state of $AlCl_3$ is (2009)

30. The number of hexagonal faces that are present in a truncated octahedron is (2011)

ANSWER KEY

- | | | | | | |
|---|--|--------------|---------------------------|--------------------------------------|--------------|
| 1. (a) | 2. (a) | 3. (d) | 4. (a) | 5. (b) | 6. (d) |
| 7. (b) | 8. (a) | 9. (a, c, d) | 10. (b, c) | 11. (a) | 12. 12 |
| 13. 2.91 \AA | 14. 1.86 \AA | 15. 26.10 % | 16. 2.16 g/cm^3 | 17. 124.27 pm, 7.30 g/cm^3 | |
| 18. 1.259 : 1 | 20. 5 kg m^{-3} , metal excess defect. | | 21. 117.16 pm | 22. 2 | 23. 216.5 pm |
| 24. $A \rightarrow p, s; B \rightarrow p, q; C \rightarrow q; D \rightarrow q, r$ | | | 25. (a) | 26. (b) | 27. (a) |
| 28. (d) | 29. (6) | 30. (8) | | | |

Explanations

1. (a): For a *bcc* structure, we have

$$\text{atomic radius } r = \frac{\sqrt{3}}{4}a \quad (a = \text{edge length})$$

$$r = \frac{\sqrt{3}}{4} \times 4.3 = 1.86$$

We know r = half the distance between two nearest neighbouring atoms

$$\therefore \text{Shortest interionic distance} = 2 \times 1.86 = 3.72$$

2. (a): In case of *hcp*, the atoms are located at the corners and centre of two hexagons placed parallel to each other, three more atoms are placed midway between these two planes. In such an arrangement each atom is surrounded by 12 others and so it has a coordination number 12.

3. (d): NaCl has a face centred cubic close packing in which lattice points are occupied by Cl^- ions whereas Na^+ ions occupy all octahedral holes. Here Na^+ and Cl^- both have a coordination number of 6.

- (i) Effective number of A^- or Cl^- (normally)

$$= \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$

From corners From faces (all face centered)

No. of A^- after removing atoms along one axes

$$= \left(8 \times \frac{1}{8}\right) + \left(4 \times \frac{1}{2}\right) = 3$$

- (ii) No. of B^+ or Na^+ = $\left(12 \times \frac{1}{4}\right)$ + $1 = 4$
 From edge centres From body centre

\therefore Formula is A_3B_4 .

4. (a): Effective number of corner atoms, $A = 8 \times \frac{1}{8} = 1$

$$\text{Effective number of face centred atom, } B = \frac{1}{2} \times 6 = 3$$

Thus the composition will be AB_3 .

5. (b): In ZnS structure, sulphide ions occupy all *fcc* lattice points while Zn^{2+} ions are present in alternate tetrahedral voids.

6. (d): Packing efficiency = $\frac{\text{Area covered by particle}}{\text{Total area}}$

Let us assume radius of circle = r

Edge length of square = a

$$\text{So, } \frac{2 \times \pi r^2}{a^2} = \frac{2\pi r^2}{(2\sqrt{2}r)^2} = \frac{\pi}{4} \Rightarrow \frac{\pi}{4} \times 100 = 78.5\%$$

7. (b) : 8 X atoms present at the corners.

$$\text{Atoms contribute to 1 unit cell} = \frac{1}{8} \times 8 = 1$$

6 X atoms present at the face centres.

$$\text{Atoms contribute to 1 unit cell} = 6 \times \frac{1}{2} = 3$$

Total X atoms = $3 + 1 = 4$

4 M atoms present at edge centres.

$$\text{Atoms present in 1 unit cell} = 4 \times \frac{1}{4} = 1$$

1 M atom present at body centre and it contribute completely to 1 unit cell.

Thus, total M atoms in one unit cell = $1 + 1 = 2$

Ratio is $M : X :: 2 : 4 :: 1 : 2$

Thus, empirical formula is MX_2 .

8. (a) : Cation A^+ occupies octahedral void arrangement by anion X^- .

$$\frac{r_{A^+}}{r_{X^-}} = 0.414$$

$$\frac{r_{A^+}}{250} = 0.414 \quad [\because \text{Radius of } X^- (r_{X^-}) = 250 \text{ pm}]$$

$$r_{A^+} = 0.414 \times 250 = 103.5 \approx 104 \text{ pm}$$

9. (a, c, d): The crystals of CsCl has *bcc* structure. In such an arrangement the coordination number of both is 8.

In case of NaCl, two interpenetrating *fcc* crystal lattices are present, out of these, two are composed of Na^+ only and the other of Cl^- ions only. Each Na^+ ion is located half-way between two Cl^- ions and each Cl^- ion is located half-way between two Na^+ ions. In a unit cell of NaCl, Cl^- occupy corners as also the face centres and Na^+ ions are located at octahedral voids. On each of a unit cell we have two Cl^- ions and one Na^+ ion. Hence

$$a = 2(r_{\text{Na}^+} + r_{\text{Cl}^-}) = 2(95 + 181) \text{ pm} = 552 \text{ pm}$$

10. (b, c) : When an ion is missing from its normal position and occupies an interstitial site between the lattice points, Frenkel defect arises, hence it is a dislocation defect.

The electrons trapped in anion vacancies are referred to as F-centers.

Schottky defects arise when some atoms or ions are missing from their normal lattice points. Due to the presence of large number of vacancies in crystals, its density (*i.e.*, physical property) is lowered.

11. (a): For *ccp*, $Z = 4 =$ no. of O-atoms

No. of octahedral voids = 4

No. of tetrahedral voids = $2 \times 4 = 8$

No. of Al^{3+} ions = $m \times 4$

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No. of Mg^{2+} ions = $n \times 8$ Thus, the formula of the mineral is $Al_{4m} Mg_{8n} O_4$

$$4m(+3) + 8n(+2) + 4(-2) = 0$$

$$12m + 16n - 8 = 0$$

$$4(3m + 4n - 2) = 0$$

$$3m + 4n = 2$$

Possible values of m and n are $\frac{1}{2}$ and $\frac{1}{8}$ respectively.

12. 12; In NaCl, each Na^+ is surrounded by 12 Na^+ ions [NaCl has rock salt structure].

13. $N_0 = 6.023 \times 10^{23}$

Atomic mass of mercury = 200

$$\therefore \text{number of atoms present in 200 g of Hg} = 6.023 \times 10^{23}$$

$$\text{So, number of atoms present in 1 g of Hg} = \frac{6.023 \times 10^{23}}{200} = 3.0115 \times 10^{21}$$

Density of Hg = 13.6 g/cc

Volume of 1 atom of mercury (Hg)

$$= \frac{1}{3.0115 \times 10^{21} \times 13.6} \text{ cc} = 2.44 \times 10^{-23} \text{ cc}$$

As each mercury atom occupies a cube of edge length equal to its diameter, therefore

$$\text{Diameter of 1 mercury atom} = (2.44 \times 10^{-23})^{1/3} \text{ cm}$$

$$= 2.905 \times 10^{-8} \text{ cm} = 2.91 \text{ \AA}$$

14. In case of *bcc*, $r = \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 4.29 \text{ \AA}$

$$= \frac{1.732}{4} \times 4.29 = 1.86 \text{ \AA}$$

15. In case of *hcp* unit cell, there are 6 atoms per unit cell. If the radius of metal atom is r_1 then

$$\text{Volume occupied by the metallic atom} = 6 \times \frac{4}{3} \times \pi r^3$$

$$= 6 \times 1.33 \times \frac{22}{7} \times r^3 = 25.08 r^3$$

It has been shown geometrically that the base area of *hcp*

$$\text{unit cell} = 6 \times \frac{\sqrt{3}}{4} \times 4 \times r^2 \text{ and the height} = 4r \times \sqrt{2/3}$$

$$\therefore \text{Volume of unit cell} = \text{Area} \times \text{Height}$$

$$= 6 \times \frac{\sqrt{3}}{4} \times 4r^2 \times 4r \times \sqrt{2/3} = 33.94 r^3$$

Volume of the empty space of one unit cell

$$= 33.94 r^3 - 25.08 r^3 = 8.86 r^3$$

$$\text{Hence percentage void} = \frac{8.86 r^3}{33.94 r^3} \times 100 \text{ or } 26.10\%$$

16. Density of NaCl, $\rho = \frac{n \times \text{weight}}{N_0 \times a^3}$
- $$= \frac{4 \times 58.5}{6.023 \times 10^{23} \times (5.64 \times 10^{-8})^3} \quad [\text{for NaCl, } n = 4, \text{fcc}]$$
- $$= 2.16 \text{ g/cm}^3$$

17. In case of *bcc*, $r = \frac{\sqrt{3}}{4} \times a = \frac{\sqrt{3}}{4} \times 287 = 124.27 \text{ pm}$

$$\text{Density, } \rho = \frac{n \times \text{at.wt.}}{V \times N_0} = \frac{n \times \text{at.wt.}}{N_0 \times a^3}$$

For *bcc*, $n = 2$, given: $a = 287 \times 10^{-10} \text{ cm}$

$$\therefore \text{Density} = \frac{2 \times 51.99}{(287 \times 10^{-10} \text{ cm})^3 \times 6.023 \times 10^{23}} = 7.30 \text{ g/cm}^3$$

18. Unit cell length for *fcc* = 3.5 \AA

Unit cell length for *bcc* = 3.0 \AA

$$\therefore \text{Density in fcc} = \frac{n_1 \times \text{at.wt.}}{V_1 \times N_0}$$

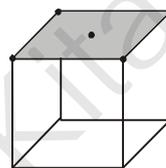
$$\text{Density in bcc} = \frac{n_2 \times \text{at.wt.}}{V_2 \times N_0}$$

$$\text{or } \frac{\text{Density (fcc)}}{\text{Density (bcc)}} = \frac{n_1 \times \frac{V_2}{V_1}}{n_2 \times \frac{V_1}{V_1}} = \frac{4}{2} \times \frac{V_2}{V_1} \left[\begin{array}{l} \text{for fcc, } n_1 = 4 \\ \text{for bcc, } n_2 = 2 \end{array} \right]$$

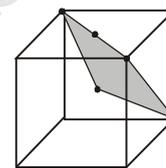
$$\text{Volume for fcc} = V_1 = a^3 = (3.5 \times 10^{-8})^3 \text{ cm}^3$$

$$\text{and volume for bcc} = V_2 = a^3 = (3.0 \times 10^{-8})^3 \text{ cm}^3$$

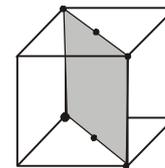
$$\therefore \frac{\text{Density (fcc)}}{\text{Density (bcc)}} = \frac{4 \times (3.0 \times 10^{-8})^3}{2 \times (3.5 \times 10^{-8})^3} = 1.259 \text{ or } 1.259 : 1$$



(i) Face Plane



(ii) Face Diagonal Plane



(iii) Diagonal Plane

19.

20. (a) Density of *AB* = $\frac{Z \times M}{N_0 \times a^3}$

$$= \frac{4 \times 6.023Y}{(2Y^{1/3} \times 10^{-9})^3 \times 6.023 \times 10^{23}}$$

$$[\because Z = 4 \text{ (for fcc)}] \quad [M = 6.023 Y, a = 2Y^{1/3} \times 10^{-9} \text{ m}]$$

$$= 5 \times 10^3 \text{ g m}^{-3} = 5 \text{ kg m}^{-3}$$

(b) As the observed density of *AB* is higher than the calculated (5.0 kg m^{-3}) which is possible if some foreign species occupy interstitial spaces hence, the defect is metal excess defect.

21. In case of *fcc*, the largest void present is octahedral.

In case the radius of void is R and the radius of lattice sphere is r , then

$$r = \frac{\sqrt{2} \times a}{4} = \frac{\sqrt{2} \times 400}{4} = 141.42 \text{ pm} \quad [\because a = 400 \text{ pm}]$$

For an octahedral void, we have $2(r + R) = a$

$$\therefore 2R = a - 2r$$

$$\text{or } 2R = 400 - 2 \times 141.42 = 117.16$$

$$\therefore \text{Diameter of greatest void} = 117.16 \text{ pm}$$

22. Pressure of $N_2 = 0.001 \text{ atm}$; $T = 300 \text{ K}$; $V = 2.46 \text{ cm}^3$

$$\therefore \text{Number of } N_2 \text{ molecules} = \frac{PV}{RT} \times N_0$$

$$= \frac{0.001 \times 2.46 \times 10^{-3}}{0.082 \times 300} \times 6.023 \times 10^{23} = 6.023 \times 10^{16}$$

Now total number of surface sites

$$= \text{Density} \times \text{Total surface area} \\ = 6.023 \times 10^{14} \times 1000 = 6.023 \times 10^{17}$$

$$\text{Site occupied by } N_2 \text{ molecules} = \frac{20}{100} \times 6.023 \times 10^{17} \\ = 12.04 \times 10^{16}$$

$$\therefore \text{Number of sites occupied by each } N_2 \text{ molecule} \\ = \frac{12.04 \times 10^{16}}{6.023 \times 10^{16}} = 2$$

$$23. \rho = \frac{Z \times m}{N_A V}$$

$$Z = \frac{\rho N_A a^3}{m} = \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8})^3}{75} \approx 2$$

Value of Z represents that the element crystallises in body centred cubic structure. For bcc structure, atomic radius

$$= \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}}{4} \times 5 \text{ \AA} = 2.165 \text{ \AA} = 216.5 \text{ pm}$$

24. A \rightarrow p, s; B \rightarrow p, q; C \rightarrow q; D \rightarrow q, r

For cubic crystal system : $a = b = c$ and $\alpha = \beta = \gamma$

For rhombohedral : $a = b = c$, $\alpha = \beta = \gamma$

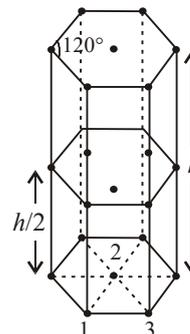
For tetragonal : $a = b \neq c$; $\alpha = \beta = \gamma$

For monoclinic : $\alpha = \gamma = 90^\circ$ and $\beta \neq 90^\circ$

For hexagonal : $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$

25. (a) : Schottky defect is caused due to a vacancy developed in anion or cation site. The number of cation and anion vacancies is same, so the ionic solid MX having Schottky defect will have the same number of cations and anions.

26. (b) : Total no. of atoms in 1 unit cell
 $= (12 \times 1/6) + 3 + (2 \times 1/2) = 6$



27. (a) : Height of unit cell = $4r\sqrt{2/3}$

$$\text{Base area} = 6 \times \sqrt{3}/4(2r)^2$$

volume = height \times base area

$$= 4r\sqrt{2/3} \times 6 \times \sqrt{3}/4(2r)^2 = 24\sqrt{2} r^3$$

28. (d) : Packing fraction = $\frac{\text{volume of the atoms in one unit cell}}{\text{volume of one unit cell}}$

$$= \frac{6 \times 4/3\pi r^3}{24\sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$$

Packing fraction = 74%

Empty space = 26%.

29. (6) : $AlCl_3$ has a 6-coordinate layer lattice with Al^{3+} occupying cubic close packed sites. Thus the coordination number of Al in $AlCl_3$ is 6.

30. (8) : Truncated octahedron contains eight hexagonal and six square faces.



6

Solutions and Colligative Properties

Multiple Choice Questions with ONE Correct Answer

- An azeotropic solution of two liquids has boiling point lower than either of them when it
 - shows negative deviation from Raoult's law
 - shows no deviation from Raoult's law
 - shows positive deviation from Raoult's law
 - is saturated. (1981)
- For a dilute solution, Raoult's law states that
 - the lowering of vapour pressure is equal to the mole fraction of solute
 - the relative lowering of vapour pressure is equal to the mole fraction of solute
 - the relative lowering of vapour pressure is proportional to the amount of solute in solution
 - the vapour pressure of the solution is equal to the mole fraction of solvent. (1985)
- When mercuric iodide is added to the aqueous solution of potassium iodide then
 - freezing point is raised
 - freezing point is lowered
 - freezing point does not change
 - boiling point does not change. (1987)
- Which of the following 0.1 M aqueous solutions will have the lowest freezing point?

(a) Potassium sulphate	(b) Sodium chloride
(c) Urea	(d) Glucose (1989)
- The freezing point of equimolar aqueous solutions will be highest for
 - $C_6H_5NH_3Cl$ (aniline hydrochloride)
 - $Ca(NO_3)_2$
 - $La(NO_3)_3$
 - $C_6H_{12}O_6$ (glucose) (1990)
- 0.2 molal acid HX is 20% ionised in solution, $K_f = 1.86 \text{ K molality}^{-1}$. The freezing point of the solution is

(a) -0.45	(b) -0.90	(c) -0.31	(d) -0.53
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 (1995)
- The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to
 - ionization of benzoic acid
 - dimerization of benzoic acid
 - trimerization of benzoic acid
 - solvation of benzoic acid. (1996)
- During depression of freezing point in a solution the following are in equilibrium
 - liquid solvent, solid solvent
 - liquid solvent, solid solute
 - liquid solute, solid solute
 - liquid solute, solid solvent. (2003)
- The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water using the following information will be (Molecular weight of $CuCl_2 = 134.4$ and $K_b = 0.52 \text{ molal}^{-1}$)

(a) 0.16	(b) 0.05	(c) 0.1	(d) 0.2
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 (2005)
- When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene ($K_f = 1.72 \text{ K kg mol}^{-1}$), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is

(a) 0.5	(b) 1	(c) 2	(d) 3
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 (2007)
- The Henry's law constant for the solubility of N_2 gas in water at 298 K is $1.0 \times 10^5 \text{ atm}$. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is

(a) 4.0×10^{-4}	(b) 4.0×10^{-5}
(c) 5.0×10^{-4}	(d) 4.0×10^{-6}

 (2009)

12. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is
 (a) 1.78 M (b) 2.00 M
 (c) 2.05 M (d) 2.22 M (2011)
13. The freezing point (in °C) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (Mol. wt. 329) in 100 g of water ($K_f = 1.86 \text{ K kg mol}^{-1}$) is
 (a) -2.3×10^{-2} (b) -5.7×10^{-2}
 (c) -5.7×10^{-3} (d) -1.2×10^{-2} (2011)
14. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solution in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is
 (take $K_b = 0.76 \text{ K kg mol}^{-1}$)
 (a) 724 (b) 740 (c) 736 (d) 718 (2012)
- Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer**
15. In the depression of freezing point experiment, it is found that the
 (a) vapour pressure of the solution is less than that of pure solvent
 (b) vapour pressure of the solution is more than that of pure solution
 (c) only solute molecules solidify at the freezing point
 (d) only solvent molecules solidify at the freezing point. (1999)
16. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are)
 (a) ΔG is positive (b) ΔS_{system} is positive
 (c) $\Delta S_{\text{surroundings}} = 0$ (d) $\Delta H = 0$ (2013)
- Fill in the Blanks**
17. Given that ΔT_f is the depression in freezing point of the solvent in a solution of a non-volatile solute of molality, m , the quantity $\lim_{m \rightarrow 0} (\Delta T_f/m)$ is equal to (1994)
- Subjective Problems**
18. What is the molarity and molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/ml? To what volume should 100 ml of this acid be diluted in order to prepare a 1.5 N solution? (1978)
19. A solution contains Na_2CO_3 and NaHCO_3 . 10 ml of the solution requires 2.5 ml of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as an indicator. Methyl orange is then added when a further 2.5 ml of 0.2 M H_2SO_4 was required. Calculate the amount of Na_2CO_3 and NaHCO_3 in one litre of the solution. (1979)
20. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. This solution is completely neutralised by 26.7 ml of 0.4 N NaOH. Find the percentage of free SO_3 in the sample of oleum. (1980)
21. The vapour pressure of pure benzene is 639.7 mm of mercury and the vapour of a solution of a solute in benzene at the temperature is 631.9 mm of mercury. Calculate the molality of the solution. (1981)
22. Two liquids A and B form ideal solutions. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states. (1982)
23. An organic compound ($\text{C}_x\text{H}_y\text{O}_z$) was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O . The hot gases when cooled to 0°C and 1 atm pressure, measured 2.24 litres. The water collected during cooling weighed 0.9 g. The vapour pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50 g of the organic compound are dissolved in 1000 g of water. Give the molecular formula of the organic compound. (1983)
24. 'Two volatile and miscible liquids can be separated by fractional distillation into pure component', is true under what conditions? (1984)
25. The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. (1986)
26. The vapour pressure of a dilute aqueous solution of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is 750 mm of mercury at 373 K. Calculate (i) molality and (ii) mole fraction of the solution. (1989)

Solutions and Colligative Properties

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27. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance? (1990)
28. The degree of dissociation of calcium nitrate in a dilute aqueous solution, containing 7.0 g of the salt per 100 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution. (1991)
29. Addition of 0.643 g of a compound to 50 ml of benzene (density: 0.879 g/ml) lowers the freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K kg mol⁻¹, calculate the molecular weight of the compound. (1992)
30. What weight of the non-volatile solute, urea (NH₂-CO-NH₂) needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? (1993)
31. Upon mixing 45 ml of 0.25 M lead nitrate solution with 25 ml of 0.1 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentration of the species left behind in the final solution. Assume that lead sulphate is completely insoluble. (1993)
32. A motor vehicle radiator was filled with 8 L of water to which 2 L of methyl alcohol (density 0.8 g/ml) were added. What is the lowest temperature at which the vehicle can be parked outdoors without a danger that water in the radiator will freeze? [K_f of water = 1.86 K m⁻¹] (1995)
33. The molar volume of liquid benzene (density = 0.877 g/ml) increases by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (density = 0.867 g/ml) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution. (1996)
34. A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm³ of benzene (density 0.889 g cm⁻³). At room temperature vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene? (1997)
35. A solution of a non-volatile solute in water freezes at -0.30°C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and K_f for water is 1.86 K kg mol⁻¹. Calculate the vapour pressure of this solution at 298 K. (1998)
36. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon: 42.86%, hydrogen: 2.40%, nitrogen: 16.67%, and oxygen: 38.07% (i) Calculate the empirical formula of the minor product. (ii) When 5.5 g of the minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84°C higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula. (Molal boiling point elevation constant of benzene is 2.53 K kg mol⁻¹.) (1999)
37. To 500 cm³ of water, 3.0 × 10⁻³ kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg⁻¹ mol⁻¹ and 0.997 g cm⁻³, respectively. (2000)
38. 1.22 g of benzoic acid is dissolved in 100 g of acetone and 100 g of benzene separately. Boiling point of the solution in acetone increases by 0.17°C, while that in the benzene increases by 0.13°C; K_b for acetone and benzene is 1.7 K kg mol⁻¹ and 2.6 K kg mol⁻¹ respectively. Find molecular weight of benzoic acid in two cases and justify your answer. (2004)
39. 75.2 g of C₆H₅OH (phenol) is dissolved in a solvent of $K_f = 14$. If the depression in freezing point is 7 K then find the % of phenol that dimerises. (2006)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension - 1

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9

Given : Freezing point depression constant of water ($K_{f \text{ water}}$)
= 1.86 K kg mol⁻¹

Freezing point depression constant of ethanol ($K_{f \text{ ethanol}}$)
= 2.0 K kg mol⁻¹

Boiling point elevation constant of water ($K_{b \text{ water}}$)
= 0.52 K kg mol⁻¹

Boiling point elevation constant of ethanol ($K_{b \text{ ethanol}}$)
= 1.2 K kg mol⁻¹

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol⁻¹

Molecular weight of ethanol = 46 g mol⁻¹

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

40. The freezing point of the solution M is
(a) 268.7 K (b) 268.5 K
(c) 234.2 K (d) 150.9 K
41. The vapour pressure of the solution M is
(a) 39.3 mm Hg (b) 36.0 mm Hg
(c) 29.5 mm Hg (d) 28.8 mm Hg
42. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is
(a) 380.4 K (b) 376.2 K
(c) 375.5 K (d) 354.7 K

(2008)

Integer Answer Type

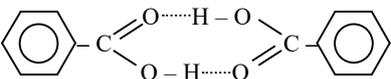
43. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is (2014)
44. If the freezing point of a 0.01 molal aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is -0.0558°C , the number of chloride(s) in the coordination sphere of the complex is [K_f of water = 1.86 K kg mol⁻¹] (2015)

ANSWER KEY

- | | | | | | |
|--|---|--|------------------------------------|--------------------|---------|
| 1. (c) | 2. (b) | 3. (a) | 4. (a) | 5. (d) | 6. (a) |
| 7. (b) | 8. (a) | 9. (a) | 10. (a) | 11. (a) | 12. (c) |
| 13. (a) | 14. (a) | 15. (a, d) | 16. (b, c, d) | 17. K_f | |
| 18. 1.52 m, 1.35 M, 80 ml | 19. 4.2 g/L | 20. 3.84 % | 21. 0.156 mol/kg | | |
| 22. $A = 400$ mm of Hg; $B = 600$ mm of Hg | 23. $\text{C}_5\text{H}_{10}\text{O}_5$ | 24. In case they form an ideal solution. | 25. 66.15 mm, 0.657 | | |
| 26. 0.7431 mol kg ⁻¹ ; 0.0132 | 27. 65.25 | 28. 746.32 mm of Hg | 29. 156.0 | 30. 111g; 18.5 m | |
| 31. 156.0 | 32. -11.625°C | 33. 0.73 | 34. 5.027 K molality ⁻¹ | 35. 23.44 mm of Hg | |
| 36. $\text{C}_3\text{H}_2\text{NO}_2$; 168 mol ⁻¹ ; $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$; C_6H_4 $\begin{matrix} \diagup \text{NO}_2 \\ \diagdown \text{NO}_2 \end{matrix}$ | 37. 0.228 K | 38. 122; 244 | 39. 75% | | |
| 40. (d) | 41. (b) | 42. (b) | 43. (2) | 44. (1) | |

Explanations

1. (c) : B.pt. $\propto \frac{1}{V.P.}$. For b.pt. to be lower, V. P. should be higher.
Thus the V.P. of the mixture is higher than either of the two liquids.
2. (b) : Raoult's law is $\frac{P^\circ - P_s}{P^\circ} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}}$ = Mole fraction of solute
3. (a) : When we add HgI_2 , a complex $\text{K}_2[\text{HgI}_4]$ is formed

$$2\text{KI} + \text{HgI}_2 \longrightarrow \text{K}_2[\text{HgI}_4]$$
 It results in a decrease in number of moles of particles, because of it ΔT_f increases.
4. (a) : In case of K_2SO_4 we get two K^+ and one SO_4^{2-} ions. A total of three ions which is maximum number of particles formed in any of the given substances. (NaCl = 2), (Urea = 1), (Glucose = 1). Hence K_2SO_4 has maximum ΔT_f or minimum freezing point.
5. (d) : Glucose is not an electrolyte and it remains undissociate thus it gives only one particle which is the minimum number of particles, hence it has minimum ΔT_f or maximum freezing point.
6. (a) : $\Delta T_f = iK_f m$ and $i = \frac{1 - \alpha + n\alpha}{1}$
 When n = number of ions formed on complete dissociation of 1 mole of HX.
 $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^- \quad i.e. n = 2$
 $\therefore i = \frac{1 - 0.2 + 2 \times 0.2}{1} = 1.2$
 or $\Delta T_f = 1.2 \times 1.86 \times 0.2 = 0.45$
 Thus the freezing point of solution = $0 - 0.45 = -0.45^\circ\text{C}$
7. (b) : In benzene, benzoic acid exists as dimer.

8. (a) : Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid. At this point, there is an equilibrium between solid and liquid states. If we cool a solute of a non-volatile solute to a temperature below the freezing point of solution, some of the liquid solvent will separate as a solid and due to this there will be an increase in concentration of the solution.
9. (a) : $\Delta T_b = iK_b \cdot m$; $\text{CuCl}_2 \rightleftharpoons \text{Cu}^{2+} + 2\text{Cl}^-$
 $\Delta T_b = 3 \times 0.52 \times 0.1 = 0.156 \approx 0.16$
 $[K_b = 0.52, m = \frac{13.44}{134.4} = 0.1]$
10. (a) : For electrolytic solution,
 $\Delta T_f = iK_f m$
i.e. $2 = i \times 1.72 \times \frac{20}{172} \times \frac{1000}{50} \Rightarrow i = 0.5$
11. (a) : According to Henry's law,
 $x_{\text{N}_2} \times K_H = p_{\text{N}_2} \quad (p_{\text{N}_2} = \text{Partial pressure of N}_2)$
 Given, total pressure = 5 atm, mole fraction of $\text{N}_2 = 0.8$
 \therefore partial pressure of $\text{N}_2 = 0.8 \times 5 = 4$.
 $\Rightarrow x_{\text{N}_2} \times 1 \times 10^5 = 4 \Rightarrow x_{\text{N}_2} = 4 \times 10^{-5}$
 no. of moles of H_2O , $n_{\text{H}_2\text{O}} = 10$
 no. of moles of N_2 , $n_{\text{N}_2} = ?$
 $\frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{H}_2\text{O}}} = x_{\text{N}_2} = 4 \times 10^{-5}$
 $\frac{n_{\text{N}_2}}{10 + n_{\text{N}_2}} = 4 \times 10^{-5} \Rightarrow n_{\text{N}_2} \approx 4 \times 10^{-4}$
12. (c) : Total mass of solution = $1000 + 120 = 1120$ g
 Total volume of solution (in mL) = $\frac{W}{\text{density}} = \frac{1120}{1.15} = 973.91$
 $M = \frac{W \times 1000}{m \times V(\text{mL})} = \frac{120 \times 1000}{60 \times 973.91} = 2.05$ M
13. (a) : $\text{K}_3[\text{Fe}(\text{CN})_6]$ is an electrolyte.
 Degree of dissociation $i = n$ (no. of ions).
 $\text{K}_3[\text{Fe}(\text{CN})_6] \longrightarrow 3\text{K}^+ + [\text{Fe}(\text{CN})_6]^{3-}; i = 4$
 $\Delta T_f = K_f \times i \times \frac{w}{m} \times \frac{1000}{W}$
 $= 1.86 \times 4 \times \frac{0.1}{329} \times \frac{1000}{100} = 2.3 \times 10^{-2}$
 $T_f = -2.3 \times 10^{-2}$
14. (a) : $\Delta T_b = K_b \times m$
 $2 = 0.76 \times m \Rightarrow m = \frac{2}{0.76}$
 $m = \frac{g / \text{M.W.}}{V} \times 1000 = \frac{2.5 / \text{M.W.}}{100} \times 1000$
 $\frac{2}{0.76} = \frac{2.5 \times 10}{\text{M.W.}} \Rightarrow \text{M.W.} = \frac{2.5 \times 10}{2} \times 0.76$
 $\frac{P^\circ_{\text{solvent}} - P_{\text{solute}}}{P^\circ_{\text{solvent}}} = x_{\text{solute}}$ (mole fraction of solute)
 $P^\circ_{\text{solvent}} = 1 \text{ atm} = 760 \text{ mm Hg}$
 $\frac{760 - P_{\text{solute}}}{760} = \frac{2.5 / \text{M.W.}}{100 / 18}$

$$760 - P_{\text{solute}} = \frac{2.5 \times 2}{2.5 \times 10 \times 0.76} \times \frac{18}{100} \times 760$$

$$760 - P_{\text{solute}} = 36 \Rightarrow P_{\text{solute}} = 724 \text{ mm Hg}$$

15. (a, d) : When a solute is added to a solvent there occurs a depression in freezing point of solvent.

Raoult's law states, "When a non-volatile solute is added to a solvent, the vapour pressure of the solvent decreases". At freezing point only the solvent molecules will solidify.

16. (b,c,d) : For an ideal solution,

(i) $\Delta G < 0$; for mixing.

(ii) $\Delta S_{\text{system}} > 0$; because disorder increases.

(iii) $\Delta S_{\text{surr}} = 0$; no heat is exchanged in case of ideal solution.

(iv) $\Delta H_{\text{mix}} = 0$.

17. K_f (molal depression constant). We know

$\Delta T_f = K_f \cdot m$. Where ΔT_f is depression in freezing point and m is molality of solution.

18. 100 g solution contains 13 g sulphuric acid (Molecular mass = 98, Equivalent mass = 49)

We know,

$$\text{molality} = \frac{\text{wt. in g}}{\text{molecular mass}} \times \frac{1000}{\text{wt. of solvent in g}}$$

$$\text{Weight of solvent} = 100 - 13 = 87 \text{ g}$$

$$\text{molality } (m) = \frac{13}{98} \times \frac{1000}{87} = 1.52 \text{ m}$$

To find out the molarity, we require the volume of 100 g of solution. For this we are given the density.

$$\text{Volume of 100 g of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100 \text{ gm}}{1.02 \text{ gm/ml}} = 98 \text{ ml}$$

Now, molarity can be calculated as follows.

$$\text{molarity} = \frac{\text{wt. in g}}{\text{molecular mass}} \times \frac{1000}{\text{volume in ml}}$$

$$\text{molarity } (M) = \frac{13}{98} \times \frac{1000}{98} = 1.35 \text{ M}$$

We know, $\frac{\text{normality}}{\text{molarity}} = \frac{\text{molecular mass}}{\text{equivalent mass}}$

$$\frac{N}{1.35} = \frac{98}{49} \quad \text{or, } N = 2.7$$

If N_1 and V_1 are the normality and volume of solution before dilution and N_2 and V_2 are the respective values after dilution then,

$$N_1 V_1 = N_2 V_2$$

100 ml solution having normality 2.7 is to be diluted to 1.5 N, means

$$100 \times 2.7 = V_2 \times 1.5$$

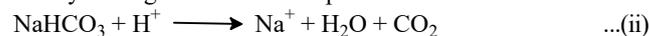
Thus, $V_2 = 180 \text{ ml}$

The solution should be diluted up to 180 ml to get 1.5 N or 80 ml of water should be added to 100 ml of the given solution to get normality value 1.5

19. Phenolphthalein indicates half neutralisation.



Methyl orange indicates complete neutralisation.



From equation (i) it is clear that the volume of 0.1 M H_2SO_4 needed for complete neutralisation = $2 \times 2.5 = 5.0 \text{ ml}$

Since molecular weight of H_2SO_4 (=98) is $2 \times$ equivalent weight (=49).

$$\therefore 0.1 \text{ M } \text{H}_2\text{SO}_4 = 0.2 \text{ N } \text{H}_2\text{SO}_4 \text{ and}$$

$$0.2 \text{ M } \text{H}_2\text{SO}_4 = 0.4 \text{ N } \text{H}_2\text{SO}_4$$

Using normality equation

$$N_{\text{Na}_2\text{CO}_3} \times 10 = 0.2 \times 5.0$$

$$\text{or } N_{\text{Na}_2\text{CO}_3} = \frac{0.2 \times 5.0}{10} = 0.1 \text{ N}$$

Equivalent weight of $\text{Na}_2\text{CO}_3 = \frac{1}{2}$ molecular weight.

$$= \frac{106}{2} = 53$$

$$\therefore \text{Strength of } \text{Na}_2\text{CO}_3 = 53 \times 0.1 = 5.3 \text{ g/L}$$

During the second stage of neutralisation volume of 0.2 M H_2SO_4 used = 2.5 ml

It is also equal to 2.5 ml of 0.4 N H_2SO_4 .

It is also equal to 5.0 ml 0.2 N H_2SO_4 .

Out of 5.0 ml of 0.2 N H_2SO_4 2.5 ml of 0.2 N H_2SO_4 is used for neutralising NaHCO_3 formed from half neutralisation of Na_2CO_3 .

Therefore, volume of H_2SO_4 used for neutralisation of NaHCO_3 originally present = $5.0 - 2.5 = 2.5 \text{ ml}$.

$$\therefore N_{\text{NaHCO}_3} \times 10 = 2.5 \times 0.2$$

$$\therefore N_{\text{NaHCO}_3} = \frac{0.2 \times 2.5}{10} = 0.05 \text{ N}$$

Equivalent weight of $\text{NaHCO}_3 = 84$

$$\therefore \text{Strength of } \text{NaHCO}_3 \text{ in the mixture} = 84 \times 0.05 = 4.2 \text{ g/L}$$

20. Molecular weight of $\text{H}_2\text{SO}_4 = (2 \times 1) + 32 + (4 \times 16) = 98$

$$\text{Equivalent weight of } \text{H}_2\text{SO}_4 = \frac{98}{2} = 49$$

26.7 ml of 0.4 N H_2SO_4 is equal to V ml of 1 N H_2SO_4 .

Using $N_1 V_1 = N_2 V_2$

$$\therefore 1 \times V_1 = 26.7 \times 0.4 = 10.68 \text{ ml of 1 N } \text{H}_2\text{SO}_4$$

49 g of H_2SO_4 will be neutralised by 1 N NaOH = 1000 ml

$\therefore 0.5 \text{ g of } \text{H}_2\text{SO}_4$ will be neutralised by 1 N NaOH

$$= \frac{1000}{49} \times 0.5 \text{ ml} = 10.20 \text{ ml}$$

Volume of 1 N NaOH used by dissolved SO_3

$$= 10.68 - 10.20 = 0.48 \text{ ml}$$



$$\text{Eq. wt. of } \text{SO}_3 = \frac{32 + (3 \times 16)}{2} = \frac{32 + 48}{2} = \frac{80}{2} = 40$$

$$\text{Weight of } \text{SO}_3 = \frac{40}{1000} \times 0.48 = 0.0192 \text{ g}$$

$$\text{Percentage of } \text{SO}_3 = \frac{0.0192}{0.5} \times 100 = 3.84\%$$

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21. Let the molality of solution = 'm'

Thus m moles of solute are present in 1000 g of benzene

V. P. of benzene (P°) = 639.7 mm of Hg

V. P. of solution (P_s) = 631.9 mm of Hg

Number of moles of benzene = $\frac{1000}{78}$

Number of moles of solute = ?

Using the relation :

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n}{N}, \text{ we get } = \frac{639.7 - 631.9}{639.7} = \frac{n \times 78}{1000}$$

$$\text{or } n = \frac{1000 \times 7.8}{78 \times 639.7} = 0.156$$

Hence molality of solution = 0.156 mol/kg.

22. At 300 K :

V. P. of solution containing 1 mole of A + 3 moles of B = 550 mm

V. P. of solution containing 1 mole of A + 4 moles of B
= (550 + 10) = 560 mm

Let the V. P. of pure A = p_A°

and the V. P. of pure B = p_B°

Then $p_{\text{Total}} = p_A^\circ \times x_A + p_B^\circ \times x_B$

$$\text{or } 550 = p_A^\circ \times x_A + p_B^\circ \times x_B$$

$$= p_A^\circ \times \frac{1}{4} + p_B^\circ \times \frac{3}{4} \left[\because x_A = \frac{1}{1+3} = \frac{1}{4}, x_B = \frac{3}{1+3} = \frac{3}{4} \right]$$

$$550 = \frac{p_A^\circ}{4} + \frac{3}{4} p_B^\circ \quad \text{or } 2200 = p_A^\circ + 3p_B^\circ \quad \dots(i)$$

Again, we have

$$560 = p_A^\circ \times \frac{1}{5} + p_B^\circ \times \frac{4}{5} \left(\because x_A = \frac{1}{1+4} = \frac{1}{5}, x_B = \frac{4}{1+4} = \frac{4}{5} \right)$$

$$2800 = p_A^\circ + 4p_B^\circ \quad \dots(ii)$$

Solving equations (i) and (ii), we get

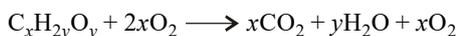
$$p_B^\circ = 600 \text{ mm of Hg}$$

$$p_A^\circ = 400 \text{ mm of Hg}$$

Hence V. P. of pure A = 400 mm of Hg

and V. P. of pure B = 600 mm of Hg

23. Combustion of $C_xH_yO_z$ can be represented as



The moles of gases obtained after cooling

$$= x + x = 2x \quad [\text{H}_2\text{O is liquid.}]$$

$$\therefore 2x = 2.24 \quad \text{or } x = \frac{2.24}{2} = 1.12 \text{ litres}$$

$$\text{Number of moles of } CO_2 = \frac{1.12}{22.4} = 0.05$$

The empirical formula of the organic compound is $C(H_2O)$.

$$\text{Now, } \frac{P^\circ - P_s}{P^\circ} = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$\text{or } \frac{0.104}{17.5} = \frac{\frac{50}{M_A}}{\frac{50}{M_A} + \frac{1000}{18}} = \frac{50}{M_A(50 \times 18 + 1000 M_A)}$$

$$\text{or } \frac{104}{17500} = \frac{50 \times 18}{900 + 1000 M_A}$$

$$\text{or } 900 + 1000 M_A = \frac{900 \times 17500}{104}$$

$$1000 M_A = \frac{900 \times 17500}{104} - 900$$

$$\text{or } 1000 M_A = \frac{900 \times 17500 - 900 \times 104}{104}$$

$$\text{or } 1000 M_A = \frac{900(17500 - 104)}{104}$$

$$\text{or } M_A = \frac{900 \times 17396}{1000 \times 104} \quad \text{or } M_A = 150.5$$

Hence molecular weight of compound = 150.5

Empirical formula weight = $12 + 2 \times 1 + 16 = 30$

$$\therefore n = \frac{150.5}{30} \quad \text{or } 5 \quad (\text{nearest whole number})$$

$$\therefore \text{Molecular formula of the given compound} = (\text{CH}_2\text{O})_5 \\ = \text{C}_5\text{H}_{10}\text{O}_5$$

24. In case they form an ideal solution, then the Raoult's law is valid,

$$\text{i.e. } \Delta H_{\text{mixing}} = 0 \quad \text{and } \Delta V_{\text{mixing}} = 0$$

25. We know $P_{\text{Total}} = P_1 + P_2$

$$\text{Also } P_1 = p_1^\circ \times x_1 \quad \text{and } P_2 = p_2^\circ \times x_2$$

$$x_1 = \text{mole fraction of } \text{CH}_3\text{OH} = \frac{\frac{40}{32}}{\frac{40}{32} + \frac{60}{46}} = 0.49$$

[Mol. wt. of CH_3OH = 32, Mol. wt. of $\text{C}_2\text{H}_5\text{OH}$ = 46]

$$x_2 = \text{Mole fraction of } \text{C}_2\text{H}_5\text{OH} = \frac{\frac{60}{46}}{\frac{40}{32} + \frac{60}{46}} = 0.51$$

P_1 = partial vapour pressure of CH_3OH = $88.7 \times 0.49 = 43.46$ mm

P_2 = partial vapour pressure of $\text{C}_2\text{H}_5\text{OH}$ = $44.5 \times 0.51 = 22.69$ mm

$$P_{\text{Total}} = P_1 + P_2 = (43.46 + 22.69) \text{ mm} = 66.15 \text{ mm}$$

$$\text{Mole fraction of } \text{CH}_3\text{OH} \text{ in vapour} = \frac{43.46}{66.15} = 0.657$$

26. Using the relation, $p_1 = p_1^\circ x_1$

$$\text{We get } x_1 = \frac{p_1}{p_1^\circ} = \frac{750}{760} \quad \text{or } 0.9868$$

$$\therefore x_2 = 1 - x_1 = 1 - 0.9868 \quad \text{or } 0.0132$$

$$\text{Molality, } m = \frac{x_2}{x_1 M_1} \times 1000 \quad (x_2 = \text{mole fraction of solute})$$

$$= \frac{0.0132 \times 1000}{0.9868 \times 18} = 0.7431 \text{ mol kg}^{-1}$$

27. From Raoult's law, $\frac{p^\circ - p_s}{p^\circ} = \frac{w/m}{w/m + W/M}$

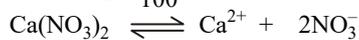
Given $p^\circ = 640 \text{ mm Hg}$; $w = 2.175 \text{ g}$; $m = ?$
 $p_s = 600 \text{ mm Hg}$; $W = 39.0 \text{ g}$; $M = 78$

Substituting the given values, we get

$$\frac{640 - 600}{640} = \frac{2.175}{\frac{2.175}{m} + \frac{39}{78}}$$

or $\frac{40}{640} = \frac{2.175}{2.175 + 0.5m}$ or $m = 65.25$

28. If we take 1 mole of $\text{Ca}(\text{NO}_3)_2$ initially, then degree of dissociation (α) of $\text{Ca}(\text{NO}_3)_2 = \frac{70}{100} \alpha = 0.7$



Initial moles	1	0	0
Eq. moles	$1 - 0.7 = 0.3$	0.7	$2 \times 0.7 = 1.4$
Total no. of moles	$0.3 + 0.7 + 1.4 = 2.4$		

Total number of moles = $1 + 0 + 0 = 1$

If the solution contains 1 g of $\text{Ca}(\text{NO}_3)_2$, then number of

moles of $\text{Ca}(\text{NO}_3)_2$ present in solution = $\frac{1}{164}$ [mol. wt. = 164]

\therefore Total number of moles present in solution at equilibrium

in such solution = $\frac{1}{164} \times 2.4$

Similarly, the total number of moles present in a solution

containing 7 g of $\text{Ca}(\text{NO}_3)_2$ will be = $\frac{7}{164} \times 2.4 = 0.102$

$$\begin{aligned} \text{Number of moles of water (N)} &= \frac{\text{Weight of water}}{\text{Mol. wt. of water}} \\ &= \frac{100}{18} = 5.55 \end{aligned}$$

Using Raoult's law, $\frac{p^\circ - p_s}{p^\circ} = \frac{n}{n + N}$, We get

or $\frac{760 - p_s}{760} = \frac{0.102}{0.102 + 5.55}$ or $\frac{760 - p_s}{760} = 0.0180$

or $p_s = 760 - (760 \times 0.0180) = 746.32 \text{ mm of Hg}$.

29. Given : $\Delta T_f = 5.51 - 5.03 = 0.48$; $w = 0.643 \text{ g}$

$$K_f = 5.12$$
; $W = 50 \times 0.879 = 43.95 \text{ g}$

Now, molecular weight of solute :

$$m = \frac{1000 \times K_f \times w}{\Delta T_f \times W} = \frac{1000 \times 5.12 \times 0.643}{0.48 \times 43.95} = 156.0$$

30. We know, $\frac{p^\circ - p_s}{p^\circ} = \frac{w/m}{w/m + W/M}$

Let the initial (normal) pressure, $p^\circ = p$, then

$$p_s = \text{pressure of solution} = \frac{75}{100} \times p \text{ or } 0.75p$$

$$m = 60, M = 18$$
; $W = 100 \text{ g}$

Substituting these values, we get

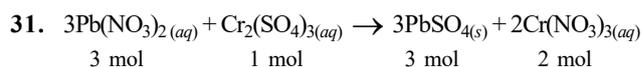
$$\frac{p - 0.75p}{p} = \frac{w/60}{w/60 + 100/18}$$

or $\frac{1}{4} = \frac{w/60}{w/60 + 5.55}$ or $\frac{4w}{60} = \frac{w}{60} + 5.55$

or $\frac{4w}{60} - \frac{w}{60} = 5.55$ or $\frac{3w}{60} = 5.55$

or $w = \frac{5.55 \times 60}{3}$ or 111 g

$$\text{Molality} = \frac{w}{60} \times \frac{1000}{100} = \frac{111}{60} \times \frac{1000}{100} = 18.5 \text{ m}$$



$$\begin{array}{cccc} 3 \text{ mol} & 1 \text{ mol} & 3 \text{ mol} & 2 \text{ mol} \end{array}$$

$$\text{Moles of Pb}(\text{NO}_3)_2 \text{ mixed} = \frac{45}{1000} \times 0.25 = 11.25 \times 10^{-3} \text{ mol}$$

$$\text{Moles of Cr}_2(\text{SO}_4)_3 \text{ mixed} = \frac{25}{1000} \times 0.1 = 2.5 \times 10^{-3} \text{ mol}$$

$$\therefore \text{Moles of PbSO}_4 \text{ precipitated} = 3 \times 2.5 \times 10^{-3} \text{ mol}$$

$$\text{or } 7.5 \times 10^{-3} \text{ mol}$$

$$\text{Moles of Pb}(\text{NO}_3)_2 \text{ reacted} = 3 \times 2.5 \times 10^{-3} = 7.5 \times 10^{-3} \text{ mol}$$

$$\text{Moles of Pb}(\text{NO}_3)_2 \text{ left unreacted} = (11.25 \times 10^{-3} - 7.5 \times 10^{-3}) \text{ mol} = 3.75 \times 10^{-3} \text{ mol}$$

$$\text{Moles of Cr}_2(\text{SO}_4)_3 \text{ left} = 0$$

$$\text{Moles of Cr}_2(\text{SO}_4)_3 \text{ in solution} = 2 \times 2.5 \times 10^{-3} \text{ moles} = 5.0 \times 10^{-3} \text{ moles}$$

$$\text{Total volume of solution} = (45 + 25) \text{ ml} = 70 \text{ ml}$$

$$\therefore \text{Molarity of Pb}(\text{NO}_3)_2 \text{ in solution} = \frac{3.75 \times 10^{-3}}{70} \times 1000 = 0.0536 \text{ M}$$

$$\text{Molarity of Cr}(\text{NO}_3)_3 \text{ in solution} = \frac{5.0 \times 10^{-3}}{70} \times 1000 = 0.0714 \text{ M}$$

32. Given $w_A = 8000 \times 1.0 = 8000 \text{ g}$ [density of water is 1g/ml]
 $w_B = 2000 \times 0.8 = 1600 \text{ g}$, $M_B = 32$

Using the relation, $\Delta T_f = \frac{K_f \times 1000 \times w_B}{w_A \times M_B}$, we get

$$\therefore \Delta T_f = \frac{1.86 \times 1000 \times 1600}{8000 \times 32} = 11.625$$

$$\text{Freezing point} = 0 - 11.625 = -11.625^\circ\text{C}$$

Vehicle may be parked outdoor not below than -11.625°C temperature.

33. Volume of 1 mol of liquid benzene = $\frac{78}{0.877} = 88.94 \text{ ml}$

$$\text{Volume of 1 mol of benzene vapour} = 88.94 \times 2750 = 244.585 \text{ L}$$

Assuming the vapour to behave like an ideal gas

$$\begin{aligned} P^\circ_{\text{Benzene}} &= \frac{RT}{V} \quad (\text{For 1 mol}) \\ &= \frac{0.082 \times 293}{244.585} \text{ atm} = 0.098 \text{ atm} \end{aligned}$$

$$\text{Volume of 1 mol of liquid toluene} = \frac{92}{0.867} = 106.11$$

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Volume of 1 mol of toluene vapour = $106.11 \times 7720 = 819.169$ L

Assuming the vapour to behave like an ideal gas

$$P_{\text{Toluene}}^{\circ} = \frac{0.082 \times 293}{819.169} = 0.029 \text{ atm}$$

$$P_{\text{Benzene}} = X_{\text{Benzene}} \times P_{\text{Benzene}}^{\circ} = X_{\text{Benzene}} \times 0.098 \text{ atm}$$

$$P_{\text{Toluene}} = X_{\text{Toluene}} \times 0.029 \\ = (1 - X_{\text{Benzene}}) \times 0.029 \text{ atm} [\because X_{\text{Toluene}} = 1 - X_{\text{Benzene}}]$$

$$P_{\text{Total}} = P_{\text{Benzene}} + P_{\text{Toluene}}$$

$$\text{or } 46 \text{ torr} = X_{\text{Benzene}} \times 0.098 + (1 - X_B) \times 0.029$$

$$\text{or } \frac{46}{760} \text{ atm} = 0.069 X_{\text{Benzene}} + 0.029$$

$$\text{or } 0.06 = 0.069 X_{\text{Benzene}} + 0.029$$

$$\text{or } X_B = \frac{0.06 - 0.029}{0.069} = \frac{0.031}{0.069} = 0.449$$

Thus mole fraction of benzene in vapour phase

$$= \frac{0.449 \times 0.098}{0.06} = 0.73$$

34. Using the relation $\frac{P^{\circ} - P_s}{P^{\circ}} = \frac{w}{m} \times \frac{M}{W}$
 [For very dilute solution $\frac{w}{m} + \frac{W}{m} \approx \frac{W}{M}$],

we get,

$$\frac{100 - 98.88}{98.88} = \frac{w \times 78 \times 1000}{m \times W \times 1000}$$

$$\text{or molality} = \frac{w}{m} \times \frac{1000}{W} = \frac{1.12 \times 1000}{78 \times 98.88} = 0.1452$$

$$\text{Since } \Delta T_f = K_f \times \text{molality}$$

$$\therefore 0.73 = K_f \times 0.1452$$

$$\text{or } K_f = \frac{0.73}{0.1452} = 5.027 \text{ K molality}^{-1}$$

35. $\Delta T_f = 0 - (-0.30) = 0.30$

$$\text{Since } \Delta T_f = K_f m$$

$$\therefore m = \frac{\Delta T_f}{K_f} = \frac{0.30}{1.86} = 0.161$$

$$\text{Using the relation, } \frac{P^{\circ} - P_s}{P^{\circ}} = X_B = \frac{n_B}{n_A + n_B}, \text{ we get}$$

$$\frac{P^{\circ} - P_s}{P^{\circ}} = \frac{n_B}{n_A} \quad [\text{For dilute solutions, } n_A + n_B = n_A]$$

$$\text{or } \frac{23.51 - P_s}{23.51} = \frac{0.161}{1000/18}$$

$$\text{or } \frac{23.51 - P_s}{23.51} = 0.002898$$

$$\text{or } P_s = 23.51 - 23.51 \times 0.002898 = 23.51 - 0.067 \\ = 23.44 \text{ mm of Hg}$$

36. Calculation of Empirical Formula

Element	%	Relative number of atoms	Simplest ratio
C	42.86	$42.86/12 = 3.57$	$3.57/1.19 = 3$
H	2.40	$2.40/1 = 2.40$	$2.40/1.19 = 2$
N	16.67	$16.67/14 = 1.19$	$1.19/1.19 = 1$
O	38.07	$38.07/16 = 2.38$	$2.38/1.19 = 2$

\therefore Empirical formula of minor product = $C_3H_2NO_2$

Empirical formula weight = $3 \times 12 + 2 \times 1 + 14 + 2 \times 16 = 84$

If molecular mass of minor product is M , then for 5.5 g of minor product dissolved in 45 g of benzene,

$$\frac{5.5}{M}$$

$$\text{the molality of solution} = \frac{5.5}{0.045}$$

Since $\Delta T_b = K_b \times \text{molality}$

$$1.84 = (2.53 \text{ kg mol}^{-1}) \left(\frac{5.5}{0.045} \right) \text{ or } M = 168 \text{ mol}^{-1}$$

$$\therefore n = \frac{168}{84} \text{ or } 2$$

\therefore Molecular formula of the compound is $C_6H_4N_2O_4$

Its structural formula is $C_6H_4 \begin{matrix} \diagup NO_2 \\ \diagdown NO_2 \end{matrix}$
o/m/p-dinitrobenzene

37. Weight of water = $500 \times 0.997 = 498.5$ g

$$\text{Number of moles of acetic acid} = \frac{3 \times 10^{-3} \times 10^3 \text{ g}}{60} = 0.05$$

Since the solution contains 0.05 moles of acetic acid (CH_3COOH) in 498.5 g of water

\therefore Moles of acetic acid present in 1000 g of water

$$= \frac{0.05}{498.5} \times 1000 = 0.1$$

Hence the molality of solution = 0.1

To Determine van't Hoff factor (i)



$$\begin{array}{l} \text{Initial} \quad 1 \quad \quad \quad 0 \quad 0 \\ \text{Equi.} \quad 1 - 0.23 \quad \quad 0.23 \quad 0.23 \end{array}$$

$$\therefore i = 1 - 0.23 + 0.23 + 0.23 = 1.23$$

$$\text{since } \Delta T_f = i \times K_f \times m$$

$$\therefore \Delta T_f = 1.23 \times 1.86 \times 0.1 = 0.228 \text{ K.}$$

38. First case

(i) $\Delta T_b = K_b \times m$

$$\text{or } 0.17 = 1.7 \times \frac{1.22}{m \times 100 \times 10^{-3}}$$

$$\text{or } m = 122 \text{ i.e. Benzoic acid exists as monomer.}$$

Second case

(ii) $\Delta T_b = K_b \times m$

$$\text{or } 0.13 = 2.6 \times \frac{1.22}{m' \times 100 \times 10^{-3}}$$

$$\text{or } m' = 244$$

i.e. the molecular weight of benzoic acid is twice its normal molecular weight so it shows that benzoic acid exists as dimer in acetone.

39. $2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$

$$\begin{array}{l} t = 0 \quad \quad \quad C \quad \quad \quad 0 \\ t_{\text{equi.}} \quad C(1 - \alpha) \quad \quad \quad C\alpha/2 \end{array}$$

$$\text{Total number of moles} = C - C\alpha + (C\alpha/2)$$

$$= C - \frac{C\alpha}{2} = \frac{2C - C\alpha}{2} = \frac{C(2 - \alpha)}{2}$$

$$C = \frac{\text{Weight}}{\text{Molecular weight}} = \frac{75.2}{(\text{C}_6\text{H}_5\text{OH})} = \frac{75.2}{92} = 0.8$$

$$\Delta T_f = K_f \times m$$

$$\Rightarrow 7 = 14 \times 0.8 \left(\frac{2-\alpha}{2} \right) \text{ or, } 1 = 0.8(2-\alpha)$$

$$\text{or, } 2-\alpha = \frac{1}{0.8} \text{ or, } -\alpha = \frac{10}{8} - 2$$

$$-\alpha = \frac{-6}{8} \text{ or, } \alpha = 0.75 = 75\%$$

40. (d): $\Delta T_f = K_f \times m = 2 \times \frac{0.1}{0.9 \times 46} \times 1000$ or $\Delta T_f = 4.83$ K

Freezing point of solution M, $T'_f = T_f^\circ - \Delta T_f = 155.7 - 4.83$

or $T'_f = 150.9$ K

41. (b): Total vapour pressure

$$P = P_A^0 X_A \quad (\text{Solute is non-volatile here})$$

$$P = 40 \times 0.9 \quad (\text{Vapour pressure of pure ethanol} = 40 \text{ mm of Hg})$$

$$= 36 \text{ mm of Hg}$$

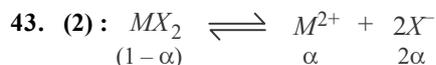
42. (b): $\Delta T_b = K_b \times m = 0.52 \times \frac{0.1}{0.9 \times 18} \times 1000$

$$\text{or } \Delta T_b = \frac{520}{9 \times 18} = 3.20$$

The boiling point of the solution, $T'_b = T_b^\circ + \Delta T_b$

$$T'_b = 373 + 3.20 \quad (\text{Standard B.P. of water} = 373 \text{ K})$$

$$T'_b = 376.2 \text{ K}$$



$$(1-\alpha) \qquad \qquad \alpha \qquad \qquad 2\alpha$$

$$i = 1 - \alpha + \alpha + 2\alpha$$

$$i = 1 + 2\alpha$$

$$i = 1 + 2 \times 0.5 = 2$$

$$(\because \alpha = 0.5)$$

44. (1): $\Delta T_f = iK_f m$

Given: $m = 0.01$ molal, $T_f = -0.0558^\circ\text{C}$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$$\Delta T_f = T_f^\circ - T_f = 0^\circ\text{C} - (-0.0558^\circ\text{C}) = 0.0558^\circ\text{C}$$

$$= \frac{\Delta T_f}{K_f m} = \frac{0.0558}{1.86 \times 0.01} = 3$$

As, three ions are produced by the complex, the molecular formula of the complex is $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Thus, only one Cl^- ion is in the coordination sphere.



7

Chemical Energetics

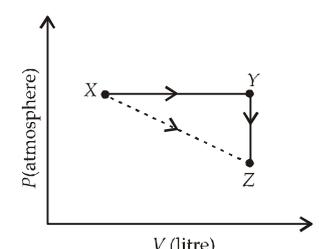
Multiple Choice Questions with ONE Correct Answer

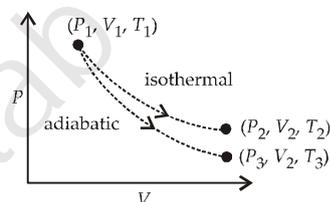
1. The difference between heats of reaction at constant pressure and constant volume for the reaction:
 $2\text{C}_6\text{H}_6(l) + 15\text{O}_2(g) \longrightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$ at 25°C in kJ is
 (a) -7.43 (b) $+3.72$ (c) -3.72 (d) $+7.43$
 (1991)
2. For an endothermic reaction where ΔH represents the enthalpy of the reaction in kJ/mole, the minimum value for the energy of activation will be
 (a) less than ΔH (b) zero
 (c) more than ΔH (d) equal to ΔH .
 (1992)
3. For which change $\Delta H \neq \Delta E$?
 (a) $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ (b) $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl}$
 (c) $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$ (d) $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$
 (1995)
4. Molar heat capacity of water in equilibrium with ice at constant pressure is
 (a) zero (b) infinity (∞)
 (c) $40.45 \text{ kJ K}^{-1} \text{ mol}^{-1}$ (d) $75.48 \text{ kJ K}^{-1} \text{ mol}^{-1}$
 (1997)
5. Standard molar enthalpy of formation of CO_2 is equal to
 (a) zero
 (b) the standard molar enthalpy of combustion of gaseous carbon
 (c) the sum of standard molar enthalpies of formation of CO and O_2
 (d) the standard molar enthalpy of combustion of carbon (graphite).
 (1997)
6. The ΔH_f° for $\text{CO}_{2(g)}$, $\text{CO}_{(g)}$ and $\text{H}_2\text{O}_{(g)}$ are -393.5 , -110.5 and $-241.8 \text{ kJ mol}^{-1}$ respectively. The standard enthalpy change (in kJ) for reaction $\text{CO}_{2(g)} + \text{H}_{2(g)} \rightarrow \text{CO}_{(g)} + \text{H}_2\text{O}_{(g)}$ is
 (a) 524.1 (b) 41.2 (c) -262.5 (d) -41.2
 (2000)
7. In thermodynamics, a process is called reversible when
 (a) surroundings and system change into each other
 (b) there is no boundary between system and surroundings
 (c) the surroundings are always in equilibrium with the system
 (d) the system changes into the surroundings spontaneously.
 (2001)
8. Which one of the following statements is false?
 (a) Work is a state function.
 (b) Temperature is a state function.
 (c) Change in the state is completely defined when the initial and final states are specified
 (d) Work appears at the boundary of the system. (2001)
9. One mole of a non-ideal gas undergoes a change of state ($2.0 \text{ atm}, 3.0 \text{ L}, 95 \text{ K}$) \rightarrow ($4.0 \text{ atm}, 5.0 \text{ L}, 245 \text{ K}$) with a change in internal energy, $\Delta U = 30.0 \text{ L atm}$. The change in enthalpy (ΔH) of the process in L atm is
 (a) 40.0 (b) 42.3
 (c) 44.0 (d) not defined, because pressure is not constant. (2002)
10. Which of the reaction defines ΔH_f° ?
 (a) $\text{C}_{(\text{diamond})} + \text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)}$
 (b) $\frac{1}{2}\text{H}_{2(g)} + \frac{1}{2}\text{F}_{2(g)} \longrightarrow \text{HF}_{(g)}$
 (c) $\text{N}_{2(g)} + 3\text{H}_{2(g)} \longrightarrow 2\text{NH}_{3(g)}$
 (d) $\text{CO}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)}$
 (2003)
11. Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K . The enthalpy change (in kJ) for the process is
 (a) 11.4 kJ (b) -11.4 kJ (c) 0 kJ (d) 4.8 kJ
 (2004)
12. The enthalpy of vapourisation of liquid is 30 kJ mol^{-1} and entropy of vapourisation is $75 \text{ J mol}^{-1} \text{ K}$. The boiling point of the liquid at 1 atm is
 (a) 250 K (b) 400 K (c) 450 K (d) 600 K
 (2004)
13. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is
 (Given: $\Delta H_r^\circ_{298 \text{ K}} = -54.07 \text{ kJ mol}^{-1}$,
 $\Delta S_r^\circ_{298 \text{ K}} = 10 \text{ JK}^{-1} \text{ mol}^{-1}$ and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$,
 $2.303 \times 8.314 \times 298 = 5705$)
 (a) 5 (b) 10 (c) 95 (d) 100
 (2007)

14. For the process
 $\text{H}_2\text{O}_{(l)} (1 \text{ bar}, 373 \text{ K}) \rightarrow \text{H}_2\text{O}_{(g)} (1 \text{ bar}, 373 \text{ K})$,
 the correct set of thermodynamic parameters is
 (a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0, \Delta S = -ve$
 (c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve.$ (2007)
15. The species which by definition has zero standard molar enthalpy of formation at 298 K is
 (a) $\text{Br}_{2(g)}$ (b) $\text{Cl}_{2(g)}$ (c) $\text{H}_2\text{O}_{(g)}$ (d) $\text{CH}_{4(g)}$ (2010)
16. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a $\text{C}\equiv\text{C}$ bond in C_2H_2 . That energy is (take the bond energy of a $\text{C}-\text{H}$ bond as 350 kJ mol^{-1}).
 $2\text{C}_{(s)} + \text{H}_{2(g)} \rightarrow \text{C}_2\text{H}_{2(g)}; \Delta H = 225 \text{ kJ mol}^{-1}$
 $2\text{C}_{(s)} \rightarrow 2\text{C}_{(g)}; \Delta H = 1410 \text{ kJ mol}^{-1}$
 $\text{H}_{2(g)} \rightarrow 2\text{H}_{(g)}; \Delta H = 330 \text{ kJ mol}^{-1}$
 (a) 1165 (b) 837 (c) 865 (d) 815 (2012)
17. The standard enthalpies of formation of $\text{CO}_{2(g)}$, $\text{H}_2\text{O}_{(l)}$ and glucose $_{(s)}$ at 25°C are -400 kJ/mol , -300 kJ/mol and -1300 kJ/mol , respectively. The standard enthalpy of combustion per gram of glucose at 25°C is
 (a) $+2900 \text{ kJ}$ (b) -2900 kJ
 (c) -16.11 kJ (d) $+16.11 \text{ kJ}$ (2013)
18. For the process:
 $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)}$
 at $T = 100^\circ\text{C}$ and 1 atmosphere pressure, the correct choice is
 (a) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$
 (b) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$
 (c) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$
 (d) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$ (2014)

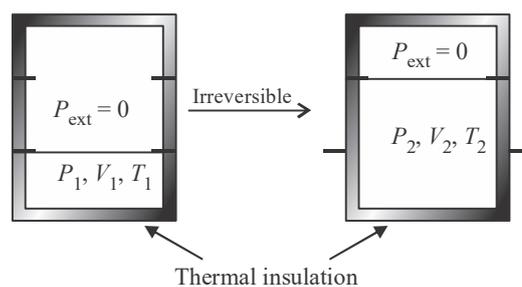
**Multiple Choice Questions with
 ONE or MORE THAN ONE Correct Answer**

19. Identify the intensive quantities from the following
 (a) enthalpy (b) temperature
 (c) volume (d) refractive index. (1993)
20. The following is (are) endothermic reaction(s)
 (a) combustion of methane
 (b) decomposition of water
 (c) dehydrogenation of ethane to ethylene
 (d) conversion of graphite to diamond. (1999)
21. Among the following, the state function(s) is(are)
 (a) internal energy
 (b) irreversible expansion work
 (c) reversible expansion work
 (d) molar enthalpy. (2009)

22. For an ideal gas, consider only P - V work in going from an initial state X to the final state Z . The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is(are) correct? [Take ΔS as change in entropy and w as work done]
- 
- (a) $\Delta S_{X \rightarrow Z} = \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z}$
 (b) $w_{X \rightarrow Z} = w_{X \rightarrow Y} + w_{Y \rightarrow Z}$
 (c) $w_{X \rightarrow Y \rightarrow Z} = w_{X \rightarrow Z}$
 (d) $\Delta S_{X \rightarrow Y \rightarrow Z} = \Delta S_{X \rightarrow Z}$ (2012)
23. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is(are) correct?



- (a) $T_1 = T_2$ (b) $T_3 > T_1$
 (c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$ (d) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$ (2012)
24. An ideal gas in a thermally insulated vessel at internal pressure = P_1 , volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of gas are P_2 , V_2 and T_2 , respectively. For this expansion,



- (a) $q = 0$ (b) $T_2 = T_1$
 (c) $P_2V_2 = P_1V_1$ (d) $P_2V_2^\gamma = P_1V_1^\gamma$ (2014)

Fill in the Blanks

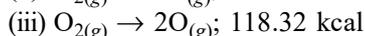
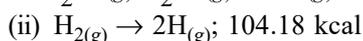
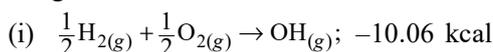
25. A system is said to be if it can neither exchange matter nor energy with the surroundings. (1993)
26. The heat content of the products is more than that of the reactants in an reaction. (1993)
27. Enthalpy is an property. (1997)

True / False

28. First law of thermodynamics is not adequate in predicting the direction of a process. (1982)
29. Heat capacity of a diatomic gas is higher than that of a monoatomic gas. (1985)

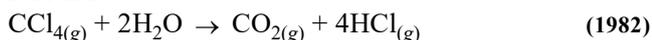
Subjective Problems

30. The enthalpy for the following reaction (ΔH°) at 25°C are given below:



Calculate the O – H bond energy in the hydroxyl radical. (1981)

31. The standard heats of formation at 298 K for $\text{CCl}_{4(g)}$, $\text{H}_2\text{O}_{(g)}$, $\text{CO}_{2(g)}$ and $\text{HCl}_{(g)}$ are -25.5, -57.8, -94.1 and -22.1 kcal/mol respectively. Calculate ΔH_{298}° for the reaction :



32. The molar heats of combustion of $\text{C}_2\text{H}_{2(g)}$, C(graphite) and $\text{H}_{2(g)}$ are 310.62 kcal, 94.05 kcal and 68.32 kcal, respectively. Calculate the standard heat of formation of $\text{C}_2\text{H}_{2(g)}$. (1983)

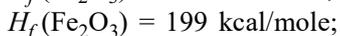
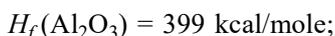
33. The heat energy, q , absorbed by a gas is ΔH is true at what condition(s)? (1984)

34. Given the following standard heats of reactions:
- (i) heat of formation of water = -68.3 kcal;
- (ii) heat of formation of acetylene = -310.6 kcal;
- (iii) heat of formation of ethylene = -337.2 kcal;
- Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25°C). (1984)

35. The bond dissociation energies of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 kcal/mole respectively. Calculate the enthalpy of formation of HCl gas. (1985)

36. The standard molar heats of formation of ethane, carbon dioxide and liquid water are -21.1, -94.1 and -68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane. (1986)

37. An intimate mixture of ferric oxide, Fe_2O_3 , and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heat of formation and densities are as follows:



38. An athlete is given 100 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) of energy equivalent to 1560 kJ. He utilizes 50 per cent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ/mole. (1989)

39. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are -241, -3800 and -3920 kJ/mole respectively. Calculate the heat of hydrogenation of cyclohexene. (1989)

40. Using the data (all values are in kcal mol⁻¹ at 25°C) given below, calculate the bond energy of C–C and C–H bonds.

$$\Delta H_{\text{combustion(ethane)}}^\circ = -372.0$$

$$\Delta H_{\text{combustion(propane)}}^\circ = -530.0$$

$$\Delta H_{\text{combustion(graphite)}}^\circ \rightarrow \text{C}_{(g)} = -172.0$$

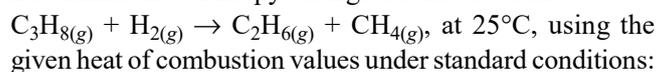
$$\text{Bond energy of H – H} = 104.0$$

$$\Delta H_f^\circ \text{ of } \text{H}_2\text{O}_{(l)} = -68.0$$

$$\Delta H_f^\circ \text{ of } \text{CO}_{2(g)} = -94.0 \quad (1990)$$

41. A gas mixture of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO_2 . Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are -1423 and -891 kJ mol⁻¹ at 25°C. (1991)

42. Determine the enthalpy change of the reaction.



Compound	$\text{H}_{2(g)}$	$\text{CH}_{4(g)}$	$\text{C}_2\text{H}_{6(g)}$	$\text{C}_{(\text{graphite})}$
$\Delta H^\circ(\text{kJ/mol})$	-285.8	-890.0	-1560.0	-393.5

The standard heat of formation of $\text{C}_3\text{H}_{8(g)}$ is -103.8 kJ/mol. (1992)

43. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and $6x$ litre/hour of O_2) is to be readjusted for butane, C_4H_{10} . In order to get the same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion, etc. are the same for both the fuels and the gases behave ideally. (Heats of combustion: $\text{CH}_4 = 809$ kJ/mol; $\text{C}_4\text{H}_{10} = 2878$ kJ/mol) (1993)

44. The polymerisation of ethylene to linear polyethylene is represented by the reaction



where n has a large integral value. Given that the average enthalpies of bond dissociation for C=C and C–C at

- 298 K are +590 and +331 kJ mol⁻¹ respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K. (1994)
45. The standard molar enthalpies of formation of cyclohexane_(l) and benzene_(l) at 25°C are -156 and +49 kJ mol⁻¹ respectively. The standard enthalpy of hydrogenation of cyclohexene_(l) at 25°C is -119 kJ mol⁻¹. Use these data to estimate the magnitude of the resonance energy of benzene. (1996)
46. The enthalpy change involved in the oxidation of glucose is -2880 kJ mol⁻¹. Twenty five per cent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 g of glucose? (1997)
47. Compute the heat of formation of liquid methyl alcohol in kilojoules per mole, using the following data. Heat of vapourisation of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states; H = 218 kJ/mol; C = 715 kJ/mol; O = 249 kJ/mol. Average bond energies: C - H = 415 kJ/mol, C - O = 365 kJ/mol, O - H = 463 kJ/mol (1997)
48. Anhydrous AlCl₃ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution.
(Ionisation energy for Al = 5137 kJ mol⁻¹;
 $\Delta H_{\text{hydration}}$ for Al³⁺ = -4665 kJ mol⁻¹;
 $\Delta H_{\text{hydration}}$ for Cl⁻ = -381 kJ mol⁻¹.) (1997)
49. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO_{2(g)}, H_{2O(l)} and propene_(g) are -393.5, -285.8 and 20.42 kJ mol⁻¹ respectively. The enthalpy of isomerisation of cyclopropane to propene is -33.0 kJ mol⁻¹. (1998)
50. Estimate the average S—F bond energy in SF₆. The values of standard enthalpy of formation of SF_{6(g)}, S_(g) and F_(g) are: -1100, 275 and 80 kJ mol⁻¹ respectively. (1999)
51. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm³ to 2.50 dm³. Calculate the enthalpy change in this process. $C_{V,m}$ for argon is 12.48 JK⁻¹ mol⁻¹. (2000)
52. Show that the reaction CO_(g) + $\frac{1}{2}$ O_{2(g)} → CO_{2(g)} at 300 K, is spontaneous and exothermic, when the standard entropy change is -0.094 kJ mol⁻¹ K⁻¹. The standard Gibbs free energies of formation for CO₂ and CO are -394.4 and -137.2 kJ mol⁻¹, respectively (2000)
53. Diborane is a potential rocket fuel which undergoes combustion according to the reaction.
B₂H_{6(g)} + 3O_{2(g)} → B₂O_{3(s)} + 3H₂O_(g)
From the following data, calculate the enthalpy change for the combustion of diborane.
2B_(s) + $\frac{3}{2}$ O_{2(g)} → B₂O_{3(s)} $\Delta H = -1273$ kJ mol⁻¹
H_{2(g)} + $\frac{1}{2}$ O_{2(g)} → H_{2O(l)} $\Delta H = -286$ kJ mol⁻¹
H_{2O(l)} → H_{2O(g)} $\Delta H = 44$ kJ mol⁻¹
2B_(s) + 3H_{2(g)} → B₂H_{6(g)} $\Delta H = 36$ kJ mol⁻¹ (2000)
54. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria:
B ⇌ A; $\Delta G_1^\circ = ?$ B ⇌ C; $\Delta G_2^\circ = ?$
From the calculated value of ΔG_1° and ΔG_2° indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C). (2001)
55. Two moles of a perfect gas undergo the following processes:
(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);
(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);
(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L);
(i) Sketch with labels each of the processes on the same P-V diagram.
(ii) Calculate the total work (W) and the total heat change (q) involved in the above processes.
(iii) What will be the values of ΔU , ΔH and ΔS for the overall process? (2002)
56. C_V value of He is always 3R/2 but C_V value of H₂ is 3R/2 at low temperature and 5R/2 at moderate temperature and more than 5R/2 at higher temperature. Explain in two to three lines. (2003)
57. An insulated container contains 1 mol of a liquid, molar volume 100 ml, at 1 bar. When liquid is steeply pressed to 100 bar, volume decreases to 99 ml. Find ΔH and ΔU for the process. (2004)
58. In the following equilibrium N₂O_{4(g)} ⇌ 2NO_{2(g)}

Chemical Energetics

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When 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar. Given: $\Delta G_f^\circ(\text{N}_2\text{O}_4) = 100 \text{ kJ}$; $\Delta G_f^\circ(\text{NO}_2) = 50 \text{ kJ}$

- (i) Find ΔG of the reaction at 298 K.
(ii) Find the direction of the reaction. (2004)

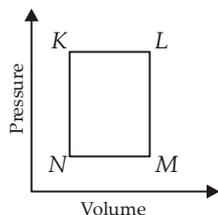
59. For the reaction, $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$; $\Delta H = -560 \text{ kJ}$. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2 , the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K. (1 atm = 0.1 kJ) (2006)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension - 1

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure



60. The pair of isochoric processes among the transformation of states is
(a) K to L and L to M (b) L to M and N to K
(c) L to M and M to N (d) M to N and N to K
61. The succeeding operations that enable this transformation of states are
(a) heating, cooling, heating, cooling
(b) cooling, heating, cooling, heating
(c) heating, cooling, cooling, heating
(d) cooling, heating, heating, cooling. (2013)

Comprehension - 2

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant ($-57.0 \text{ kJ mol}^{-1}$), this experiment could be used to measure the calorimeter constant.

In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured. (Consider heat capacity of all solutions as $4.2 \text{ J g}^{-1} \text{ K}^{-1}$ and

density of all solutions as 1.0 g mL^{-1})

62. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt. 2 is
(a) 1.0 (b) 10.0 (c) 24.5 (d) 51.4
63. The pH of the solution after Expt. 2 is
(a) 2.8 (b) 4.7 (c) 5.0 (d) 7.0 (2015)

Matrix Match Type

64. Match the transformations in Column I with appropriate options in Column II.

Column I	Column II
A. $\text{CO}_{2(s)} \rightarrow \text{CO}_{2(g)}$	p. Phase transition
B. $\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$	q. allotropic change
C. $2\text{H}\cdot \rightarrow \text{H}_{2(g)}$	r. ΔH is positive
D. $\text{P}_{(\text{white, solid})} \rightarrow \text{P}_{(\text{red, solid})}$	s. ΔS is positive
	t. ΔS is negative

(2011)

65. Match the thermodynamic processes given under Column I with the expressions given under Column II.

Column I	Column II
(A) Freezing of water at 273 K and 1 atm	(P) $q = 0$
(B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q) $w = 0$
(C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(R) $\Delta S_{\text{sys}} < 0$
(D) Reversible heating of $\text{H}_{2(g)}$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(S) $\Delta U = 0$
	(T) $\Delta G = 0$

(2015)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
(c) Statement-1 is true, statement-2 is false.
(d) Statement-1 is false, statement-2 is true.

66. **Statement-1** : The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
Statement-2 : The volume occupied by the molecules of an ideal gas is zero. (2000)

67. Statement-1 : For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

Statement-2 : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. (2008)

68. Statement-1 : There is a natural asymmetry between converting work to heat and converting heat to work.

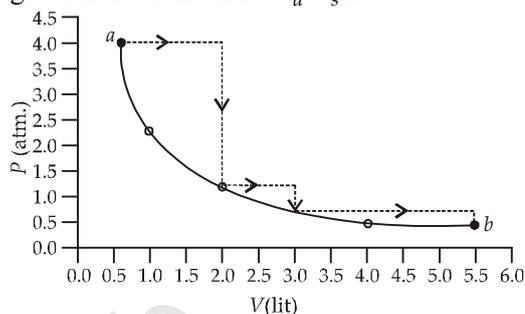
Statement-2 : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. (2008)

Integer Answer Type

69. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process.

Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1} , the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is (2009)

70. One mole of an ideal gas is taken from *a* to *b* along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d , the integer closest to the ratio w_d/w_s is



(2010)

ANSWER KEY

- | | | | | | |
|--|--|---|---|-------------------------------|-----------------|
| 1. (a) | 2. (c) | 3. (d) | 4. (b) | 5. (d) | 6. (b) |
| 7. (c) | 8. (a) | 9. (c) | 10. (b) | 11. (c) | 12. (b) |
| 13. (b) | 14. (a) | 15. (b) | 16. (d) | 17. (c) | 18. (b) |
| 19. (b, d) | 20. (b, c, d) | 21. (a, d) | 22. (a, c) | 23. (a, c, d) | 24. (a, b, c) |
| 25. Isolated | 26. Endothermic | 27. Extensive | 28. True | 29. True | 30. 101.19 kcal |
| 31. -41.4 kcal | 32. 54.20 kcal | 33. Heat is absorbed at constant pressure; ΔH | | | |
| 34. -41.104 kcal | 35. -22 kcal | 36. -372 kcal/mole. | | 37. 0.9346 kcal/g; 3.94 kcal | |
| 38. 319.1 g | 39. -121 kJ | 40. C-C = 82 kcal; C-H = 99 kcal | 41. 55.57 kJ | 42. -55.7 kJ/mole | |
| 43. 5.48 (X) litre O_2 | 44. -72 kJ mol^{-1} | 45. -152 kJ | 46. 4.8 km | 47. -275 kJ mol^{-1} | |
| 48. -671 kJ mol^{-1} | 49. 2091.32 kJ mol^{-1} | 50. 309.16 kJ mol^{-1} | | | |
| 51. -115.96 Joules | 52. ΔG° is negative; ΔH is negative | 53. -2035 kJ | | | |
| 54. $\Delta G^\circ_1 = 15.992 \text{ kJ mol}^{-1}$; $\Delta G^\circ_2 = 12.312 \text{ kJ mol}^{-1}$; $B > C > A$. | | | | | |
| 55. (W) = -6.15 L atm; q = -6.15 L atm; $\Delta S = 0$; $\Delta H = 0$; $\Delta U = 0$ | | | | | |
| 57. $\Delta U = 100 \text{ bar mL}$; $\Delta H = 9900 \text{ bar mL}$ | | | 58. $5.0705 \times 10^3 \text{ kJ mol}^{-1}$, reverse direction. | | |
| 59. -557 kJ | 60. (b) | 61. (c) | 62. (a) | 63. (b) | |
| 64. (A) \rightarrow (p, r, s); B \rightarrow (r, s), C \rightarrow (t), D \rightarrow (p, q, t) | | | | | |
| 65. (A) \rightarrow (R and T); B \rightarrow (P, Q and S), C \rightarrow (P, Q and S), D \rightarrow (P, Q, S and T) | | | | | |
| 66. (b) | 67. (d) | 68. (a) | 69. (9) | 70. (2) | |

Explanations

1. (a): $q = \Delta E - W$ (First law of thermodynamics)

At constant volume, $\Delta V = 0$

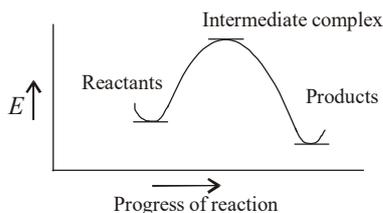
At constant pressure, $\Delta P = 0$

$$\begin{aligned} \therefore q_p &= \Delta E - (-P\Delta V) & (\because W &= -P\Delta V) \\ &= (E_2 - E_1) + P(V_2 - V_1) \\ &= (E_2 + PV_2) - (E_1 + PV_1) \\ &= H_2 - H_1 & (\because H &= E + PV) = \Delta H \end{aligned}$$

$$\begin{aligned} \text{or } q_p - q_v &= \Delta H - \Delta E & (\because q_v &= \Delta E, W = 0) = \Delta n.RT \\ &= -3 \times 8.314 \times 10^{-3} \times 298 & (\Delta n = 12 - 15 = -3) \\ &= -7.43 \text{ kJ.} \end{aligned}$$

2. (c): $E_{\text{activation}}$ = (Energy intermediate complex) - (Average energy of reactants)

The energy of intermediate complex generally lies above the energy of products.



3. (d): $\Delta H = \Delta E + (\Delta n)RT$

For $\Delta H \neq \Delta E$, $\Delta n \neq 0$

For (a), (b) and (c), $\Delta n = 0$

4. (b): $C_p = \frac{H_2 - H_1}{\Delta T} = \frac{\Delta H}{0} = \infty$ (infinity)

[$\Delta T = 0$, because two states (liquid and solid) of water are in equilibrium]

5. (d): ΔH_f° for CO_2 is given by $\text{C}_{(\text{graphite})} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})}$

6. (b): $\Delta H = (\Sigma\Delta H_p - \Sigma\Delta H_R)$
 $= (-110.5 - 241.8) - (-393.5) \text{ kJ mol}^{-1} = 41.2 \text{ kJ mol}^{-1}$

7. (c): Since the driving and opposite forces are equal in case of a reversible process so in such a process, the surroundings are always in equilibrium with the system.

8. (a): Work done depends upon the path adopted so it is not a state function.

9. (c): $\Delta H = H_2 - H_1 = (E_2 + P_2V_2) - (E_1 + P_1V_1)$
 $= (E_2 - E_1) + P_2V_2 - P_1V_1$
 $= 30 + 4 \times 5 - 2 \times 3 = 44 \text{ L atm.}$

10. (b): (a) is not correct because $\text{C}_{(\text{graphite})}$ and not $\text{C}_{(\text{diamond})}$ is the standard state.

(b) is correct because in it one mole of HF in its standard state is formed from its elements in their standard states.

(c) is incorrect because in it 2 moles of NH_3 are formed.

(d) is incorrect as it involves CO (not an element).

11. (c): $\Delta H = nC_p\Delta T$; Since $\Delta T = 0$ hence, $\Delta H = 0$

12. (b): $dS = \frac{dq_{\text{rev}}}{T}$ or $75 = \frac{30 \times 10^3}{T}$ or $T = 400 \text{ K}$

13. (b): For the equilibrium, $A \rightleftharpoons B$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -2.303RT \log_{10}K \quad (K \text{ is equilibrium constant.})$$

$$-2.303RT \log_{10}K = \Delta H^\circ - T\Delta S^\circ$$

$$2.303RT \log_{10}K = T\Delta S^\circ - \Delta H^\circ$$

$$\log_{10}K = \frac{T\Delta S^\circ - \Delta H^\circ}{2.303RT} = \frac{298 \times 10 + 54.07 \times 1000}{2.303 \times 8.314 \times 298} = 10$$

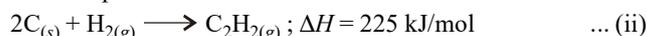
14. (a): The change given is occurring at the boiling point of the liquid, where, at given pressure and temperature, the liquid-vapour system virtually remains at equilibrium and hence $\Delta G = 0$. Also due to absorption of heat as latent heat of vaporisation, or due to change from liquid to gaseous state where randomness has also increased, $\Delta S > 0$.

15. (b): ΔH_f° is generally zero for elements, and in standard conditions, bromine is in liquid state while chlorine is in gaseous state.

16. (d): Ethyne molecule breaks as



Given equations are



Eqn. (i) can be obtained by adding equation (iii) and (iv) and then subtracting eq. (ii).

$$\begin{aligned} \Delta H \text{ for (i)} &= \Delta H_{(\text{iii})} + \Delta H_{(\text{iv})} - \Delta H_{(\text{ii})} \\ &= 1410 + 330 - 225 = 1515 \text{ kJ/mol.} \end{aligned}$$

Equation (i) involves breaking of 2C-H bonds and 1 $\text{C}\equiv\text{C}$ bonds, thus

ΔH of eq. (i) = 2 × bond energy of C-H + bond energy of $\text{C}\equiv\text{C}$ bond.

$$1515 = 2 \times 350 + \text{C}\equiv\text{C bond energy}$$

$$\text{Bond energy of C}\equiv\text{C} = 815 \text{ kJ/mol}$$

17. (c): $\text{C}_6\text{H}_{12}\text{O}_{6(\text{s})} + 6\text{O}_{2(\text{g})} \rightarrow 6\text{CO}_{2(\text{g})} + 6\text{H}_2\text{O}_{(\text{l})}$

$$\begin{aligned} \Delta H_c^\circ &= \Sigma\Delta H_f^\circ(\text{products}) - \Sigma\Delta H_f^\circ(\text{reactants}) \\ &= [6 \times \Delta H_f^\circ(\text{CO}_2) + 6 \times \Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6) \\ &\quad + 6 \times \Delta H_f^\circ(\text{O}_2)] \\ &= [6 \times (-400) + 6 \times (-300)] - [-1300 + 6(0)] \\ &= [(-2400 - 1800)] - [-1300] = -4200 + 1300 \\ &= -2900 \text{ kJ/mol} \end{aligned}$$

The standard enthalpy of combustion per gram of glucose is

$$= \frac{-2900}{180} = -16.11 \text{ kJ/g}$$

18. (b): $\text{H}_2\text{O}_{(l)} \xrightarrow{\text{Boiling}} \text{H}_2\text{O}_{(g)}$
 For this, $\Delta S_{\text{total}} = 0$
 $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$
 $\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$
 Hence, $\Delta S_{\text{system}} > 0$; $\Delta S_{\text{surroundings}} < 0$
19. (b, d): Intensive properties are those which are independent of the mass of the system.
20. (b, c, d): All combustion reactions are accompanied by evolution of heat *i.e.* they are exothermic.
21. (a, d): A state function is a property of a system whose value depends only upon the state of the system and is independent of the path or manner by which the state is reached. Thus internal energy and molar enthalpy are state functions. Work is a path dependent function and hence is not a state function.
22. (a, c): As ΔS does not depend on path and only depends on initial and final stages *i.e.*, it is a state function thus
 $\Delta S_{X \rightarrow Z} = \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z}$
 and $\Delta S_{Y \rightarrow Z}$ is not zero thus
 $\Delta S_{X \rightarrow Y \rightarrow Z} \neq \Delta S_{X \rightarrow Y}$
 As we know that work is not a state function and depends on path,
 Thus, $w_{X \rightarrow Z} \neq w_{X \rightarrow Y} + w_{Y \rightarrow Z}$
 $w_{X \rightarrow Y} = PdV$ (P is constant.)
 $w_{Y \rightarrow Z} = 0$ (V is constant.)
 $w_{X \rightarrow Z} = 2.303nRT \log \frac{V_2}{V_1}$
 $w_{X \rightarrow Y \rightarrow Z} = w_{X \rightarrow Y} + w_{Y \rightarrow Z}$
 As $w_{Y \rightarrow Z} = 0$, hence $w_{X \rightarrow Y \rightarrow Z} = w_{X \rightarrow Y}$
23. (a, c, d): (a) $T_1 = T_2$ as the process is isothermal. Hence, (a) is correct.
 (b) $T_3 < T_1$ because cooling takes place on adiabatic expansion. Hence (b) is incorrect.
 (c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$ because area under the isothermal curve is greater than under the adiabatic curve. Hence (c) is correct.
 (d) $\Delta U_{\text{adiabatic}} = -ve$ because when adiabatic expansion occurs, internal energy decreases. Thus, $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$. Hence (d) is correct.
24. (a, b, c): Since vessel is thermally insulated, *i.e.* the process is adiabatic hence, $q = 0$
 Also, $P_{\text{ext}} = 0$, hence $w = 0$
 From 1st law of thermodynamics, $\Delta E = q + w$
 $\therefore \Delta E = 0$ (for ideal gas)
 $\therefore \Delta T = 0$ or $T_2 = T_1$
 [\because Internal energy of an ideal gas is a function of temperature.]
 Applying ideal gas equation, $PV = nRT$
 where n , R and T are constant.
 then $P_1V_1 = P_2V_2$

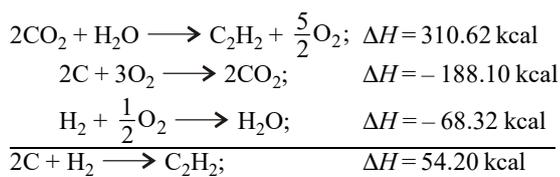
Equation, $PV^\gamma = \text{constant}$, is applicable only for ideal gas in reversible adiabatic process.

Hence, $P_2V_2^\gamma = P_1V_1^\gamma$ equation is not applicable.

25. Isolated; When the boundary is both sealed and insulated, no interaction is possible with the surroundings.
26. Endothermic; Since $H_P > H_R$ or $H_P - H_R = \Delta H = +ve$
27. Extensive; A property which depends upon the quantity of matter present in the system is called an extensive property.
28. True
 First law fails to predict the direction of reaction.
29. True
 In case of polyatomic gases, a part of energy supplied is used in increasing the internal energy of the system, and thus some additional energy is needed to raise the temperature of the gas through 1°C. It means that the heat capacity (amount of heat required to raise the temperature of the system by 1°C) is higher in case of polyatomic gases as compared to that for monoatomic gases.
30. The desired reaction is
 $\text{OH}_{(g)} \longrightarrow \text{O}_{(g)} + \text{H}_{(g)}; \Delta H = ?$
 To get this equation, divide equations (ii) and (iii) each by 2 and reverse equation (i). Now add all the new equations.
 $\text{OH}_{(g)} \longrightarrow \frac{1}{2} \text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)}; \Delta H = +10.06 \text{ kcal}$
 $\frac{1}{2} \text{H}_{2(g)} \longrightarrow \text{H}_{(g)}; \Delta H = -52.09 \text{ kcal}$
 $\frac{1}{2} \text{O}_{2(g)} \longrightarrow \text{O}_{(g)}; \Delta H = -59.16 \text{ kcal}$
 $\text{OH}_{(g)} \longrightarrow \text{O}_{(g)} + \text{H}_{(g)}; \Delta H = 10.06 + (-52.09) + (-59.16)$
 $= -101.19 \text{ kcal}$
 Hence the bond energy of O–H bond is 101.19 kcal
31. Heat content of a compound = Heat of formation (ΔH_f°)
 $= (\text{Heat content of products}) - (\text{Heat content of reactants})$
 From the given chemical reactions
 $\text{CCl}_4(g) + 2\text{H}_2\text{O}(g) \longrightarrow \text{CO}_2(g) + 4 \text{HCl}; \Delta H_{298}^\circ = ?$
 $\Delta H_{298}^\circ = [H_{\text{CO}_2} + 4 \times H_{\text{HCl}}] - [H_{\text{CCl}_4} + 2 \times H_{\text{H}_2\text{O}}]$
 or $\Delta H_{298}^\circ = [(-94.1) + 4(-22.1)] - [(-25.5) + 2(-57.8)]$
 $= [(-94.1 - 88.4) - (-25.5 - 115.6)]$
 $= -182.5 + 141.1 = -41.4 \text{ kcal}$
32. In this case the desired equation is
 $2\text{C} + \text{H}_2 \longrightarrow \text{C}_2\text{H}_2; \Delta H = ?$
 From the given data following reactions may be written as
 (i) $\text{C}_2\text{H}_2 + \frac{5}{2} \text{O}_2 \longrightarrow 2\text{CO}_2 + \text{H}_2\text{O}; \Delta H = -310.62 \text{ kcal}$
 (ii) $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2; \Delta H = -94.05 \text{ kcal}$
 (iii) $\text{H}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{H}_2\text{O}; \Delta H = -68.32 \text{ kcal}$
 To get the desired equation, reverse equation (i) and multiply equation (ii) by 2.
 Now add all the three new equations *i.e.*

Chemical Energetics

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33. In case heat is absorbed at constant pressure, we have

$$q_p = \Delta E - W$$

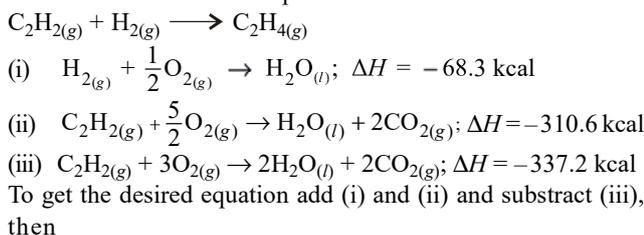
$$= \Delta E + P\Delta V \quad [\because W = -P\Delta V]$$

$$= (E_2 - E_1) + P(V_2 - V_1) = (E_2 + PV_2) - (E_1 + PV_1)$$

$$= H_2 - H_1 \quad [H = E + PV]$$

$$= \Delta H$$

34. In this case the desired equation is



$$\Delta H = -68.3 + (-310.6) - (-337.2) \text{ kcal}$$

$$\text{or } \Delta H = -41.7 \text{ kcal}$$

$$\Delta H = \Delta E + \Delta n.RT$$

$$\therefore \Delta E = \Delta H - \Delta n.RT$$

$$= -41.7 - (-1 \times 2 \times 10^{-3} \times 298) \text{ kcal}$$

$$= (-41.7 + 0.596) \text{ kcal} \quad [\because R = 2 \times 10^{-3} \text{ kcal/K/mole}]$$

$$= -41.104 \text{ kcal}$$

35. Given bond dissociation energy for

$$\text{H}-\text{H} = 10.4 \text{ kcal}$$

$$\text{Cl}-\text{Cl} = 58 \text{ kcal}$$

$$\text{H}-\text{Cl} = 103 \text{ kcal}$$

The reaction of formation of HCl is



In the formation of 2 moles of HCl,

one mole of H-H bonds are broken

one mole of Cl-Cl bonds are broken

and two moles of H-Cl bonds are formed.

$$\text{Thus } \Delta H \text{ of reaction} = (104 + 58) - 2 \times 103$$

$$= 162 - 206 = -44 \text{ kcal}$$

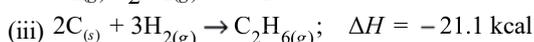
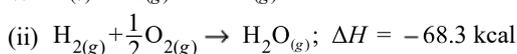
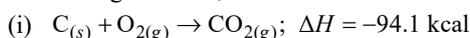
Thus $\Delta H = -44 \text{ kcal}$ for 2 moles of HCl

$$\text{Hence } \Delta H_f \text{ (i.e. for one mole)} = -\frac{44}{2} \text{ kcal} = -22 \text{ kcal}$$

36. In this case the desired equation is

Since in the above equation 2 moles of C_2H_6 are involved so ΔH_{comb} for C_2H_6 (i.e. ΔH_{comb} is the heat evolved when onemole is oxidised) will be half of the above i.e. $\frac{x}{2}$.

From the given data, we can write

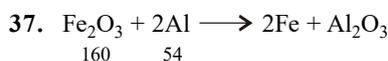
Since $\Delta H = \Delta_p - \Delta_R$

$$\therefore \Delta H = [4 \times (-94.1) + 6 \times (-68.3)] - [2 \times (-21.1) + 0]$$

$$\Delta H = [-376.4 - 409.8] + 42.2$$

$$\Delta H = -744.0 \text{ kcal}$$

$$\text{or } \frac{x}{2} = \frac{\Delta H}{2} = \frac{-744}{2} = -372 \text{ kcal/mole}$$



$$\text{Heat of reaction} = H_f(\text{Al}_2\text{O}_3) - H_f(\text{Fe}_2\text{O}_3)$$

$$= (399 - 199) \text{ kcal} = 200 \text{ kcal}$$

$$\text{Total weight of reactants} = (160 + 54) = 214 \text{ g}$$

$$\text{Fuel value / gram} = \frac{200}{214} = 0.9346 \text{ kcal/g}$$

$$\text{Volume of Al} = \frac{\text{Mass}}{\text{Density}} = \frac{54}{2.7} = 20.0 \text{ cc}$$

$$\text{Volume of Fe}_2\text{O}_3 = \frac{\text{Mass}}{\text{Density}} = \frac{160}{5.2} = 30.77 \text{ cc}$$

$$\text{Total volume} = (20.0 + 30.77) \text{ cc} = 50.77 \text{ cc}$$

$$\therefore \text{Fuel value per cc} = \frac{200}{50.77} = 3.94 \text{ kcal}$$

38. 100 g glucose = 1560 kJ

$$\therefore \text{Energy used up} = \frac{50}{100} \times 1560 = 780 \text{ kJ}$$

Hence energy to be given out = 780 kJ

Enthalpy of evaporation of water = 44 kJ / mole

$$= 44 \text{ kJ} / 18 \text{ g of water}$$

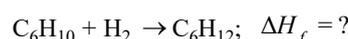
Thus 44 kJ energy is given by water = 18 g

$$1 \text{ kJ energy is given by water} = \frac{18}{44} \text{ g}$$

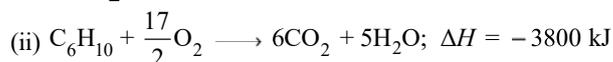
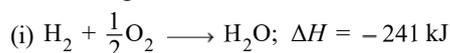
$$780 \text{ kJ energy will be given by water} = \frac{18}{44} \times 780 \text{ g} = 319.1 \text{ g}$$

Hence water to be perspired = 319.1 g

39. In this case the desired reaction is



From the given data, we can write following equations:

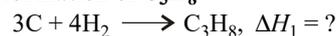
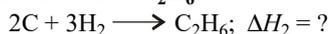


To get the desired equation, add (i) and (ii) and subtract (iii).

$$\text{Then } \Delta H = -241 + (-3800) - (-3920)$$

$$= -4041 + 3920 = -121 \text{ kJ}$$

40. For formation of
- C_3H_8

For formation of C_2H_6 

$$\text{Thus (i) } \Delta H_1 = -[2(\text{C}-\text{C}) + 8(\text{C}-\text{H})] + [3\text{C}_{s \rightarrow g} + 4(\text{H}-\text{H})]$$

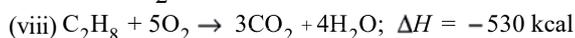
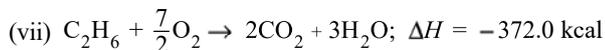
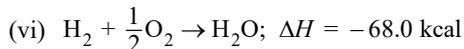
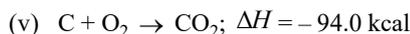
$$\text{(ii) } \Delta H_2 = -[1(\text{C}-\text{C}) + 6(\text{C}-\text{H})] + [2\text{C}_{s \rightarrow g} + 3(\text{H}-\text{H})]$$

Let the bond energy of C-C and C-H bonds be x kcal and y kcal respectively. Then, we have

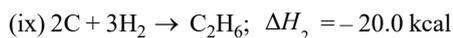
$$\text{(iii) } \Delta H_1 = -(2x + 8y) + [3 \times 172 + 4 \times 104]$$

$$\text{and (iv) } \Delta H_2 = -(x + 6y) + [2 \times 172 + 3 \times 104]$$

Given:



If we multiply (v) by 2 and (vi) by 3 and then from the sum of these new equations subtract (vii), we get (ix)



Again $3 \times (v) + 4 \times (vi) - (viii)$ gives;



Solving equations (iii), (iv), (ix) and (x), we get

$$x + 6y = 676$$

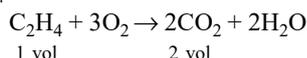
$$2x + 8y = 956$$

or $x = 82 \text{ kcal}$ and $y = 99 \text{ kcal}$

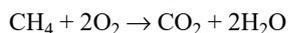
Hence bond energy of C - C bond = 82 kcal

and bond energy of C - H bond = 99 kcal

41. Following equations represent the combustion of C_2H_4 and CH_4



1 vol 2 vol



1 vol 1 vol

Let the volume of CH_4 in the mixture be x litre.

Then volume of C_2H_6 in the mixture = $(3.67 - x)$ litre

volume of CO_2 produced by x L of $\text{CH}_4 = x$ L

volume of CO_2 produced by $(3.67 - x)$ L of C_2H_4
 $= 2(3.67 - x)$ L

\therefore Total volume of CO_2 produced = $x + 2(3.67 - x)$ L

or $6.11 = x + 2(3.67 - x)$ L

or $x = 1.23$ L

Thus volume of CH_4 in mixture = 1.23 L

So volume of C_2H_4 in mixture = $(3.67 - 1.23)$ L = 2.44 L

Volume of CH_4 / litre of mixture = $\frac{1.23}{3.67}$ or 0.335 L

Volume of C_2H_4 / litre of mixture = $\frac{2.44}{3.67}$ or 0.665 L

Since volume of 1 mole of a gas at NTP = 22.4 L

So heat evolved due to combustion of 0.335 L of CH_4

$$= - \frac{0.335 \times 891}{22.40} = -13.32 \text{ kJ}$$

and heat evolved due to combustion of 0.665 L of C_2H_4

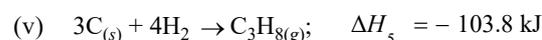
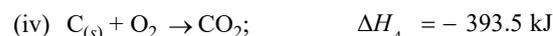
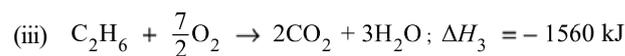
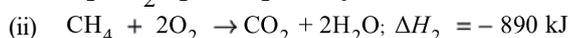
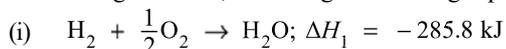
$$= - \frac{0.665 \times 1423}{22.40} = -42.25 \text{ kJ}$$

Hence total heat evolved = $-13.32 + (-42.25) = -55.57 \text{ kJ}$

i.e. heat evolved = 55.57 kJ

Negative sign indicates evolution of heat.

42. From the given data, we can get following equations



The desired equation is



We can get the desired equation using the manipulations given below

$$[3 \times (iv) + 5 \times (i)] - [(v) + (iii) + (ii)]$$

$$\therefore \Delta H = (3\Delta H_4 + 5\Delta H_1) - (\Delta H_5 + \Delta H_3 + \Delta H_2)$$

$$= [3 \times (-393.5) + 5 \times (-285.8)] - [-103.8 - 1560 - 890]$$

$$= (-1180.5 - 1429.0) - (-2553.8)$$

$$= 2553.8 - 2609.5 = -55.7 \text{ kJ / mole}$$

43. The reaction of combustion of CH_4 and C_4H_{10} can be written as follows:



Initial volume x $6x$
 (in litre)

Let the temperature be T and assume volume of 1 mole of a gas is V litre at this condition.

$\therefore V$ litre or 1 mole CH_4 gives energy on combustion = 809 kJ

$\therefore x$ litre of CH_4 gives energy on combustion = $\frac{808(x)}{V}$ kJ

$\therefore 2878$ kJ energy is obtained by 1 mole or V litre C_4H_{10}

$\therefore \frac{809(x)}{V}$ kJ energy is obtained by

$$= \frac{809(x) \times V}{V \times 2878} \text{ litre } \text{C}_4\text{H}_{10} = 0.281(X) \text{ litre } \text{C}_4\text{H}_{10}$$

Thus, butane supplied for same calorific output

$$= 0.281(x) \text{ litre}$$

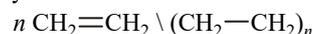
$\therefore \text{C}_4\text{H}_{10} + \frac{13}{2}\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}; \Delta H = -2878 \text{ kJ/mol}$

Volume of O_2 required = 3 \times volume of O_2 for combustion of C_4H_{10}

$$= 3 \times \frac{13}{2} \times \text{volume of } \text{C}_4\text{H}_{10}$$

$$= 3 \times \frac{13}{2} \times 0.281(X) = 5.48(x) \text{ litre } \text{O}_2$$

44. The polymerisation reaction is



In this process, one double bond ($\text{C}=\text{C}$) breaks and two $-\text{CH}_2$ groups are linked with single bonds thus forming three single bonds (two single bonds are formed when each CH_2 group of ethylene ($\text{CH}_2=\text{CH}_2$) links with another CH_2- group of another ethylene molecule).

Therefore in polymerisation reaction one $\text{C}=\text{C}$ is replaced by two $\text{C}-\text{C}$ bonds or one mole of $\text{C}=\text{C}$ bonds are replaced by 2 moles of $\text{C}-\text{C}$ bonds

Energy released in formation of 2 moles $\text{C}-\text{C}$ bonds

$$= (2 \times 331) \text{ kJ} = 662 \text{ kJ}$$

Energy needed to dissociate one mole of $\text{C}=\text{C}$ bonds = 590 kJ

\therefore Enthalpy of polymerisation = $(590 - 662) \text{ kJ} = -72 \text{ kJ mol}^{-1}$

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45. $C_6H_{10} + H_2 \longrightarrow C_6H_{12}; \Delta H = -119 \text{ kJ}$
(involves breaking up of three double bond and addition of three H_2 molecule)

$$\therefore C_6H_6 + 3H_2 \longrightarrow C_6H_{12}; \Delta H = 3 \times (-119) = -357 \text{ kJ}$$

(involves breaking up of three double bond and addition of three H_2 molecule)

$$\text{Also given } 6C + 6H_2 \longrightarrow C_6H_{12(l)}; \Delta H = -156$$

$$\text{we have } C_6H_6 + 3H_2 \longrightarrow C_6H_{12(l)}; \Delta H = -357$$

$$\frac{6C + 3H_2 \longrightarrow C_6H_6; \Delta H = +201 \text{ kJ}}$$

Therefore, resonance energy = $49 - 201 = -152 \text{ kJ}$

46. Energy provided by 1 mole of glucose = $\frac{2880 \times 25}{100} = 720 \text{ kJ}$

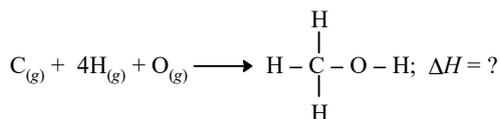
So 180 g (1 mole) of glucose ($C_6H_{12}O_6$) supplies energy = 720 kJ

$$\text{Total energy available from 120 g glucose} = \frac{720}{180} \times 120 = 480 \text{ kJ}$$

Distance covered by 100 kJ energy = 1 km

$$\therefore \text{Distance covered by 480 kJ energy} = \frac{1}{100} \times 480 = 4.8 \text{ km}$$

47. The desired equation is



$$\begin{aligned} \therefore \Delta H_f &= \left[\Delta H_{C(s) \rightarrow C(g)} + 2\Delta H_{\text{H-H}} + \frac{1}{2}\Delta H_{\text{O=O}} \right] - \\ &\quad [3\Delta H_{\text{C-H}} + \Delta H_{\text{C-O}} + \Delta H_{\text{O-H}} + \Delta H_{\text{vap}}(\text{CH}_3\text{OH})] \\ &= [715 + 2 \times 436 + 249] - [3 \times 415 + 365 + 463 + 38] \\ &= -275 \text{ kJ mol}^{-1} \end{aligned}$$

48. Total energy of hydration of Al^{3+} and $3Cl^-$ ions of $AlCl_3$
($\Delta H_{\text{Hydration}}$) = Hydration energy of Al^{3+} + $3 \times$ Hydration energy of Cl^-
- $$= [-4665 + 3 \times (-381)] \text{ kJ mol}^{-1}$$
- $$= -5808 \text{ kJ mol}^{-1}$$

This amount of energy exceeds the energy needed for the ionisation of Al to Al^{3+} (*i.e.* $5808 > 5137$). Because of this $AlCl_3$ becomes less ionic in aqueous solution.

In aqueous solution $AlCl_3$ exists in ionic form as $[Al(\text{H}_2\text{O})_6]^{3+}$ and $3Cl^-$

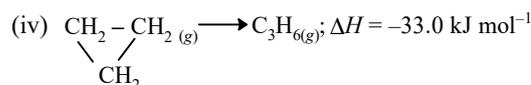
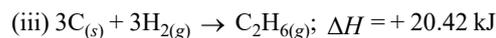
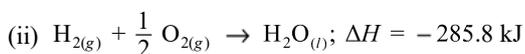


$$\Delta H = (\text{Energy released during hydration}) - (\text{Energy used during hydration}).$$

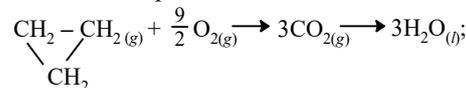
$$= (-4665) - (3 \times 381) + 5137 = -671 \text{ kJ mol}^{-1}$$

Hence formation of ions will take place.

49. Following equation can be obtained from the available data



The desired equation is

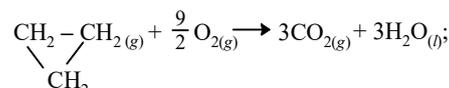


$$\Delta H = 2091.32 \text{ kJ mol}^{-1}$$

To get the desired equation compute as follows

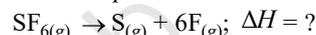
$$[3 \times (i) + 3 \times (ii)] + [(iv) - (iii)]$$

or we have

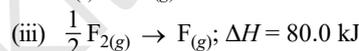
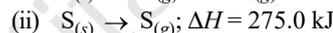


$$\Delta H = 2091.32 \text{ kJ mol}^{-1} \approx 2.091 \times 10^3 \text{ kJ mol}^{-1}$$

50. The desired equation is



From the available data, we can write the following equation



To get the desired equation carry out the following computation

$$[6 \times (iii) + (ii)] - (i)$$

$$\text{i.e. } \Delta H = (6 \times 80 + 275) - (-1100.0) = 1855 \text{ kJ}$$

Now in SF_6 we find six S - F bonds, therefore the bond energy

$$(\text{average}) \text{ of S - F bond} = \frac{1855}{6} = 309.16 \text{ kJ mol}^{-1}$$

51. In case of an adiabatic expansion of a gas, we have

$$\ln \frac{T_1}{T_2} = \frac{R}{C_v} \ln \frac{V_2}{V_1} \quad \text{or} \quad \ln \frac{300}{T_2} = \frac{8.31}{12.48} \ln \frac{2.50}{1.25}$$

solving the above equation, we get $T_2 = 188.5 \text{ K}$

$$\begin{aligned} \text{Number of moles of argon gas, } n &= \frac{PV}{RT} \\ &= \frac{1 \times 1.25}{0.082 \times 300} = 0.05 \end{aligned}$$

Since $\Delta H = n.C_p.\Delta T$

$$\begin{aligned} \therefore \Delta H &= 0.05 \times 20.8 (188.5 - 300) \\ &\quad [C_p = C_v + R = (12.48 + 8.314) \approx 20.8] \\ &= -0.05 \times 20.8 \times 111.5 = -115.96 \text{ Joules} \end{aligned}$$

52. We know, $\Delta G^\circ = \Delta G^\circ_{(\text{Products})} - \Delta G^\circ_{(\text{Reactants})}$

$$= -394.4 - [-137.2 + 0] = -257.2 \text{ kJ mol}^{-1}$$

Since ΔG° is negative so the reaction is feasible *i.e.* spontaneous.

Again $\Delta G^\circ = \Delta H^\circ - T\Delta S$

$$\therefore -257.2 = \Delta H^\circ - 300(-0.094)$$

$$\text{or } \Delta H^\circ = (-257.2 - 28.2) \text{ kJ} = -285.4 \text{ kJ mol}^{-1}$$

Since the value of ΔH is negative so the reaction is exothermic.

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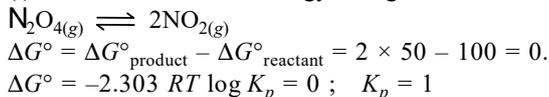
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$$\text{Also } \Delta H = \Delta U + \Delta(PV)$$

$$= \Delta U + P_2 V_2 - P_1 V_1 = 100 + (99 \times 100 - 100 \times 1)$$

$$= 100 + 9900 - 100 = 9900 \text{ bar mL}$$

58. (i) Standard Gibbs free energy change for the reaction,



$$\text{Initially, } P_{\text{N}_2\text{O}_4} = P_{\text{NO}_2} = 10 \text{ bar}$$

$$\text{So, } Q_p \text{ initial} = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = 10$$

Initial Gibbs free energy of the above reaction,

$$\Delta G = \Delta G^\circ + 2.303 RT \log Q_p$$

$$\Delta G = 0 + 2.303 \times 8.314 \times 298 \log 10$$

$$= 5.0705 \times 10^3 \text{ kJ mol}^{-1}.$$

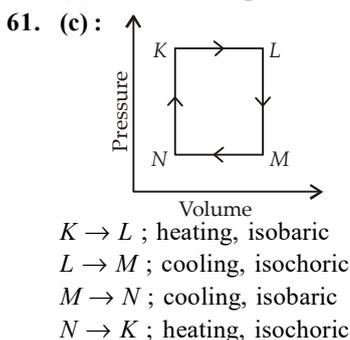
(ii) Since initial Gibbs free energy change of the reaction is positive, so the reverse reaction will take place.

59. $\Delta H = \Delta U + V\Delta P$

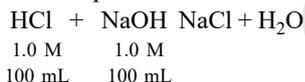
$$\Delta U = \Delta H - V\Delta P = -560 - [0.1(40 - 70)]$$

$$= -560 - (-3) = -560 + 3 = -557 \text{ kJ}.$$

60. (b): In isochoric process, volume is constant.



62. (a): From exp. 1



$$\text{Enthalpy of neutralisation} = -57.0 \text{ kJ mol}^{-1}$$

For $(1.0 \times 100 \Rightarrow)$ 100 millimoles or 0.1 moles, energy evolved due to neutralisation

$$= 0.1 \times 57 = 5.7 \text{ kJ} = 5700 \text{ J}$$

$$\text{Mass of solution} = 100 + 100 = 200 \text{ g} \quad (\because d = 1.0 \text{ g mL}^{-1})$$

$$\text{Heat capacity of solution} = 4.2 \text{ J g}^{-1} \text{ K}^{-1}$$

$$\text{Rise in temperature} = 5.7^\circ\text{C}$$

$$\text{Energy used to increase the temperature of solution} = \text{Mass of solution} \times \text{heat capacity} \times \text{rise in temp.}$$

$$= 200 \times 4.2 \times 5.7 = 4788 \text{ J}$$

$$\text{Energy used to increase the temperature of calorimeter}$$

$$= 5700 - 4788 = 912 \text{ J}$$

$$\text{Calorimeter constant} = \frac{912 \text{ J}}{5.7^\circ\text{C}} = 160 \text{ J}^\circ\text{C}$$

From expt. 2

Energy evolved by neutralization of CH_3COOH and NaOH

$$= 200 \times 4.2 \times 5.6 + 160 \times 5.6$$

$$= 4704 + 896 = 5600 \text{ J}$$

Thus, energy used for dissociation of 0.1 mole of CH_3COOH

$$= 5700 - 5600 = 100 \text{ J}$$

$$\text{Enthalpy of dissociation for 1 mole of } \text{CH}_3\text{COOH} = \frac{100}{0.1} = 1000 \text{ J}$$

i.e., enthalpy of dissociation = 1 kJ mol^{-1}

63. (b): $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$[\text{CH}_3\text{COOH}] = \frac{1 \times 100}{200} = \frac{1}{2} = 0.5 \text{ M}$$

$$[\text{CH}_3\text{COONa}] = \frac{1 \times 100}{200} = \frac{1}{2} = 0.5 \text{ M}$$

$$\text{pK}_a = -\log K_a = -\log(2.0 \times 10^{-5})$$

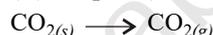
$$\text{pK}_a = 4.69$$

$$\text{pH} = 4.69 + \log \left(\frac{0.5}{0.5} \right)$$

$$\therefore \text{pH} = 4.69 \approx 4.7$$

64. (A) \rightarrow (p, r, s); (B) \rightarrow (r, s); (C) \rightarrow (t); (D) \rightarrow (p, q, t)

$$(A) \rightarrow (p, r, s)$$

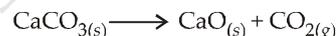


(i) It is an example of phase transition.

(ii) Conversion of solid into gas *i.e.*, sublimation, which is endothermic, therefore, $\Delta H = \text{positive}$

(iii) For $S \rightarrow g$ $\Delta S = \text{positive}$
 because, $\Delta S = S_g - S_{(s)}$ $S_g > S_{(s)}$

$$(B) \rightarrow (r, s)$$



It is endothermic process so, $\Delta H = \text{positive}$

When any product is gas and reactant is solid then, $\Delta S = \text{positive}$

$$(C) \rightarrow (t)$$



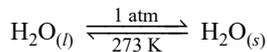
Conversion of radical in molecular form is exothermic. Two particles give one gaseous particle. So, $\Delta S = -\text{ve}$.

$$(D) \rightarrow (p, q, t)$$

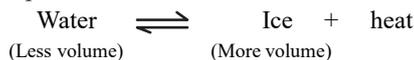
$$\Delta H = +\text{ve}; \Delta S = +\text{ve} \text{ (allotropic change)}$$

65. (A) \rightarrow (R and T)

Freezing of water,



The system is cooled *i.e.*; heat is released during the process so, $q < 0$.



Volume is increased *i.e.*; $\Delta V = +\text{ve}$.

$$w = -P\Delta V = -\text{ve}$$

i.e.; $w < 0$ (expansion)

Entropy of system is decreased, $\Delta S_{\text{sys}} < 0$.

$$\Delta U = q + w$$

As $q < 0$, $w < 0$ so, $\Delta U < 0$.

At equilibrium, $\Delta G = 0$.

(B) → (P, Q and S)

Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions,

$$w = 0, q = 0 \text{ so, } \Delta U = 0$$

For expansion, $\Delta S_{\text{sys}} > 0$ as entropy increases.

$$\Delta G = -nRT \ln \frac{V_2}{V_1}$$

For expansion, $V_2 > V_1$

$$\Delta G = -ve \text{ i.e.; } \Delta G < 0.$$

(C) → (P, Q and S)

Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container.

$$q = 0 \text{ (isolated)}$$

$$w = -P\Delta V$$

$$w = 0 \text{ (}\because \Delta V = 0\text{)}$$

$$\Delta S_{\text{sys}} > 0 \text{ (mixing of gases)}$$

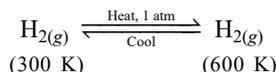
$$\Delta U = q + w = 0$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = q_p - T\Delta S \text{ (at constant } P, T\text{)}$$

$$\Delta G = 0 - T\Delta S = -T\Delta S$$

$$\Delta G < 0 \text{ (}\because \Delta S_{\text{sys}} > 0\text{)}$$

(D) → (P, Q, S and T)

Internal energy (U), entropy (S) and free energy (G) are state functions which depend only upon the state of the system and do not depend upon the path by which the state is attained.

Thus, $\Delta U = 0$, $\Delta S = 0$ and $\Delta G = 0$

Work and heat are path functions but the same path is retraced so, $q = 0$ and $w = 0$.

66. **(b):** By first law of thermodynamics $dq = dE + dW$. Under isothermal condition for ideal gas $dW = 0$ as volume occupied

by the molecules of ideal gas is zero. Also $(dE)_T = 0$ as for ideal gas there is no change in internal energy at constant T due to no force of attraction between the molecules.

$$\therefore dq = 0 + 0 = 0.$$

67. **(d):** At equilibrium

$\Delta G = 0$, but standard Gibb's energy (ΔG°) of a reaction may or may not be zero. For reaction to be spontaneous ΔG (Gibbs energy) should be more negative. i.e., $\Delta G < 0$.

68. **(a):** Second law of thermodynamics states that total heat can never be converted into equivalent amount of work.

69. **(9):** Given, $C_V = 2.5 \text{ kJ K}^{-1} = 2500 \text{ J K}^{-1}$

$$\Delta T = T_2 - T_1 = 298.45 - 298 = 0.45 \text{ K}$$

$$\Delta H \text{ due to combustion of 3.5 g gas} = C_V \times \Delta T = 2500 \times 0.45 = 1125 \text{ J}$$

Given, molecular weight of gas = 28. $\therefore 28 \equiv 1 \text{ mole}$

Hence, ΔH due to combustion of 1 mole of gas

$$= \frac{1125}{3.5} \times 28 = 9000 \text{ J}$$

$$\therefore \Delta H \text{ in kJ mol}^{-1} = 9 \text{ kJ mol}^{-1}.$$

70. **(2):** Solid line path work done (w_s) is isothermal because PV is constant (Boyle's law) and dashed line (horizontal) path work done w_d is isobaric. Work done in vertical line is zero as $\Delta V = 0$.

$$\begin{aligned} \text{Total work done on solid line path } (w_s) &= 2.303 nRT \log \frac{V_2}{V_1} \\ &= 2.303 PV \log \frac{V_2}{V_1} = 2.303 \times 4 \times 0.5 \log \frac{5.5}{0.5} = 4.8 \text{ L atm.} \end{aligned}$$

$$\begin{aligned} \text{Total work done on dash line path } (w_d) &= P\Delta V \\ &= 4 \times (2 - 0.5) + 1(3 - 2) + 0.5(5.5 - 3) = 6 + 1 + 1.25 = 8.25 \end{aligned}$$

$$\text{So, } \frac{w_d}{w_s} = \frac{8.25}{4.8} \approx 2.$$



8

Chemical Kinetics

Multiple Choice Questions with ONE Correct Answer

- The rate constant of a reaction depends on
 - temperature
 - initial concentration of the reactants
 - time of reaction
 - extent of reaction. (1981)
- The specific rate constant of a first order reaction depends on the
 - concentration of the reactant
 - concentration of the product
 - time
 - temperature. (1983)
- A catalyst is a substance which
 - increases the equilibrium concentration of the product
 - changes the equilibrium constant of the reaction
 - shortens the time to reach equilibrium
 - supplies energy to the reaction (1983)
- The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is
 - $2.0 \times 10^{18} \text{ s}^{-1}$
 - $6.0 \times 10^{14} \text{ s}^{-1}$
 - infinity
 - $3.6 \times 10^{30} \text{ s}^{-1}$ (1996)
- The rate constant for the reaction, $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, is $3.0 \times 10^{-5} \text{ sec}^{-1}$. If the rate is $2.40 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$, then the concentration of N_2O_5 (in mol litre^{-1}) is
 - 1.4
 - 1.2
 - 0.04
 - 0.8 (2000)
- If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process, $AB + h\nu \longrightarrow AB$, the rate of formation of AB is directly proportional to
 - C
 - I
 - I^2
 - $C.I$ (2001)
- Consider the chemical reaction, $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$. The rate of this reaction can be expressed in terms of time derivative of concentration of $\text{N}_{2(g)}$, $\text{H}_{2(g)}$ or $\text{NH}_{3(g)}$. Identify the correct relationship amongst the rate expressions.
 - Rate = $-d[\text{N}_2]/dt = -1/3d[\text{H}_2]/dt = 1/2d[\text{NH}_3]/dt$
 - Rate = $-d[\text{N}_2]/dt = -3d[\text{H}_2]/dt = 2d[\text{NH}_3]/dt$
 - Rate = $d[\text{N}_2]/dt = -1/3d[\text{H}_2]/dt = 1/2d[\text{NH}_3]/dt$
 - Rate = $d[\text{N}_2]/dt = -d[\text{H}_2]/dt = 1/2d[\text{NH}_3]/dt$ (2002)
- In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in $2 \times 10^4 \text{ sec}$. The rate constant of reaction in sec^{-1} is
 - 2×10^4
 - 3.45×10^{-5}
 - 1.386×10^{-4}
 - 2×10^{-4} (2003)
- The reaction, $X \rightarrow \text{Product}$, follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 to 0.025 M. The rate of reaction, when concentration of X is 0.01 M is
 - $1.73 \times 10^{-4} \text{ M min}^{-1}$
 - $3.47 \times 10^{-5} \text{ M min}^{-1}$
 - $3.47 \times 10^{-4} \text{ M min}^{-1}$
 - $1.73 \times 10^{-5} \text{ M min}^{-1}$ (2004)
- Which one of the following statement for order of reaction is not correct?
 - Order can be determined experimentally.
 - Order of reaction is equal to sum of the powers of concentration terms in differential rate law.
 - It is not affected with the stoichiometric coefficient of the reactants.
 - Order cannot be fractional. (2005)
- Consider a reaction $aG + bH \rightarrow \text{products}$. When concentration of both the reactants G and H is doubled, the rate increases eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is
 - 0
 - 1
 - 2
 - 3 (2007)

12. Under the same reaction conditions, initial concentration of $1.386 \text{ mol dm}^{-3}$ of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constant for first order (k_1) and zero order (k_0) of the reactions is

- (a) $0.5 \text{ mol}^{-1} \text{ dm}^3$ (b) 1.0 mol dm^{-3}
(c) 1.5 mol dm^{-3} (d) $2.0 \text{ mol}^{-1} \text{ dm}^3$

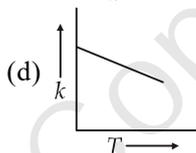
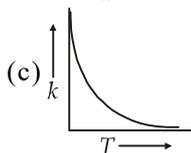
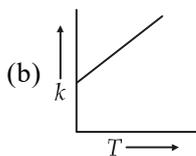
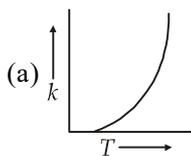
(2008)

13. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation $\log k = -(2000) \frac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a , respectively, are

- (a) $1.0 \times 10^6 \text{ s}^{-1}$ and 9.2 kJ mol^{-1}
(b) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(c) $1.0 \times 10^6 \text{ s}^{-1}$ and 16.6 kJ mol^{-1}
(d) $1.0 \times 10^6 \text{ s}^{-1}$ and 38.3 kJ mol^{-1} .

(2009)

14. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is



(2010)

15. In the reaction, $P + Q \rightarrow R + S$ the time taken for 75% reaction of P is twice the time taken for 50% reaction of P . The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is

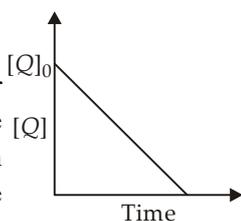
- (a) 2 (b) 3 (c) 0 (d) 1

(2013)

16. For the elementary reaction $M \rightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M . The order of the reaction with respect to M is

- (a) 4 (b) 3 (c) 2 (d) 1

(2014)



Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

17. A catalyst
- (a) increases the average kinetic energy of reaction molecules
(b) decreases the activation energy
(c) alters the reaction mechanism
(d) increases the frequency of collisions of reacting species (1984)
18. The rate law for the reaction:
 $\text{RCl} + \text{NaOH}_{(aq)} \rightarrow \text{ROH} + \text{NaCl}$ is given by,
Rate = $k [\text{RCl}]$. The rate of the reaction will be
- (a) doubled on doubling the concentration of sodium hydroxide
(b) halved on reducing the concentration of alkyl halide to one half
(c) increased on increasing the temperature of the reaction
(d) unaffected by increasing the temperature of the reaction (1988)
19. For a first order reaction,
- (a) the degree of dissociation is equal to $(1 - e^{-kt})$
(b) a plot of reciprocal concentration of the reactant vs time gives a straight line
(c) the time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction
(d) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1} . (1998)
20. The following statement(s) is(are) correct
- (a) a plot of $\log K_p$ versus $1/T$ is linear
(b) a plot of $\log [X]$ versus time is linear for a first order reaction, $X \rightarrow P$
(c) a plot of p versus $1/T$ is linear at constant volume
(d) a plot of p versus $1/V$ is linear at constant temperature (1999)
21. For the first order reaction
- (a) the concentration of the reactant decreases exponentially with time
(b) the half-life of the reaction decreases with increasing temperature
(c) the half-life of the reaction depends on the initial concentration of the reactant
(d) the reaction proceeds to 99.6% completion in eight half-life duration. (2011)

Fill in the Blanks

22. For the reaction $\text{N}_{2(g)} + 3\text{H}_{2(g)} \longrightarrow 2\text{NH}_{3(g)}$, under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 0.001 kg h^{-1} . The rate of conversion of H_2 under the same condition is kg h^{-1} . (1994)
23. In the Arrhenius equation, $k = A \exp(-E/RT)$, A may be termed as the rate constant at (1997)

True / False

24. For a first order reaction, the rate of the reaction doubles as the concentration of the reactant(s) doubles. (1986)
25. Catalyst makes a reaction more exothermic. (1987)
26. Catalyst does not affect the energy of activation in a chemical reaction. (1989)
27. The rate of an exothermic reaction increases with increasing temperature. (1990)

Subjective Problems

28. Rate of reaction $A + B \rightarrow$ products, is given below as a function of different initial concentrations of A and B :
- | $[A]$ (mol/L) | $[B]$ (mol/L) | Initial rate (mol/L/min) |
|---------------|---------------|--------------------------|
| 0.01 | 0.01 | 0.005 |
| 0.02 | 0.01 | 0.010 |
| 0.01 | 0.02 | 0.005 |

Determine the order of the reaction with respect to A and with respect to B . What is the half-life of A in the reaction? (1982)

29. A first order reaction is 20% complete in 10 minutes. Calculate (i) the specific rate constant of the reaction, and (ii) the time taken for the reaction to go to 75% completion. (1983)
30. While studying the decomposition of gaseous N_2O_5 it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameters can be obtained from this observation? (1985)
31. A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C . If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed in the product? What is the half life of this reaction? (1987)

32. A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C . Calculate the reaction rate constant at 27°C and the energy of activation of the reaction in kJ/mole . (1988)

33. In the Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period be ten minutes? (1990)

34. The decomposition of N_2O_5 according to the equation:

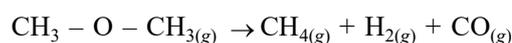


is a first order reaction. After 30 min. from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction. (1991)

35. Two reactions (I) $A \rightarrow$ products, (II) $B \rightarrow$ products, follow first order kinetics. The rate of the reaction (I) is doubled when the temperature is raised from 300 K to 310 K. The half life for this reaction at 310 K is 30 minutes. At the same temperature B decomposes twice as fast as A . If the energy of activation for the reaction (II) is half that of reaction (I), calculate the rate constant of the reaction (II) at 300 K. (1992)

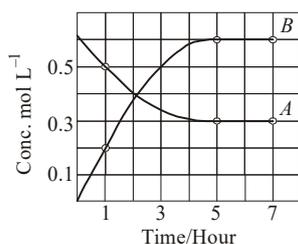
36. A first order reaction $A \rightarrow B$, requires activation energy of 70 kJ mol^{-1} . When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the per cent decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature. (1993)

37. The gas phase decomposition of dimethyl ether follows first order kinetics.



The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minutes. Initially, only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes? Assume ideal gas behaviour. (1993)

38. The progress of the reaction, $A \rightleftharpoons nB$, with time, is presented in figure given below.



Determine

- the value of n
- the equilibrium constant, K and
- the initial rate of conversion of A . (1994)

39. From the following data for the reaction between A and B .

Exp. No.	[A], mol lit ⁻¹	[B], mol lit ⁻¹	initial rate mole lit ⁻¹ s ⁻¹ at	
			300 K	320 K
I	2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
II	5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	—
III	1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	—

Calculate

- the order of the reaction with respect to A and with respect to B ,
 - the rate constant at 300 K
 - the energy of activation, and
 - the pre-exponential factor (1994)
40. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol⁻¹. Calculate the time required for 75% decomposition at 450°C. (1995)
41. The ionisation constant of NH_4^+ in water is 5.6×10^{-10} at 25°C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} L mol⁻¹ s⁻¹. Calculate the rate constant for proton transfer from water to NH_3 . (1996)
42. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is 3.56×10^9 s⁻¹, calculate its rate constant at 318 K and also the energy of activation. (1997)
43. The rate constant for the first order decomposition of a certain reaction is described by the equation

$$\log(k) = 14.34 - \frac{1.25 \times 10^4}{T}$$

- What is the energy of activation for this reaction?
- At what temperature will its half-life period be 256 minutes? (1997)

44. The rate constant of a reaction is 1.5×10^7 s⁻¹ at 50°C and 4.5×10^7 s⁻¹ at 100°C. Evaluate the Arrhenius parameters A and E_a . (1998)
45. The rate constant for an isomerisation reaction, $A \rightarrow B$ is 4.5×10^{-3} min⁻¹. If the initial concentration of A is 1M, calculate the rate of the reaction after 1 hr. (1999)
46. A hydrogenation reaction is carried out at 500 K. If same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol⁻¹. (2000)
47. The rate of a first-order reaction is 0.04 mol litre⁻¹s⁻¹ at 10 minutes and 0.03 mol litre⁻¹ s⁻¹ at 20 minutes after initiation. Find the half-life of the reaction. (2001)
48. The vapour pressure of the two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 moles of (A) is mixed with 12 moles of (B). However, as soon as (B) is added, (A) starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 minutes, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate of constant of the polymerisation reaction. Assume negligible volume change of mixing and polymerisation and ideal behaviour for the final solution. (2001)
49. For the given reactions, $A + B \rightarrow$ Products, following data were obtained.

	$[A_0]$	$[B_0]$	R_0 (mol l ⁻¹ s ⁻¹)
1.	0.1	0.2	0.05
2.	0.2	0.2	0.10
3.	0.1	0.1	0.05

- Write the rate law expression.
 - Find the rate constant. (2004)
50. At constant temperature and volume, X decomposes as $2X_{(g)} \longrightarrow 3Y_{(g)} + 2Z_{(g)}$; P_x is the partial pressure of X .

Observation No.	Time (in minute)	P_x (in mm of Hg)
1	0	800
2	100	400
3	200	200

Chemical Kinetics

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- (i) What is the order of reaction with respect to X ?
 (ii) Find the rate constant.
 (iii) Find the time for 75% completion of the reaction.
 (iv) Find the total pressure when pressure of X is 700 mm of Hg. (2005)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

51. **Statement-1** : For each ten degree rise of temperature the specific rate constant is nearly doubled.

Statement-2: Energy-wise distribution of molecules in a gas is an exponential function of temperature. (1989)

Integer Answer Type

52. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data is obtained :

$[R]$ (molar)	1.0	0.75	0.40	0.10
t (min.)	0.0	0.05	0.12	0.18

The order of the reaction is (2010)

53. An organic compound undergoes first-order decomposition. The time taken for decomposition to $1/8$ and $1/10$ of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$?

(take $\log_{10} 2 = 0.3$) (2012)

ANSWER KEY

1. (a) 2. (d) 3. (c) 4. (b) 5. (d) 6. (b)
 7. (a) 8. (c) 9. (c) 10. (d) 11. (d) 12. (a)
 13. (d) 14. (a) 15. (d) 16. (b) 17. (b, c) 18. (b, c)
 19. (a, d) 20. (a, b, d) 21. (a, b, d) 22. 1.765×10^{-4} kg/hr
 23. Very high temperature and zero activation energy 24. True 25. False 26. False
 27. False 28. With respect to $A = 1$; with respect to $B = 0$; 1.386 minutes
 29. 0.02231 min^{-1} ; 62.15 min 30. decomposition of N_2O_5 is a first order reaction.
 31. 5.2%; 128.33 hours 32. $k_{27^\circ} = 0.0231 \text{ min}^{-1}$; 43.848 kJ mol $^{-1}$
 33. 313.80 K 34. $5.2 \times 10^{-3} \text{ min}^{-1}$ 35. 0.0327 min^{-1}
 36. 67.17% 37. 0.749 atm 38. $n = 2$; 1.2; 0.1 mol litre $^{-1}$ hour $^{-1}$
 39. With respect to $A = 2$; with respect to $B = 1$; $2.67 \times 10^8 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$; 55.33 kJ mol $^{-1}$; 1.140×10^{18}
 40. 20.36 min 41. $6.07 \times 10^5 \text{ s}^{-1}$ 42. $E_a = 76.623 \text{ kJ mol}^{-1}$; $k_{318} = 9.27 \times 10^{-4} \text{ s}^{-1}$
 43. 239 kJ mol $^{-1}$, 669 K 44. $E_a = 2.2 \times 10^4 \text{ J mol}^{-1}$; $A = 5.42 \times 10^{10} \text{ s}^{-1}$
 45. $3.44 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$ 46. 100 kJ mol $^{-1}$ 47. 24.14 min 48. $1.005 \times 10^{-4} \text{ min}^{-1}$
 49. $R_0 = k [A_0]$; 0.5 sec^{-1} 50. 1; $6.93 \times 10^{-3} \text{ min}^{-1}$; 200 min; 950 mm of Hg
 51. (a) 52. (0) 53. (9)

Explanations

1. (a): At any given temperature the value of rate constant is fixed. It is independent of initial concentration of reactants, time of reaction, extent of reaction, etc.

2. (d): Refer to Q. 1.

3. (c): A catalyst provides an alternative path with lower activation energy and in this way shortens the time to reach equilibrium.

4. (b): The Arrhenius equation is; $k = A \cdot e^{-\frac{E_a}{RT}}$

As $T \rightarrow \infty$, the value of $e^{-\frac{E_a}{RT}} \rightarrow 1$, Thus $k = A$
Thus $k = 6.0 \times 10^{14} \text{ s}^{-1}$

5. (d): Since the unit of k is sec^{-1} , so it is a first order reaction.
Thus $r = k [\text{N}_2\text{O}_5]$

$$\text{or } \frac{r}{k} = [\text{N}_2\text{O}_5] = \frac{2.4 \times 10^{-5}}{3 \times 10^{-5}} = 0.8 \text{ mol litre}^{-1}$$

6. (b): In case of photochemical reaction, the rate varies with change in intensity of absorption. For such a reaction, rate $\propto I$ (intensity of absorption).

7. (a): From the given equation, we have

$$-\frac{d}{dt}[\text{N}_2] = -\frac{1}{3} \frac{d}{dt}[\text{H}_2] = \frac{1}{2} \frac{d}{dt}[\text{NH}_3].$$

8. (c): $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$ [For first order reaction]

Substituting the given values, we have

$$k = \frac{2.303}{2 \times 10^4} \log \frac{800}{50} = 1.386 \times 10^{-4} \text{ sec}^{-1}$$

9. (c): Since the concentration of 'X' changes from 0.1 M to 0.025M (i.e. it becomes 1/4 or it is equal to two times $t_{1/2}$) in 40 minutes.

$$\therefore 2 \times t_{1/2} = 40 \text{ min} \quad \text{or} \quad t_{1/2} = 40/2 = 20 \text{ min.}$$

$$r = k[X] = \frac{0.693}{t_{1/2}} \times 0.01 = \frac{0.693}{20} \times 0.01 \\ = 3.465 \times 10^{-4} \text{ M min}^{-1}$$

10. (d): It is not correct because order of a reaction can be fractional.

11. (d):

Exp. No.	[G] mole/lit	[H] mole/lit	Rate mole lit ⁻¹ time ⁻¹
1	a	b	r
2	2a	2b	8r
3	2a	b	2r

Applying $r = k[G]^x[H]^y$... (i)

$$8r = k[2G]^x \cdot [2H]^y$$

$$8r = k \cdot 2^{x+y} [G]^x [H]^y$$

Substituting the value of r from eq. (i)

$$8k [G]^x \cdot [H]^y = k \cdot 2^{x+y} [G]^x [H]^y$$

$$2^{x+y} = 8 \Rightarrow 2^{x+y} = 2^3$$

$$\Rightarrow x + y = 3.$$

\therefore Overall order is 3.

12. (a): For first order reaction

$$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{0.5a} = \frac{2.303}{t_{1/2}} \log_{10} 2 = \frac{0.693}{t_{1/2}}$$

$$\therefore t_{1/2} = \frac{0.693}{k}; \therefore k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40}$$

For zero order reaction, $t_{1/2} = \frac{A_0}{2k}$

$$\therefore k_0 = \frac{A_0}{2 \times t_{1/2}} = \frac{1.386}{2 \times 20}$$

$$\text{Now, } \frac{k_1}{k_0} = \frac{0.693}{40} \times \frac{40}{1.386} = 0.5 \text{ mol}^{-1} \text{ dm}^3$$

13. (d): According to Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303 RT} \quad \dots(i)$$

$$\text{given, } \log k = -(2000) \frac{1}{T} + 6.0 \quad \dots(ii)$$

Comparing equations (i) and (ii),

$$\log A = 6 \Rightarrow A = 1 \times 10^6 \text{ s}^{-1}$$

$$\frac{-E_a}{2.303 RT} = -\frac{2000}{T} \Rightarrow E_a = 2000 \times 2.303 \times 8.314$$

$$\Rightarrow E_a = 38294 \text{ J/mole or } E_a \approx 38.3 \text{ kJ mol}^{-1}$$

14. (a): According to the Arrhenius equation, $k = Ae^{-E_a/RT}$

where, k = rate constant, E_a = activation energy and T = temperature.

Increasing the temperature, leads to doubling of the rate of reaction alongwith decrease in activation energy and an exponential increase in the rate constant.

15. (d): For P , if $t_{50\%} = x$ then $t_{75\%} = 2x$. So order with respect to P is 1. From the given graph, concentration of Q decreases linearly with time. So, rate with respect to Q , remains constant. Hence, order of reaction with respect to Q is zero.

The rate law expression;

$$r = k[P]^1[Q]^0$$

So, overall order is $1 + 0 = 1$.

16. (b): $M \longrightarrow N$

$$r = k[M]^x \quad \dots(i)$$

$$8r = k[2M]^x \quad \dots(ii)$$

On dividing eqn. (ii) by (i), we get

$$\text{or } 8 = (2)^x \Rightarrow (2)^3 = (2)^x \Rightarrow x = 3$$

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17. (b, c): (b) is correct because a catalyst provides a path with lower activation energy.

(c) is correct, since in the presence of catalyst, an intermediate of low activation energy is formed (between catalyst and reactants) which then decomposes to form the products and catalyst is regenerated.

18. (b, c) : Since rate = $k[RCl]$

If we decrease the concentration of RCl to half, the rate will also become halved.

In most of the reactions rate increases with increase of temperature.

19. (a,d): For a first order reaction, α is the degree of dissociation

$$\therefore k \cdot t = \ln \frac{1}{1-\alpha} = -\ln(1-\alpha)$$

$$\text{or } e^{-k \cdot t} = (1-\alpha) \quad \text{or } \alpha = 1 - e^{-k \cdot t}$$

As, Arrhenius equation is, $k = A \cdot e^{-E_a/RT}$

The dimensions of pre-exponential factor (A) are the same as those of k , which is T^{-1} for a first order reaction.

20. (a,b,d): (a) is correct because the plot of $\log K_p$ vs $1/T$ is linear.

The expression is

$$\log K_p = -\frac{\Delta H}{R} \cdot \frac{1}{T} + I$$

It is the expression of a straight line similar to $y = m x + c$

(b) For a first order reaction the plot of $\log [x]$ vs time is linear.

The expression is

$$\log [x] = \log [x_0] + k t \quad \text{[First order reaction]}$$

(c) is incorrect because at constant volume we have $P/T = \text{constant}$

(d) is correct because at constant temperature

$$P \cdot V = \text{constant} \quad \text{[Boyle's law]}$$

21. (a, b, d) : For a reaction, concentration of reactant decreases exponentially with time. It is true statement.

$$[A] = [A]_0 e^{-kt} \quad \text{Also, } t_{1/2} = \frac{0.693}{K}$$

This relation shows that half life is independent of concentration and $t_{1/2}$ decreases with the increase of temperature.

The reaction proceeds to 99.6% completion in eight half-life duration.

$$K = \frac{0.693}{t_{1/2}} \quad \dots (i)$$

For 99.6% $a=100$ $x=99.6$ $a-x=0.4$

$$K = \frac{2.303}{t_{99.6\%}} \log \frac{100}{0.4} = \frac{2.303}{t_{99.6\%}} \log 250 = \frac{2.303}{t_{99.6\%}} \times 2.4 \quad \dots (ii)$$

From eq. (i) and (ii), $\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{99.6\%}} \times 2.4$

$$t_{99.6\%} = \frac{2.303}{0.693} \times 2.4 \times t_{1/2} = 7.975 \times t_{1/2} \approx 8 \times t_{1/2}$$

22. $1.765 \times 10^{-4} \text{ kg/hr}; \quad N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

$$\text{or } -\frac{1}{3} \frac{d}{dt} [H_2] = \frac{1}{2} \frac{d}{dt} [NH_3]$$

$$\text{or } -\frac{d}{dt} [H_2] = \frac{3}{2} \frac{d}{dt} [NH_3]$$

$$\text{Since } \frac{d}{dt} [NH_3] = 0.001 \text{ kg/hr}$$

$$= \frac{0.001 \times 1000}{17} \text{ mol/hr} = \frac{1}{17} \text{ mol/hr}$$

$$\therefore -\frac{d}{dt} [H_2] = \frac{1}{17} \times \frac{3}{2} \text{ mol/hr} = \frac{3}{34} \text{ mol/hr}$$

$$= \frac{3}{34} \times \frac{2}{1000} \text{ kg/hr} = 1.765 \times 10^{-4} \text{ kg/hr}$$

23. Very high temperature and zero activation energy;

For Arrhenius equation $k = A \cdot e^{-E_a/RT}$

A represents frequency factor. It may be termed as rate constant at very high temperature and activation energy equal to zero.

24. True

In case of first order reaction, the rate of reaction is directly proportional to the concentration of reacting substance.

25. False

Catalyst provides an alternate path with lower activation energy and hence increases the rate of the reaction.

26. False

Catalyst lowers the activation energy.

27. False

The rate of a reaction increases with increase in temperature. For every 10°C rise in temperature the rate of reaction doubles.

28. From comparison of data (i) and (ii), it is obvious that if $[A]$ is doubled (from 0.01 to 0.02 mol L^{-1}) keeping $[B]$ constant, the rate of reaction is doubled (from 0.005 to 0.010 mol $\text{lit}^{-1} \text{min}^{-1}$). From this we can conclude that

$$\text{rate} \propto [A]^1$$

\therefore Order of reaction with respect to $A = 1$.

Similarly from a comparison of data (i) and (iii), it is obvious that when $[B]$ is doubled (from 0.01 to 0.02 mol litre^{-1}) keeping $[A]$ constant, the rate of reaction remains unchanged. From this one may conclude that $\text{rate} \propto [B]^0$ i.e. rate is independent of $[B]$. Thus the order of reaction with respect to $B = \text{zero}$.

Thus for the reaction

$A + B \longrightarrow \text{Products}$, we have

$$\text{rate} = k [A] [B]^0$$

$$\text{or } \text{rate} = k [A]$$

$$\text{or } k = \frac{\text{rate}}{[A]} = \frac{0.005}{0.01} = 0.5 \text{ min}^{-1}$$

$$\text{Again since } t_{1/2} = \frac{0.693}{k}$$

$$\therefore t_{1/2} = \frac{0.693}{0.5} = 1.386 \text{ minutes}$$

29. (i) : Let the initial concentration = 100

Then, $a = 100, x = 20, t = 10$ min.

For a first order reaction, we have

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{10} \log \frac{100}{(100-20)}$$

$$= \frac{2.303}{10} \log \frac{100}{80} = \frac{2.303}{10} \times 0.0969 = 0.02231 \text{ min}^{-1}$$

- (ii) Let 75% of reaction get completed in time = t min.

Then $a = 100, x = 75, t = t$ min., $k = 0.02231 \text{ min}^{-1}$

For a first order reaction, we have

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\therefore 0.02231 = \frac{2.303}{t} \log \frac{100}{100-75}$$

$$\text{or } 0.02231 = \frac{2.303}{t} \log 4 = \frac{2.303}{t} \times 0.6021$$

$$\text{or } t = \frac{2.303 \times 0.6021}{0.02231} = 62.15 \text{ min.}$$

30. Let us assume the decomposition of N_2O_5 to be a first order reaction, then

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{P_0}{P}$$

$$\text{or } \log P = \frac{-kt}{2.303} + \log P_0$$

Thus a graph of $\log P$ vs t will be linear.

This is in accordance with given statement so the decomposition of N_2O_5 is a first order reaction.

31. For a first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Given : $t = 10 \times 60 \times 60$ sec., Let initial concentration (a) = 1,

$$\text{Then, } k = \frac{2.303}{10 \times 60 \times 60} \log \frac{1}{(1-x)}$$

$$\text{or } 1.5 \times 10^{-6} = \frac{2.303}{10 \times 60 \times 60} \log \frac{1}{(1-x)}$$

$$\text{or } \log \frac{1}{(1-x)} = \frac{1.5 \times 10^{-6} \times 10 \times 60 \times 60}{2.303}$$

$$\text{or } \log \frac{1}{(1-x)} = 0.0234 \quad \text{or} \quad \frac{1}{(1-x)} = 1.055$$

$$\text{or } 1.055 - 1.055x = 1$$

$$\text{or } x = \frac{1.055 - 1}{1.055} = 0.052$$

Thus 5.2% ($0.052 \times 100 = 5.2$) of the initial concentration of reactants has changed into products.

$$\text{Since } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-6}}$$

$$= 462000 \text{ s or } 128.33 \text{ hours}$$

32. Since $t_{1/2} = \frac{0.693}{k}$, $\therefore k = \frac{0.693}{t_{1/2}}$

Given: $t_{1/2} = 30$ min at 27°C and $t_{1/2} = 10$ min at 47°C

$$\therefore k_{27^\circ} = \frac{0.693}{30} \text{ min}^{-1} = 0.0231 \text{ min}^{-1}$$

$$\text{and } k_{47^\circ} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$$

$$\text{We know that } \log \frac{k_{47}}{k_{27}} = \frac{E_a}{2.303 R} \times \frac{(T_2 - T_1)}{T_2 \times T_1}$$

$$\therefore E_a = \frac{2.303 R \times T_1 \times T_2}{(T_2 - T_1)} \log \frac{k_{47}}{k_{27}}$$

$$\text{or } E_a = \frac{2.303 \times 8.314 \times 10^{-3} \times 300 \times 320}{(320 - 300)} \log \frac{0.0693}{0.0231}$$

$$= 43.848 \text{ kJ mol}^{-1}$$

33. Using the relation, $k = \frac{0.693}{t_{1/2}}$

$$\text{We get, } k = \frac{0.693}{10 \times 60} = 1.155 \times 10^{-3}$$

From Arrhenius equation, we have

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

$$\therefore \log (1.155 \times 10^{-3}) = (\log 4 \times 10^{13}) - \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times T}$$

$$\text{or } -3 + \log (1.155) = 13 + \log 4 - \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times T}$$

$$\text{or } -3 + 0.1917 = 13 + 0.6021 - \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times T}$$

$$\text{or } \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times T} = 16.6021 - 0.1917 = 16.4104$$

$$\text{or } T = \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times 16.4104} = 313.80 \text{ K}$$

34. $2\text{N}_2\text{O}_{5(g)} \longrightarrow 4\text{NO}_{2(g)} + \text{O}_{2(g)}$

From the above equation it is evident that 2 moles of $\text{N}_2\text{O}_{5(g)}$ on complete decomposition will yield 5 moles of gaseous products.

$$\therefore \text{Initial pressure of } \text{N}_2\text{O}_5 = 584.5 \times \frac{2}{5} = 233.8 \text{ mm of Hg}$$

Let the amount of N_2O_5 decomposed after 30 min = x

Then, after 30 minutes

$$\text{Pressure due of } \text{N}_2\text{O}_5 = (233.8 - x)$$

$$\text{Pressure due to } \text{NO}_2 = 2x$$

$$\text{Pressure due to } \text{O}_2 = x/2$$

$$\text{Thus, total pressure after 30 min.} = (233.8 - x) + 2x + x/2$$

$$\text{or } (233.8 - x) + 2x + x/2 = 284.5$$

$$\text{or } x = 33.8 \text{ mm of Hg}$$

$$\text{Hence pressure due to } \text{N}_2\text{O}_5 \text{ after 30 min.} = (233.8 - 33.8)$$

$$= 200 \text{ mm of Hg}$$

Now for a first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$\text{or } k = \frac{2.303}{30} \log \frac{233.8}{200}$$

$$= \frac{2.303}{30} \times 0.0679 = 5.2 \times 10^{-3} \text{ min}^{-1}$$

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35. (I) $A \rightarrow$ Products(II) $B \rightarrow$ Products $\therefore t_{1/2}$ for (I) at 310 K = 30 minute

$$\therefore k_{(I)} \text{ at } 310 = \frac{0.693}{30} = 0.0231 \text{ min}^{-1} \quad \dots (i)$$

 \therefore both reactions are of I order

$$\text{Also given, } \frac{k_I \text{ at } 310}{k_I \text{ at } 300} = 2 \quad \dots (ii)$$

$$\text{Also given, } \frac{k_{II} \text{ at } 310}{k_I \text{ at } 310} = 2 \quad \dots (iii)$$

$$\text{Also we have, } \frac{E_{a_{II}}}{E_{a_I}} = \frac{1}{2} \quad \dots (iv)$$

$$\text{For I: } 2.303 \log_{10} \frac{k_I \text{ at } 310}{k_I \text{ at } 300} = \frac{E_{a_I}}{R} \left[\frac{310 - 300}{310 \times 300} \right] \dots (v)$$

$$\text{For II: } 2.303 \log_{10} \frac{k_{II} \text{ at } 310}{k_{II} \text{ at } 300} = \frac{E_{a_{II}}}{R} \left[\frac{310 - 300}{310 \times 300} \right] \dots (vi)$$

Dividing equation (v) by (vi),

$$\therefore \frac{\log_{10} \frac{k_I \text{ at } 310}{k_I \text{ at } 300}}{\log_{10} \frac{k_{II} \text{ at } 310}{k_{II} \text{ at } 300}} = \frac{E_{a_I}}{E_{a_{II}}} = 2 \quad \text{by eq. (iv) ... (vii)}$$

$$\text{or } \log_{10} \frac{k_I \text{ at } 310}{k_I \text{ at } 300} = 2 \log_{10} \left[\frac{k_{II} \text{ at } 310}{k_{II} \text{ at } 300} \right]$$

$$\text{or } \frac{k_I \text{ at } 310}{k_I \text{ at } 300} = \left[\frac{k_{II} \text{ at } 310}{k_{II} \text{ at } 300} \right]^2 \quad \dots (viii)$$

By equations (ii) and (viii),

$$\text{or } \left[\frac{k_{II} \text{ at } 310}{k_{II} \text{ at } 300} \right]^2 = 2$$

$$\text{or } k_{II} \text{ at } 310 \text{ K} = \sqrt{2} k_{II} \text{ at } 300 \text{ K} \quad \dots (ix)$$

By equations (iii) and (ix),

$$2 \times k_I \text{ at } 310 \text{ K} = \sqrt{2} (k_{II} \text{ at } 300 \text{ K}) \quad \dots (x)$$

$$k_{II} \text{ at } 300 \text{ K} = \frac{2 \times k_I \text{ at } 310}{\sqrt{2}}$$

By equations (i) and (x),

$$k_{II} \text{ at } 300 \text{ K} = \sqrt{2} \times 0.0231$$

$$k_{II} \text{ at } 300 \text{ K} = 3.27 \times 10^{-2} \text{ min}^{-1} = 0.0327 \text{ min}^{-1}$$

36. Given : $a = 100$, $(a - x) = 100 - 25 = 75$; $t = 20$ min.

Using the relation

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)},$$

We get

$$\text{at } 25^\circ\text{C (298 K)}; k_1 = \frac{2.303}{20} \log \frac{100}{75} = 0.014386 \text{ min}^{-1}$$

at $40^\circ\text{C (313 K)}; k_2 = ?$

$$\text{We know that } \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$$

$$\therefore \log \frac{k_2}{0.014386} = \frac{70 \times 10^3}{2.303 \times 8.314} \times \left(\frac{313 - 298}{298 \times 313} \right)$$

$$\text{or } \log \frac{k_2}{0.014386} = \frac{70 \times 10^3}{2.303 \times 8.314} \times \frac{15}{298 \times 313} = 0.587$$

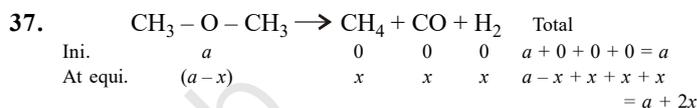
$$\text{or } \frac{k_2}{0.014386} = 3.864 \quad \text{or } k_2 = 0.0556$$

Now, for % age decomposition at 40°C (313 K) Given, $a = 100$, $(a - x) = (100 - x)$; $t = 20$ min; $k = 0.05570$

$$\text{Thus } k_{313} = \frac{2.303}{20} \log \frac{100}{(100 - x)}$$

$$\text{or } 0.0556 = \frac{2.303}{20} \log \frac{100}{(100 - x)}$$

$$\text{or } x = 67.169 \text{ or } 67.17 \%$$

Initial concentration of CH_3OCH_3 (i.e. a) can be found by using the relation $PV = nRT$

$$\text{or } \frac{n}{V} = \frac{P}{RT}$$

$$\text{or } a = \frac{P}{RT} = \frac{0.4}{0.082 \times 773} \quad [500^\circ\text{C} = 500 + 273 = 773 \text{ K}]$$

$$= 6.31 \times 10^{-3} \text{ mol lit}^{-1}$$

$$\text{To find the value of } k, \text{ use the relation, } k = 0.693 / t_{1/2}$$

$$= \frac{0.693}{14.5} = 4.78 \times 10^{-2}$$

For a first order reaction, we have

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$\therefore 4.78 \times 10^{-2} = \frac{2.303}{12} \log \frac{a}{(a-x)}$$

$$\text{or } \frac{a}{(a-x)} = 1.77446 \quad \text{or } (a-x) = \frac{a}{1.77446}$$

$$(a-x) = \frac{6.31 \times 10^{-3}}{1.77446} \text{ mol L}^{-1} \quad [\because a = 6.31 \times 10^{-3}]$$

$$\text{or } (a-x) = 3.556 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{or } x = 6.31 \times 10^{-3} - 3.556 \times 10^{-3}$$

$$= 10^{-3} \times (6.31 - 3.556) = 2.754 \times 10^{-3} \text{ mol L}^{-1}$$

After 12 minutesTotal number of moles/litre = $a + 2x$

$$= 6.31 \times 10^{-3} + 2 \times 2.754 \times 10^{-3} = 11.818 \times 10^{-3}$$

Since $PV = nRT$

$$\therefore P = \frac{n}{V} \cdot RT$$

$$= 11.818 \times 10^{-3} \times 0.082 \times 773 \quad [\because \frac{n}{V} = 11.818 \times 10^{-3}]$$

$$= 0.749 \text{ atm.}$$

38. (i) : From the graph we can see that in 4 hour (1 to 5) concentration of A decreases to 0.3 M from 0.5 M whereas concentration of B increases to 0.6 M from 0.2 M.

$$\therefore \text{Loss of conc. of } A \text{ in 4 hours} = (0.5 - 0.3) = 0.2 \text{ M}$$

Gain in concentration of B in 4 hours = $(0.6 - 0.2) = 0.4$ M

So, the increase in concentration of ' B ' in the same time (4 hours) is twice the decrease in concentration of ' A '.

Thus $n = 2$

$$(ii) \quad K = \frac{[B_{eq}]^2}{[A_{eq}]} = \frac{(0.6)^2}{(0.3)} = \frac{0.6 \times 0.6}{0.3} = 1.2$$

(iii) Initial rate of conversion of A = Change in conc. of ' A ' during 1 hour = $\frac{0.6 - 0.5}{1} = 0.1 \text{ mol litre}^{-1} \text{ hour}^{-1}$

39. (i) To calculate the order of the reaction :

we can write the rate law as follows:

$$\text{Rate} = k [A]^p [B]^q$$

From experiments I, II and III

$$(\text{Rate})_1 = k [2.5 \times 10^{-4}]^p [3.0 \times 10^{-5}]^q = 5.0 \times 10^{-4} \quad \dots(i)$$

$$(\text{Rate})_2 = k [5.0 \times 10^{-4}]^p [6.0 \times 10^{-5}]^q = 4.0 \times 10^{-3} \quad \dots(ii)$$

$$(\text{Rate})_3 = k [1.0 \times 10^{-3}]^p [6.0 \times 10^{-5}]^q = 1.6 \times 10^{-2} \quad \dots(iii)$$

Dividing equation (iii) by equation (ii)

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{(1.0 \times 10^{-3})^p}{(5.0 \times 10^{-4})^p} = \frac{1.6 \times 10^{-2}}{4.0 \times 10^{-3}}$$

$$\text{or } 2^p = 4 \quad \text{or } 2^p = 2^2 \quad \text{i. e. } p = 2$$

Dividing equation (ii) by equation (i),

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{(5.0 \times 10^{-4})^p (6.0 \times 10^{-5})^q}{(2.5 \times 10^{-4})^p (3.0 \times 10^{-5})^q} = \frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}}$$

$$\text{or } 2^p \cdot 2^q = 8 \quad \text{or } 2^2 \cdot 2^q = 8$$

$$\text{or } 2^q = 8/2^2 \quad \text{or } 2^q = 2^1$$

$$\text{or } q = 1$$

Thus the rate equation is $\text{Rate} = k[A]^2[B]$

\therefore Order of reaction with respect to $A = 2$

Order of reaction with respect to $B = 1$

(ii) To calculate rate constant (k) at 300 K

From experiment 1, we have

$$\text{Rate} = k (2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})$$

$$\text{or } 5.0 \times 10^{-4} = k (2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})$$

$$\text{or } k = \frac{5.0 \times 10^{-4}}{(2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})} = 2.67 \times 10^8 \text{ mol}^{-2} \text{L}^2 \text{s}^{-1}$$

(iii) To calculate activation energy:

$$\text{We know, } \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$$

$$\text{Given: } T_1 = 300 \text{ K, } k_1 = 5.0 \times 10^{-4};$$

$$T_2 = 320 \text{ K, } k_2 = 2.0 \times 10^{-3}$$

$$\therefore \log \frac{2.0 \times 10^{-3}}{5.0 \times 10^{-4}} = \frac{E_a}{2.303 \times 8.314} \times \frac{(320 - 300)}{(300 \times 320)}$$

$$\text{or } 0.6020 = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{300 \times 320}$$

$$\text{or } E_a = \frac{0.6020 \times 2.303 \times 8.314 \times 300 \times 320}{20}$$

$$= 55328 \text{ J mol}^{-1} = 55.33 \text{ kJ mol}^{-1}$$

(iv) To find the value of A (pre-exponential factor) :

$$\text{Use the relation; } \log k = -\frac{E_a}{2.303 R} \times \frac{1}{T} + \log A$$

$$\log 2.67 \times 10^8 = -\frac{55.33 \times 10^3}{2.303 \times 8.314} \times \frac{1}{300} + \log A$$

$$\text{or } 8.425 = -9.632 + \log A$$

$$\text{or } \log A = 8.425 + 9.632 = 18.057$$

$$\text{or } A = 1.140 \times 10^{18}$$

$$40. \text{ We know, } k = \frac{0.693}{t_{1/2}}$$

$$\therefore k = \frac{0.693}{360} = 1.925 \times 10^{-3} \text{ min}^{-1}$$

Value of k_2 at 450°C or 723 K :

$$\text{Using } \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right], \text{ we get}$$

$$\log \frac{k_2}{1.925 \times 10^{-3}} = \frac{200 \times 10^3}{2.303 \times 8.314} \left[\frac{723 - 653}{723 \times 653} \right]$$

$$\text{or } \log \frac{k_2}{1.925 \times 10^{-3}} = 1.5487$$

$$\text{or } \frac{k_2}{1.925 \times 10^{-3}} = 35.375$$

$$\text{or } k_2 = 35.375 \times 1.925 \times 10^{-3} = 6.81 \times 10^{-2} \text{ min}^{-1}$$

Calculation of time for 75% decomposition at 723 K :

$$\text{Let } [A]_0 = 1, \text{ then } [A] = 1 - \frac{75}{100} = 0.25$$

$$\text{or } t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

$$\text{or } t = \frac{2.303}{6.81 \times 10^{-2}} \log \frac{1}{0.25} = 33.82 \log 4 = 33.82 \times 0.6021 = 20.36 \text{ min.}$$

41. (i) $\text{NH}_4^+ + aq \rightleftharpoons \text{NH}_3 + \text{H}^+$

$$K = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}$$

(ii) $\text{NH}_4^+ + \text{OH}^- \longrightarrow \text{NH}_3 + \text{H}_2\text{O}$

$$\text{Rate constant, } k = 3.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$$

(iii) $\text{NH}_3 + \text{H}_2\text{O} \longrightarrow \text{NH}_4^+ + \text{OH}^-$

The rate constant for above reaction is to be calculated.

The above reaction represents backward reaction as represented by eq (ii). If rate constant of eq (ii) is k_f the rate constant for eq (iii) will be k_b .

$$\text{Equilibrium constant } K' = \frac{k_f}{k_b} \quad \text{or} \quad K' = \frac{[\text{NH}_3][\text{H}_2\text{O}]}{[\text{NH}_4^+][\text{OH}^-]}$$

Dividing K' by K

$$\frac{K'}{K} = \frac{1}{[\text{H}^+][\text{OH}^-]}$$

$$\text{or } K' = \frac{K}{[\text{H}^+][\text{OH}^-]} = \frac{5.6 \times 10^{-10}}{1.0 \times 10^{-14}} = 5.6 \times 10^4$$

$$\therefore K' = \frac{k_f}{k_b} \quad \text{or} \quad 5.6 \times 10^4 = \frac{3.4 \times 10^{10}}{k_b}$$

$$\text{or } k_b = \frac{3.4 \times 10^{10}}{5.6 \times 10^4} = 6.07 \times 10^5 \text{ s}^{-1}$$

42. For 10% completion of the reaction:

$$k_{298} = \frac{2.303}{t(10\%)} \log \frac{100}{90} \quad \dots(i)$$

For 25% completion of the reaction

$$k_{308} = \frac{2.303}{t(25\%)} \log \frac{100}{75} \quad \dots(ii)$$

From (i) and (ii), we have

$$\frac{k_{308}}{k_{298}} = \frac{\frac{2.303}{t(25\%)} \log \frac{100}{75}}{\frac{2.303}{t(10\%)} \log \frac{100}{90}}$$

Since $t(10\%) = t(25\%)$

$$\therefore \frac{k_{308}}{k_{298}} = \frac{\log \frac{100}{75}}{\log \frac{100}{90}} = 2.73$$

$$\text{Using the relation } \log \frac{k_{308}}{k_{298}} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$$

$$\log 2.73 = \frac{E_a}{2.303 \times 8.314} \left[\frac{308 - 298}{298 \times 308} \right]$$

$$\text{or } 0.436 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{298 \times 308}$$

$$\text{or } E_a = \frac{0.436 \times 2.303 \times 8.314 \times 298 \times 308}{10}$$

$$E_a = 76.623 \text{ kJ mol}^{-1}$$

Now $k = A \cdot e^{-E_a/RT}$

$$\text{or } \log k = \log A - \frac{E_a}{2.303 RT}$$

$$\therefore \log k_{318} = \log (3.56 \times 10^9) - \frac{76.623 \times 10^3}{2.303 \times 8.314 \times 318}$$

$$\text{or } \log k_{318} = 9.551 - 12.584 = -3.033 \text{ or } \bar{4}.967$$

$$\text{or } k_{318} = 9.27 \times 10^{-4} \text{ s}^{-1}$$

43. (i): We know $k = A \cdot e^{-E_a/RT}$

$$\text{or } \log k = \log A - \frac{E_a}{2.303 RT}$$

Comparing this equation with the given equation,

$$\text{we get, } \frac{E_a}{2.303 R} = 1.25 \times 10^4$$

$$\text{Hence, } E_a = 1.25 \times 10^4 \times 2.303 \times 8.314$$

$$= 2.39 \times 10^5 \text{ J mol}^{-1} \text{ or } 239 \text{ kJ mol}^{-1}$$

(ii) Since the unit of rate constant is s^{-1} , therefore the reaction is of first order.

$$\therefore t_{1/2} = \frac{0.693}{k}$$

$$\text{or } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256 \times 60} = 4.51 \times 10^{-5} \text{ s}^{-1}$$

Substituting this value in the given expression, we get

$$\log (4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$\text{or } -4.346 = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$\text{or } \frac{1.25 \times 10^4}{T} = 14.34 + 4.346$$

$$\text{or } = 18.686 \quad \text{or } T = \frac{1.25 \times 10^4}{18.686} = 669 \text{ K}$$

44. Using the relation : $\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$, we get

$$\log \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{8.314 \times 2.303} \left[\frac{373 - 323}{323 \times 373} \right]$$

$$\text{or } \log 3 = \frac{E_a \times 50}{8.314 \times 2.303 \times 323 \times 373}$$

$$\text{or } E_a = 2.2 \times 10^4 \text{ J mol}^{-1}$$

Again $k = A e^{-E_a/RT}$

$$\therefore 4.5 \times 10^7 = A \cdot e^{-\frac{2.2 \times 10^4}{8.314 \times 373}}$$

$$\therefore A = 5.42 \times 10^{10} \text{ s}^{-1}$$

45. From the units of rate constant, (min^{-1}), it is evident that the given isomerisation reaction is of first order.

$$\therefore k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

Given: $k = 4.5 \times 10^{-3} \text{ min}^{-1}$, $a = 1 \text{ M}$; $(a-x) = ?$,
 $t = 1 \text{ hr} = 60 \text{ min}$.

$$\text{Thus, } 4.5 \times 10^{-3} = \frac{2.303}{60} \log \frac{1}{(a-x)}$$

$$\text{or } \log \frac{1}{(a-x)} = \frac{60 \times 4.5 \times 10^{-3}}{2.303} \text{ or } \frac{1}{(a-x)} = 1.310$$

$$\therefore (a-x) = 0.7634 \text{ M.}$$

Rate of reaction after 1 hour

$$k[A] = 4.5 \times 10^{-3} \times 0.7634 \\ = 3.44 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

46. $k = A \cdot e^{-E_a/RT}$ [Arrhenius Equation]

Let the activation energy (E_a) in the absence of catalyst
 $= x \text{ kJ mol}^{-1}$

and activation energy in the presence of catalyst
 $= (x - 20) \text{ kJ mol}^{-1}$

Then

$$\text{at } 500 \text{ K ; } k = A \cdot e^{-x/500R} \quad \dots (i)$$

$$\text{at } 400 \text{ K ; } k = A \cdot e^{-(x-20)/400R} \quad \dots (ii)$$

Dividing (i) by (ii),

$$1 = \frac{e^{-x/500R}}{e^{-(x-20)/400R}} \quad \text{or } e^{-x/500R} = e^{-(x-20)/400R}$$

$$\text{or } \frac{x}{500 R} = \frac{x-20}{400 R} \quad \text{or } 100x = 10000$$

$$\text{or } x = 100 \text{ kJ mol}^{-1}$$

47. Rate = $k \cdot C$.

$$\therefore \text{Rate, } r_1 = k \cdot C_1 \quad [k \text{ is same}]$$

$$\text{and Rate } r_2 = k \cdot C_2$$

$$\therefore \frac{r_1}{r_2} = \frac{C_1}{C_2}$$

$$\therefore \frac{r_1 \text{ (at 10 min)}}{r_2 \text{ (at 20 min)}} = \frac{0.04}{0.03} = \frac{C_1}{C_2}$$

$$\text{Now } t = \frac{2.303}{k} \log \frac{C_1}{C_2} \quad [\text{For first order reaction}]$$

$$\text{or } k = \frac{2.303}{t} \log \frac{C_1}{C_2}$$

When $t = 10$ min.

$$k = \frac{2.303}{10} \log \frac{0.04}{0.03}$$

$$\text{or } k = \frac{2.303}{10} \log \frac{4}{3} = 0.0287 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287} = 24.14 \text{ min.}$$

48. When polymerization process was ceased by adding 0.525 mole of solute, let by that time x mole of liquid A was left behind unpolymerised.

Since total vapour pressure at that instant is 400 mm of Hg and the solute also helps to suppress the vapour pressure so,

$$\left(\frac{x}{x+12+0.525} \times 300 \right) + \left(\frac{12}{x+12+0.525} \times 500 \right) = 400$$

[Here we have assumed that the solute added is non-volatile but miscible and the mole of B that vapourises upto equilibrium stage is negligible]

On solving, we get $x = 9.9$

Since polymerization follows a first order kinetics

$$\therefore k = \frac{2.303}{100} \log \frac{10}{9.9} = \frac{2.303}{100} \times 4.365 \times 10^{-3} \\ = 1.005 \times 10^{-4} \text{ min}^{-1}.$$

49. (a): From the given data in table and $R_0 = k [A_0]^a [B_0]^b$ we can easily conclude that

(i) The rate doubles if we double the conc. of $[A_0]$ keeping that of $[B_0]$ constant. From this we find that rate $\propto [A_0]$ or rate = $k [A_0]^1$ or $a = 1$

(ii) The rate remains unchanged when conc. of $[B_0]$ is reduced keeping $[A_0]$ constant *i.e.* rate is independent of $[B_0]$ or rate = $k [B_0]^0$ or $b = 0$

Thus rate equation becomes $R_0 = k [A_0]$

(b) Since $R_0 = k [A_0]$

$$\therefore \frac{R_0}{[A_0]} = \frac{0.05}{0.10} = 0.5 \text{ sec}^{-1}$$

50. (i): From the given data we find that $t_{1/2}$ for decomposition of $X_{(g)}$ is constant (*i.e.* 100 min). Hence order of reaction is 1.

$$\text{(ii) Rate constant, } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ min}^{-1}$$

$$\text{(iii) Time taken for 75\% completion of reaction} = 2 \times t_{1/2} \\ = 2 \times 100 = 200 \text{ min.}$$



Initially	800	0	0
After time t	$(800 - 2p)$	$3p$	$2p$

When the pressure of X is 700 mm of mercury

$$\text{Then, } (800 - 2p) = 700$$

$$\text{or } 2p = 800 - 700 = 100$$

$$\text{or } p = 100/2 = 50 \text{ mm of Hg.}$$

$$\text{Total pressure} = (800 - 2p) + 3p + 2p$$

$$= 800 + 3p = 800 + 3 \times 50$$

$$= 800 + 150 = 950 \text{ mm of Hg.}$$

51. (a): Statement-1 is correct (In most of the reactions the specific rate constant, k , nearly doubles for every 10°C rise in temperature). Statement-2 is true and it explains statement-1.

52. (0): For the given reaction,

$$-\frac{d[R]}{dt} = -\left(\frac{0.75 - 1}{0.05 - 0} \right) = \frac{0.25}{0.05} = 5 \quad \dots\text{(i)}$$

$$-\frac{d[R]}{dt} = -\left(\frac{0.40 - 0.75}{0.12 - 0.05} \right) = \frac{0.35}{0.07} = 5 \quad \dots\text{(ii)}$$

Thus the value of $\frac{d[R]}{dt} = k$ is constant, and the reaction follows zero order kinetics.

53. (9): $k = \frac{2.303}{t} \log \frac{a_0}{a}$. $a = a_0/8$ at $t_{1/8}$

$$t_{1/8} = \frac{2.303}{k} \log \frac{a_0}{a_0/8} = \frac{2.303}{k} \log 8 \quad \dots\text{(i)}$$

When $t = t_{1/10}$, $a = a_0/10$

$$t_{1/10} = \frac{2.303}{k} \log \frac{a_0}{a_0/10} = \frac{2.303}{k} \log 10 \quad \dots\text{(ii)}$$

From eq. (i) and (ii),

$$\frac{[t_{1/8}]}{[t_{1/10}]} \times 10 = \frac{2.303}{k} \log 8 \times \frac{k}{2.303 \times \log 10} \times 10 \\ = \frac{\log 8}{\log 10} \times 10 = \frac{\log 2^3}{\log 10} \times 10 = \frac{3 \log 2}{\log 10} \times 10 \\ = \frac{3 \times 0.3 \times 10}{1} = 9$$



9

Equilibrium

Multiple Choice Questions with ONE Correct Answer

- An acidic buffer solution can be prepared by mixing the solutions of
 - ammonium acetate and acetic acid
 - ammonium chloride and ammonium hydroxide
 - sulphuric acid and sodium sulphate
 - sodium chloride and sodium hydroxide (1981)
- The pH of a 10^{-8} molar solution of HCl in water is
 - 8
 - 8
 - between 7 and 8
 - between 6 and 7 (1981)
- The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if
 - temperature is increased and pressure is kept constant
 - temperature is reduced and pressure is increased
 - both temperature and pressure are increased
 - both temperature and pressure are reduced (1981)
- For the reaction:

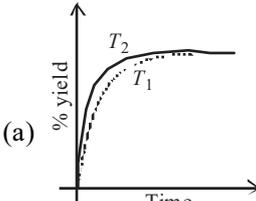
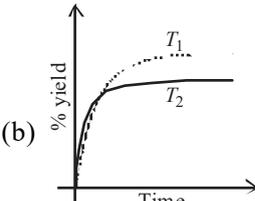
$$\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$$
 the equilibrium constant K_p changes with
 - total pressure
 - catalyst
 - the amounts of H_2 and I_2 present
 - temperature (1981)
- Of the given anions, the strongest Bronsted base is
 - ClO^-
 - ClO_2^-
 - ClO_3^-
 - ClO_4^- (1981)
- At 90°C , pure water has $[\text{H}_3\text{O}^+]$ as 10^{-6} mole litre $^{-1}$. What is the value of K_w at 90°C ?
 - 10^{-6}
 - 10^{-12}
 - 10^{-14}
 - 10^{-8} (1981)
- The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed
 - 10^{-4} M Ca^{2+} + 10^{-4} M F^-
 - 10^{-2} M Ca^{2+} + 10^{-3} M F^-
 - 10^{-5} M Ca^{2+} + 10^{-3} M F^-
 - 10^{-3} M Ca^{2+} + 10^{-5} M F^- (1982)
- A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal
 - inter-molecular forces
 - potential energy
 - total energy
 - kinetic energy (1984)
- Pure ammonia is placed in a vessel at a temperature where its dissociation constant (α) is appreciable. At equilibrium
 - K_p does not change significantly with pressure
 - α does not change with pressure
 - concentration of NH_3 does not change with pressure
 - concentration of hydrogen is less than that of nitrogen (1984)
- A certain buffer solution contains equal concentration of X^- and HX . The K_b for X^- is 10^{-10} . The pH of the buffer is
 - 4
 - 7
 - 10
 - 14 (1984)
- A certain weak acid has a dissociation constant of 1.0×10^{-4} . The equilibrium constant for its reaction with a strong base is
 - 1.0×10^{-4}
 - 1.0×10^{-10}
 - 1.0×10^{10}
 - 1.0×10^{14} (1984)
- An example of a reversible reaction is
 - $\text{Pb}(\text{NO}_3)_2(aq) + 2\text{NaI}(aq) = \text{PbI}_{2(s)} + 2\text{NaNO}_3(aq)$
 - $\text{AgNO}_3(aq) + \text{HCl}(aq) = \text{AgCl}(s) + \text{HNO}_3(aq)$
 - $2\text{Na}(s) + 2\text{H}_2\text{O}(l) = 2\text{NaOH}(aq) + \text{H}_2(g)$
 - $\text{KNO}_3(aq) + \text{NaCl}(aq) = \text{KCl}(aq) + \text{NaNO}_3(aq)$ (1985)
- The best indicator for detection of end point in titration of a weak acid and a strong base is
 - methyl orange (3 to 4)
 - methyl red (5 to 6)
 - bromothymol blue (6 to 7)
 - phenolphthalein (8 to 9.6) (1985)
- The conjugate acid of NH_2^- is
 - NH_3
 - NH_2OH
 - NH_4^+
 - N_2H_4 (1985)
- The compound that is not a Lewis acid is
 - BF_3
 - AlCl_3
 - BeCl_2
 - SnCl_4 (1985)

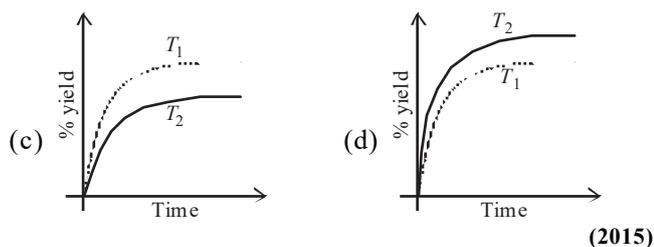
16. The compound insoluble in acetic acid is
 (a) calcium oxide (b) calcium carbonate
 (c) calcium oxalate (d) calcium hydroxide
 (1986)
17. The compound whose 0.1 M solution is basic is
 (a) ammonium acetate (b) ammonium chloride
 (c) ammonium sulphate (d) sodium acetate (1986)
18. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with
 (a) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)
 (b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
 (c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)
 (d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-) (1988)
19. The $\text{p}K_a$ of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be
 (a) unionised in the small intestine and in the stomach
 (b) completely ionised in the small intestine and in the stomach
 (c) ionised in the stomach and almost unionised in the small intestine
 (d) ionised in the small intestine and almost unionised in the stomach (1988)
20. Which one of the following is the strongest acid?
 (a) $\text{ClO}_3(\text{OH})$ (b) $\text{ClO}_2(\text{OH})$
 (c) $\text{SO}(\text{OH})_2$ (d) $\text{SO}_2(\text{OH})_2$ (1989)
21. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25°C) is
 (a) $\text{Mg}(\text{OH})_2$ (b) $\text{Ca}(\text{OH})_2$
 (c) $\text{Ba}(\text{OH})_2$ (d) $\text{Be}(\text{OH})_2$ (1990)
22. The reaction which proceeds in the forward direction is
 (a) $\text{Fe}_2\text{O}_3 + 6\text{HCl} = 2\text{FeCl}_3 + 3\text{H}_2\text{O}$
 (b) $\text{NH}_3 + \text{H}_2\text{O} + \text{NaCl} = \text{NH}_4\text{Cl} + \text{NaOH}$
 (c) $\text{SnCl}_4 + \text{Hg}_2\text{Cl}_2 = \text{SnCl}_2 + 2\text{HgCl}_2$
 (d) $2\text{CuI} + \text{I}_2 + 4\text{K}^+ = 2\text{Cu}^{2+} + 4\text{KI}$ (1991)
23. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid.

$$\text{HCl} + \text{CH}_3\text{COOH} \rightleftharpoons \text{Cl}^- + \text{CH}_3\text{COOH}_2^+$$
 The set that characterises the conjugate acid-base pairs is:
 (a) (HCl , CH_3COOH) and ($\text{CH}_3\text{COOH}_2^+$, Cl^-)
 (b) (HCl , $\text{CH}_3\text{COOH}_2^+$) and (CH_3COOH , Cl^-)
 (c) ($\text{CH}_3\text{COOH}_2^+$, HCl) and (Cl^- , CH_3COOH)
 (d) (HCl , Cl^-) and ($\text{CH}_3\text{COOH}_2^+$, CH_3COOH) (1992)
24. Which of the following solutions will have pH close to 1.0?
 (a) 100 ml of (M/10) HCl + 100 ml of (M/10) NaOH
 (b) 55 ml of (M/10) HCl + 45 ml of (M/10) NaOH
 (c) 10 ml of (M/10) HCl + 90 ml of (M/10) NaOH
 (d) 75 ml of (M/5) HCl + 25 ml of (M/5) NaOH (1992)
25. The degree of dissociation of water at 25°C is $1.9 \times 10^{-7}\%$ and density is 1.0 g cm^{-3} . The ionic constant for water is
 (a) 1.0×10^{-14} (b) 2.0×10^{-16}
 (c) 1.0×10^{-16} (d) 1.0×10^{-8} (1995)
26. Which one is more acidic in aqueous solutions?
 (a) NiCl_2 (b) FeCl_3 (c) AlCl_3 (d) BeCl_2 (1995)
27. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order.
 ClOH (I), BrOH (II), IOH (III)
 (a) $\text{I} > \text{II} > \text{III}$ (b) $\text{II} > \text{I} > \text{III}$
 (c) $\text{III} > \text{II} > \text{I}$ (d) $\text{I} > \text{III} > \text{II}$ (1996)
28. If $\text{p}K_b$ for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is
 (a) 1.74×10^{-5} (b) 3.52×10^{-3}
 (c) 6.75×10^{-4} (d) 5.38×10^{-2} (1997)
29. The solubility of A_2X_3 is $y \text{ mol dm}^{-3}$. Its solubility product is
 (a) $6y^4$ (b) $64y^4$ (c) $36y^5$ (d) $108y^5$ (1997)
30. The pH of 0.1 M solution of the following salts increases in the order
 (a) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$
 (b) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$
 (c) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
 (d) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$ (1992)
31. For the chemical reaction $3X_{(g)} + Y_{(g)} \rightleftharpoons X_3Y_{(g)}$, the amount of X_3Y at equilibrium is affected by
 (a) temperature and pressure
 (b) temperature only
 (c) pressure only
 (d) temperature, pressure and catalyst (1999)
32. For the reversible reaction, $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$ at 500°C , the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c , with concentration in mole litre $^{-1}$, is
 (a) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ (b) $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$
 (c) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$ (d) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$ (2000)
33. When two reactants, A and B are mixed to give products C and D , the reaction quotient Q , at the initial stages of the reaction

Equilibrium

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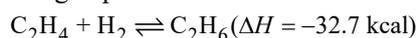
- (a) is zero (b) decreases with time
(c) is independent of time (d) increases with time (2000)
34. The set with correct order of acidity is
(a) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
(b) $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$
(c) $\text{HClO} < \text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2$
(d) $\text{HClO}_4 < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}$ (2001)
35. For a sparingly soluble salt A_pB_q , the relationship of its solubility product (L_s) with its solubility (S) is
(a) $L_s = S^{p+q} \cdot p^p \cdot q^q$ (b) $L_s = S^{p+q} \cdot p^q \cdot q^p$
(c) $L_s = S^{pq} \cdot p^p \cdot q^q$ (d) $L_s = S^{pq} \cdot (pq)^{p+q}$ (2001)
36. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ is expressed by $K_p = (4x^2P)/(1-x^2)$, where P = pressure, x = extent of decomposition. Which one of the following statements is true?
(a) K_p increases with increase of P
(b) K_p increases with increase of x
(c) K_p increases with decrease of x
(d) K_p remains constant with change in P and x (2001)
37. Consider the following equilibrium in a closed container
 $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$
At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?
(a) Neither K_p nor α changes
(b) Both K_p and α changes
(c) K_p changes, but α does not change
(d) K_p does not change, but α changes (2002)
38. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 0.1 M solution of NaX is
(a) 0.0001% (b) 0.01% (c) 0.1% (d) 0.15% (2004)
39. A 0.004 M solution of Na_2SO_4 is isotonic with 0.010 M solution of glucose at same temperature. The percentage dissociation of Na_2SO_4 is
(a) 25% (b) 50% (c) 75% (d) 85% (2004)
40. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution?
(a) 8×10^{-2} M (b) 8×10^{-11} M
(c) 8×10^{-15} M (d) 8×10^{-5} M (2005)
41. $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]^+$; $k_1 = 6.8 \times 10^{-3}$
 $[\text{Ag}(\text{NH}_3)]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$; $k_2 = 1.6 \times 10^{-3}$
then the formation constant of $[\text{Ag}(\text{NH}_3)_2]^+$ is
(a) 1.08×10^{-7} (b) 1.08×10^{-5}
(c) 1.08×10^{-9} (d) none of these. (2006)
42. $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
Which is correct statement if N_2 is added at equilibrium condition?
(a) The equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy must increase in the direction of spontaneous reaction.
(b) The condition for equilibrium is $G_{\text{N}_2} + 3G_{\text{H}_2} = 2G_{\text{NH}_3}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward directions to the same extent.
(c) The catalyst will increase the rate of forward reaction by β .
(d) Catalyst will not alter the rate of either of the reaction. (2006)
43. 2.5 mL of (2/5) M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with (2/15) M HCl in water at 25°C . The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)
(a) 3.7×10^{-13} M (b) 3.2×10^{-7} M
(c) 3.2×10^{-2} M (d) 2.7×10^{-2} M (2008)
44. Solubility product constants (K_{sp}) of salts of types MX , MX_2 and M_3X at temperature T are 4.0×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} respectively. Solubility (mol dm^{-3}) of the salts at temperature ' T ' are in the order
(a) $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$ (b) $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$
(c) $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$ (d) $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$ (2008)
45. The % yield of ammonia as a function of time in the reaction
 $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$, $\Delta H < 0$
at (P, T_1) is given below.
If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by
-
- (a)  (b) 



(2015)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

46. For the gas phase reaction



carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by

- (a) increasing the temperature
 (b) decreasing the pressure
 (c) removing some H_2
 (d) adding some C_2H_6

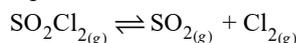
(1984)

47. When NaNO_3 is heated in a closed vessel, oxygen is liberated and NaNO_2 is left behind. At equilibrium

- (a) addition of NaNO_2 favours reverse reaction
 (b) addition of NaNO_3 favours forward reaction
 (c) increasing temperature favours forward reaction
 (d) increasing pressure favours reverse reaction

(1986)

48. The equilibrium

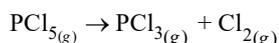


is attained at 25°C in a closed container and an inert gas, helium is introduced. Which of the following statements are correct?

- (a) Concentration of SO_2 , Cl_2 and SO_2Cl_2 do not change
 (b) More chlorine is formed
 (c) Concentration of SO_2 is reduced
 (d) More SO_2Cl_2 is formed

(1989)

49. For the reaction:



The forward reaction at constant temperature is favoured by

- (a) introducing chlorine gas at constant volume
 (b) introducing an inert gas at constant pressure
 (c) increasing the volume of the container
 (d) introducing PCl_5 at constant volume

(1991)

50. For the reaction $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{2(g)} + \text{H}_{2(g)}$ at a given temperature the equilibrium amount of $\text{CO}_{2(g)}$ can be increased by

- (a) adding a suitable catalyst
 (b) adding an inert gas
 (c) decreasing the volume of the container
 (d) increasing the amount of $\text{CO}_{(g)}$

(1998)

51. Which of the following statement(s) is (are) correct?

- (a) The pH of 1.0×10^{-8} M solution of HCl is 8.
 (b) The conjugate base of H_2PO_4^- is HPO_4^{2-} .
 (c) Autoprotolysis constant of water increases with temperature.
 (d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point $\text{pH} = (1/2) \text{p}K_a$.

(1998)

52. A buffer solution can be prepared from a mixture of

- (a) sodium acetate and acetic acid in water
 (b) sodium acetate and hydrochloric acid in water
 (c) ammonia and ammonium chloride in water
 (d) ammonia and sodium hydroxide in water

(1999)

53. Aqueous solutions of HNO_3 , KOH , CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are)

- (a) HNO_3 and CH_3COOH
 (b) KOH and CH_3COONa
 (c) HNO_3 and CH_3COONa
 (d) CH_3COOH and CH_3COONa

(2010)

54. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA , 1 M) is $1/100$ th of that of a strong acid (HX , 1 M), at 25°C . The K_a of HA is

- (a) 1×10^{-4} (b) 1×10^{-5}
 (c) 1×10^{-6} (d) 1×10^{-3}

(2013)

55. The thermal dissociation equilibrium of $\text{CaCO}_{3(s)}$ is studied under different conditions.

For this equilibrium, the correct statement(s) is (are)

- (a) ΔH is dependent on T
 (b) K is independent of the initial amount of CaCO_3
 (c) K is dependent on the pressure of CO_2 at a given T
 (d) ΔH is independent of the catalyst, if any.

(2013)

56. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M AgNO_3 solution is

- (a) 1.1×10^{-11} (b) 1.1×10^{-10}
 (c) 1.1×10^{-12} (d) 1.1×10^{-9}

(2013)

Fill in the Blanks

57. The conjugate base of HSO_4^- in aqueous solution is

(1982)

58. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be.....

(1984)

Equilibrium

103

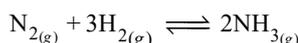
59. For a given reversible reaction at a fixed temperature, equilibrium constant K_p and K_c are related by.....
(1994)
60. A ten-fold increase in pressure on the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ at equilibrium results in in K_p .
(1996)
61. $(CH_3OH_2)^+$ is acidic than $(CH_3NH_3^+)$.
(1997)
62. For a gaseous reaction $2B \rightarrow A$, the equilibrium constant K_p is to/than K_c .
(1997)
63. In the reaction $I^- + I_2 \rightarrow I_3^-$, the Lewis acid is
(1997)

True / False

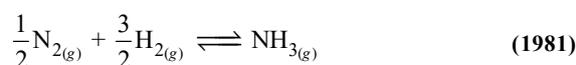
64. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons.
(1982)
65. If equilibrium constant for $A_2 + B_2 \rightleftharpoons 2AB$, is K , then for the backward reaction $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$, the equilibrium constant is $1/K$.
(1984)
66. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs.
(1984)
67. Solubility of sodium hydroxide increases with increase in temperature.
(1985)

Subjective Problems

68. How many moles of sodium propionate should be added to one litre of an aqueous solution containing 0.020 mole of propionic acid to obtain a buffer solution of pH 4.75? What will be pH if 0.010 mole of hydrogen chloride is dissolved in the above buffer solution. Compare the last pH value with the pH of 0.010 molar HCl solution. Dissociation constant of propionic acid, K_a at $25^\circ C = 1.34 \times 10^{-5}$.
(1981)
69. One mole of nitrogen is mixed with three moles of hydrogen in a 4 litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction.



Calculate the equilibrium constant (K_c) in concentration units. What will be the value of K_c for the following equilibrium?



70. Twenty ml of 0.2 M sodium hydroxide is added to 50 ml of 0.2 M acetic acid to give 70 ml of the solution.

What is the pH of this solution? Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74. The ionization constant of acetic acid is 1.8×10^{-5} .
(1982)

71. Give reasons for the following:
(i) The pH of an aqueous solution of sodium acetate is more than seven.
(1982)
(ii) Acetic acid is less acidic in sodium acetate solution than in sodium chloride solution.
(1986)
(iii) Between Na^+ and Ag^+ , which is a stronger Lewis acid and why?
(1997)
(iv) Will the pH of water be same at $4^\circ C$ and $25^\circ C$? Explain.
(2003)
72. The dissociation constant of a weak acid HA is 4.9×10^{-8} . After making the necessary approximations, calculate (i) percentage ionization, (ii) pH and (iii) OH^- concentration in a decimolar solution of the acid. Water has a pH of 7.
(1983)
73. A solution contains a mixture of Ag^+ (0.10 M) and Hg_2^{++} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated?
 $[K_{sp} : AgI = 8.5 \times 10^{-17}; Hg_2I_2 = 2.5 \times 10^{-26}]$
(1984)
74. One mole of Cl_2 and 3 moles of PCl_5 are placed in a 100 litre vessel heated at $227^\circ C$. The equilibrium pressure is 2.05 atmosphere. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction
 $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$.
(1984)
75. Arrange the following in
(i) increasing acid strength: $HClO_3, HClO_4, HClO_2, HClO$
(1986)
(ii) increasing basicity: $H_2O, OH^-, CH_3OH, CH_3O^-$
(1992)
(iii) decreasing order of Bronsted basicity
 $BaO, SO_3, CO_2, Cl_2O_7, B_2O_3$
(2004)
76. The $[H^+]$ in 0.2 M solution of formic acid is 6.4×10^{-3} mole litre $^{-1}$. To this solution sodium formate is added so as to adjust the concentration of sodium formate to one mole litre $^{-1}$. What will be pH of this solution? K_a for $HCOOH$ is 2.4×10^{-4} and degree of dissociation of $HCOONa$ is 0.75.
(1985)
77. The equilibrium constant of the reaction $A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$ at $100^\circ C$ is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2 , how many mole of AB will be formed at $373^\circ C$?
(1985)

78. The solubility of Mg(OH)_2 in pure water is 9.57×10^{-3} g/litre. Calculate its solubility (in g/litre) in 0.02 M $\text{Mg(NO}_3)_2$ solution. (1986)
79. What is the pH of the solution when 0.2 mole of hydrochloric acid is added to one litre of a solution containing
(i) 1 M each of acetic acid and acetate ion?
(ii) 0.1 M each of acetic acid and acetate ion?
Assume the total volume is one litre. K_a for acetic acid = 1.8×10^{-5} . (1987)
80. At a certain temperature equilibrium constant (K_c) is 16 for the reaction.
$$\text{SO}_{2(g)} + \text{NO}_{2(g)} \rightleftharpoons \text{SO}_{3(g)} + \text{NO}_{(g)}$$

If we take one mole each of all the four gases in a one litre container, what would be the equilibrium concentrations of $\text{NO}_{(g)}$ and $\text{NO}_{2(g)}$? (1987)
81. N_2O_4 is 25% dissociated at 37°C and one atmosphere pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C . (1988)
82. How many gram-mole of HCl will be required to prepare one litre of buffer solution (containing NaCN and HCl) of pH 8.5 using 0.01 gram formula weight of NaCN? $K_{\text{dissociation}}(\text{HCN}) = 4.1 \times 10^{-10}$. (1988)
83. The equilibrium constant K_p of the reaction:
$$2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$$

is 900 atm at 800 K. A mixture containing SO_3 and O_2 having initial partial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K. (1989)
84. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mole/L of ammonium chloride and 0.05 mole/L of ammonium hydroxide. Calculate the concentration of aluminium and magnesium ions in solution:
$$K_b[\text{NH}_4\text{OH}] = 1.80 \times 10^{-5}$$

$$K_{sp}[\text{Mg(OH)}_2] = 6 \times 10^{-10}$$

$$K_{sp}[\text{Al(OH)}_3] = 6 \times 10^{-32}$$
 (1989)
85. For the reaction: $\text{CO}_{(g)} + 2\text{H}_{2(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$
hydrogen gas is introduced into a five litre flask at 327°C , containing 0.2 mole of $\text{CO}_{(g)}$ and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of $\text{CH}_3\text{OH}_{(g)}$ is formed. Calculate the equilibrium constant K_p and K_c . (1990)
86. What is the pH of 1.0 M solution of acetic acid? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given: $K_a = 1.8 \times 10^{-5}$. (1990)
87. The solubility product of $\text{Ag}_2\text{C}_2\text{O}_4$ at 25°C is $1.29 \times 10^{-11} \text{ mol}^3 \text{ L}^{-3}$. A solution of $\text{K}_2\text{C}_2\text{O}_4$ containing 0.1520 mole in 500 ml water is shaken at 25°C with excess of Ag_2CO_3 till the following equilibrium is reached:
$$\text{Ag}_2\text{CO}_3 + \text{K}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{Ag}_2\text{C}_2\text{O}_4 + \text{K}_2\text{CO}_3$$

At equilibrium the solution contains 0.0358 mole of K_2CO_3 . Assuming the degree of dissociation of $\text{K}_2\text{C}_2\text{O}_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3 . (1991)
88. A 40.0 ml solution of weak base, BOH is titrated with 0.1 N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after adding 5.0 ml and 20.0 ml of the acid respectively. Find out the dissociation constant of the base. (1991)
89. The solubility product (K_{sp}) of Ca(OH)_2 at 25°C is 4.42×10^{-5} . A 500 ml of saturated solution of Ca(OH)_2 is mixed with equal volume of 0.4 M NaOH. How much Ca(OH)_2 in milligrams is precipitated? (1992)
90. 0.15 mole of CO taken in a 2.5 L flask is maintained at 750 K along with a catalyst so that the following reaction can take place
$$\text{CO}_{(g)} + 2\text{H}_{2(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$$

Hydrogen is introduced until the total pressure of the system is 8.5 atmosphere at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. (1993)
91. The pH of blood stream is maintained by a proper balance of H_2CO_3 and NaHCO_3 concentrations. What volume of 5M NaHCO_3 solution should be mixed with a 10 ml sample of blood which is 2M in H_2CO_3 in order to maintain a pH of 7.4? K_a for H_2CO_3 in blood is 7.8×10^{-7} . (1993)
92. An aqueous solution of a metal bromide MBr_2 (0.05M) is saturated with H_2S . What is the minimum pH at which MS will precipitate?
 K_{sp} for MS = 6.0×10^{-21} ; concentration of saturated $\text{H}_2\text{S} = 0.1 \text{ M}$, $K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$, for H_2S . (1993)
93. At temperature T , a compound $\text{AB}_{2(g)}$ dissociates according to the reaction
$$2\text{AB}_{2(g)} \rightleftharpoons 2\text{AB}_{(g)} + \text{B}_{2(g)}$$

with a degree of dissociation x which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant K_p and the total pressure, P . (1994)
94. For the reaction: $[\text{Ag(CN)}_2]^- \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$
the equilibrium constant, at 25°C , is 4.0×10^{-19} . Calculate

Equilibrium

105

the silver ion concentration in a solution which was originally 0.10 molar in KCN and 0.03 molar in AgNO₃.

(1994)

95. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation.

(pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8.)

(1995)

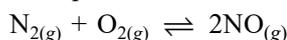
96. What is the pH of a 0.50 M aqueous NaCN solution? pK_b of CN⁻ is 4.70.

(1996)

97. A sample of hard water contains 96 ppm of SO₄²⁻ and 183 ppm of HCO₃⁻ with Ca²⁺ as the only cation. How many moles of CaO will be required to remove HCO₃⁻ from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca²⁺ ions? (Assume CaCO₃ to be completely insoluble in water). If the Ca²⁺ ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH? (One ppm means one part of the substance in one million parts of water).

(1997)

98. A sample of air consisting of N₂ and O₂ was heated to 2500 K until the equilibrium



was established with an equilibrium constant K_c = 2.1 × 10⁻³. At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fraction of N₂ and O₂.

(1997)

99. A sample of AgCl was treated with 5.00 ml of 1.5 M Na₂CO₃ solution to give Ag₂CO₃. The remaining solution contained 0.0026 g of Cl⁻ per litre. Calculate the solubility product of AgCl (K_{sp}(Ag₂CO₃) = 8.2 × 10⁻¹²).

(1997)

100. An acid type indicator, HIn differs in colour from its conjugate base (In⁻). The human eye is sensitive to colour differences only when the ratio [In⁻]/[HIn] is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change (K_a = 1.0 × 10⁻⁵)?

(1997)

101. Given: Ag(NH₃)₂⁺ ⇌ Ag⁺ + 2NH₃, K_c = 6.2 × 10⁻⁸ and K_{sp} of AgCl = 1.8 × 10⁻¹⁰ at 298 K. If ammonia is added to a water solution containing excess of AgCl(s) only, calculate the concentration of the complex in 1.0 M aqueous ammonia.

(1998)

102. The degree of dissociation is 0.4 at 400 K and 1.0 atm for gaseous reaction



Assuming ideal gas behaviour for all the gases, calculate the density of the equilibrium mixture at 400 K and 1.0 atm pressure.

(1998)

103. What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0)?

(1998)

104. When 3.06 g of solid NH₄HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_c and K_p for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH₄HS is introduced into the flask?

(1999)

105. The solubility of Pb(OH)₂ in water is 6.7 × 10⁻⁶ M. Calculate the solubility of Pb(OH)₂ in a buffer solution of pH = 8.

(1999)

106. The average concentration of SO₂ in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO₂ in water at 298 K is 1.3653 moles litre⁻¹ and the pK_a of H₂SO₃ is 1.92, estimate the pH of rain on that day.

(2000)

107. 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 ml of 0.2 M HCl at 25°C.

(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(ii) If 6 g of NaOH is added to the above solution, determine the final pH. [Assume there is no change in volume on mixing; K_a of acetic acid is 1.75 × 10⁻⁵ mol L⁻¹.]

(2002)

108. Match the following if the molecular weights of X, Y and Z are same.

Solvent	Boiling Point	K _b
X	100	0.68
Y	27	0.53
Z	235	0.98

(2003)

109. 0.1 M NaOH is titrated with 0.1 M HA till the end point; K_a for HA is 5 × 10⁻⁶ and degree of hydrolysis is less compared to 1. Calculate pH of the resulting solution at the end point.

(2004)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement - 1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.

(c) Statement-1 is true, statement-2 is false.

(d) Statement-1 is false, statement-2 is true.

110. Statement-1 : HNO_3 is a stronger acid than HNO_2 .

Statement-2 : In HNO_3 there are two nitrogen-oxygen bonds whereas in HNO_2 there is only one.

(1998)

111. Statement-1 : The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.

Statement-2 : When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change.

(1991)

Integer Answer Type

112. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4} . The pH of a 0.01 M solution of its sodium salt is

(2009)

113. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is
 KCN K_2SO_4 $(\text{NH}_4)_2\text{C}_2\text{O}_4$ NaCl $\text{Zn}(\text{NO}_3)_2$
 FeCl_3 K_2CO_3 NH_4NO_3 LiCN

(2010)

114. In 1 L saturated solution of AgCl [$K_{sp}(\text{AgCl}) = 1.6 \times 10^{-10}$], 0.1 mol of CuCl [$K_{sp}(\text{CuCl}) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x} . The value of x is

(2011)

115. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda_{\text{X}^-}^\circ \approx \lambda_{\text{Y}^-}^\circ$ the difference in their $\text{p}K_a$ values, $\text{p}K_a(\text{HX}) - \text{p}K_a(\text{HY})$, is (consider degree of ionization of both acids to be $\ll 1$)

(2015)

ANSWER KEY

- | | | | | | |
|---|---|---|--|--------------------------------|-----------|
| 1. (a) | 2. (d) | 3. (b) | 4. (d) | 5. (a) | 6. (b) |
| 7. (b) | 8. (c) | 9. (a) | 10. (a) | 11. (c) | 12. (d) |
| 13. (d) | 14. (a) | 15. (d) | 16. (c) | 17. (d) | 18. (a) |
| 19. (d) | 20. (a) | 21. (d) | 22. (a) | 23. (d) | 24. (d) |
| 25. (a) | 26. (c) | 27. (a) | 28. (c) | 29. (d) | 30. (b) |
| 31. (a) | 32. (d) | 33. (d) | 34. (a) | 35. (a) | 36. (d) |
| 37. (d) | 38. (b) | 39. (c) | 40. (b) | 41. (b) | 42. (b) |
| 43. (c) | 44. (d) | 45. (b) | 46. (a, b, c, d) | 47. (c, d) | 48. (a) |
| 49. (b, c, d) | 50. (d) | 51. (b, c) | 52. (a, c) | 53. (d) | 54. (a) |
| 55. (a, b, d) | 56. (b) | 57. SO_4^{2-} | 58. Amphoteric | 59. $K_p = K_c(RT)^{\Delta n}$ | |
| 60. No change | 61. More | 62. Less | 63. I_2 | 64. False | 65. False |
| 66. True | 67. False | 68. 2 | 69. 3.82×10^{-3} litre mol^{-1} | 70. 4.87 ml | |
| 72. (i) 0.07% (ii) 4.15 (iii) 1.43×10^{-10} mol litre $^{-1}$ | | | 73. 99.83% | 74. 0.41 | |
| 75. (i) $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$; (ii) $\text{CH}_3\text{O}^- > \text{OH}^- > \text{CH}_3\text{OH} > \text{H}_2\text{O}$; (iii) $\text{BaO} > \text{B}_2\text{O}_3 > \text{CO}_2 > \text{SO}_3 > \text{Cl}_2\text{O}_7$ | | | | | |
| 76. 4.19 | 77. 1.86 | 78. 8.7×10^{-4} g/litre | | 79. 4.5686; 1 | |
| 80. $\text{NO} = 1.6$ moles; $\text{NO}_2 = 0.4$ moles | 81. 0.266 atm; 63% | | | 82. 8.85×10^{-3} M | |
| 83. $P_{\text{SO}_2} = 0.0236$ atm; $P_{\text{O}_2} = 2.0118$ atm; $P_{\text{SO}_3} = 0.976$ atm | | | | | |
| 84. $\text{Mg}^{2+} = 46.29$ mol/L; $\text{Al}^{3+} = 1.286 \times 10^{-15}$ mol/L | 85. 0.115 atm $^{-2}$ | 86. 2.3724; 2.78×10^4 L | | | |
| 87. 3.9×10^{-12} mol 3 L $^{-3}$ | 88. 1.828×10^{-4} | 89. 742.1 mg | 90. $K_p = 0.05$ atm $^{-2}$, $P = 12.438$ atm | | |
| 91. 78.36 ml | 92. 0.983 | 93. $\left(\frac{2K_p}{P}\right)^{\frac{1}{3}}$ | 94. 7.5×10^{-18} M | 95. 6.5 | 96. 11.5 |
| 97. 2.4×10^{-3} moles/L; 2.62 | 98. $\text{N}_2 = 79\%$; $\text{O}_2 = 21\%$ | 99. 1.71×10^{-10} | 100. 2 | | |
| 101. 0.0538 M | 102. 4.54 g L $^{-1}$ | 103. 11.3010 | 104. Addition of more NH_4HS will have no effect | | |
| 105. 1.203×10^{-3} mol litre $^{-1}$ | 106. 3.39 | 107. 1; 4.75 | 109. 9 | 110. (c) | |
| 111. (d) | 112. (8) | 113. (3) | 114. (7) | 115. (3) | |

Explanations

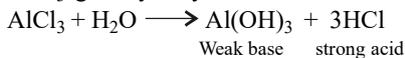
1. (a): Acidic buffer consists of a weak acid and its conjugate base. In the present case it consists of CH_3COOH (weak acid) and its conjugate base (CH_3COO^-) provided by $\text{CH}_3\text{COONH}_4$ (salt of the weak acid).
2. (d): $\text{H}^+ = 10^{-8}$ M, but pH = 8 is not possible because it is an acid. Now, $[\text{H}^+] = 10^{-7}$ M are already present in solution and since $10^{-8} < 10^{-7}$ and thus it should not be neglected.
 \therefore Total $[\text{H}^+] = 10^{-8} + 10^{-7} = 10^{-7} (0.1 + 1) = 1.1 \times 10^{-7}$
 or pH = 6.9586
3. (b): Since it is an exothermic reaction so the forward reaction ($2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 + \text{Heat}$) will be favoured by decrease in temperature in accordance with Le Chatelier's principle. Since the number of gaseous products decreases ($\Delta n = 2 - 3 = -1$) so the forward reaction will be favoured by increased pressure.
4. (d): K_p depends on temperature.
5. (a): The strongest conjugated base has the weakest corresponding acid. HClO is weakest acid because in it the oxidation state of Cl is +1 which is the least as the oxidation state of Cl in other species are like in HClO_2 (+3), HClO_3 (+5) and HClO_4 (+7). In case of oxyacids higher the oxidation state stronger is the acid.
6. (b): In case of pure water, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$
 or $K_w = 10^{-6} \times 10^{-6} = 10^{-12}$
7. (b): It is only in this case that ionic product exceeds the solubility product.
8. (c): They have equal total energy because both vapours and liquid are at the same temperature.
9. (a): Since temperature is constant so K_p remains unchanged.
10. (a): $\text{pH} = 14 - \text{p}K_b - \log \frac{[\text{salt}]}{[\text{base}]}$
 $= 14 - (-\log 10^{-10}) - \log 1 = 14 - 10 = 4$
11. (c): In case of neutralisation of a weak acid with a strong base, $K = \frac{K_a}{K_w} = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-14}}$ or 1×10^{10}
12. (d): In this case all the reactants and products exist in aqueous form so it is a reversible reaction. In case any precipitate or an insoluble gaseous product is formed then the reaction becomes unidirectional.
13. (d): In this case that indicator which gives colour on basic side will be preferred because the pH of solution at equivalence point will be more than 7 (*i.e.*, it will be a basic solution).
14. (a): $\text{NH}_2^- + \text{H}^+ \longrightarrow \text{NH}_3$
Base Conjugate acid
15. (d): In case of SnCl_4 , there is a complete octet. A Lewis acid is electron deficient compound.
16. (c): CaC_2O_4 (calcium oxalate) in CH_3COOH because CH_3COO^- is a stronger conjugate base than $\text{C}_2\text{O}_4^{2-}$.
17. (d): $\text{CH}_3\text{COONa} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{COOH} + \text{NaOH}$
Weak acid Strong alkali
 So, $\text{OH}^- > \text{H}^+$ and the solution is basic.
18. (a): For precipitation, ionic product $> K_{sp}$. In this case ionic product = $[\text{Ag}^+][\text{Cl}^-]$
 $= \frac{10^{-4}}{2} \times \frac{10^{-4}}{2} = 2.5 \times 10^{-9}$
 Thus $2.5 \times 10^{-9} > 1.8 \times 10^{-10}$ (K_{sp})
19. (d): In acidic solutions (*i.e.* pH = 2–3) it remains unionised but under basic conditions (pH = 8) that exists in small intestine it is ionised.
20. (a): Higher the electronegativity of central atom higher will be the acidic strength.
 In case of same atom higher the value of oxidation state of the central atom, higher will be its acidic strength.
 The electronegativity of Cl $>$ S
 In $\text{ClO}_3(\text{OH})$ (O.N of Cl is +7) and in $\text{ClO}_2(\text{OH})$ (O.N. of Cl is +5). Thus, $\text{ClO}_3(\text{OH})$ is strongest acid.
21. (d): $\text{Be}(\text{OH})_2$ is least soluble and so its K_{sp} is least.
22. (a): Since FeCl_3 is not hydrolysed.
23. (d): HCl is stronger acid than CH_3COOH .
 Cl^- is stronger base than $\text{CH}_3\text{COOH}_2^+$

$$\begin{array}{c} \text{HCl} + \text{CH}_3\text{COOH} \rightleftharpoons \text{Cl}^- + \text{CH}_3\text{COOH}_2^+ \\ \text{Acid} \quad \quad \quad \text{Conjugate base} \\ \text{Conjugate acid} \quad \quad \quad \text{Base} \end{array}$$
24. (d): From the given data
 (a) will be neutral pH = 7
 (b) will produce acidic solution pH $<$ 7
 (c) will produce basic solution pH $>$ 7
 (d) will produce acidic solution pH $<$ 7
 making calculation of pH in case of (b) and (d) we find that in (d), the remaining solution contains 50 ml of $\frac{M}{5}\text{HCl}$.
 or 100 ml of $\frac{M}{10}\text{HCl}$ (Total solution = 100 ml)
 $\therefore \text{pH} = -\log [\text{H}^+] = -\log \left(\frac{1}{10}\right) = 1$
25. (a): For water $[\text{H}^+] = [\text{OH}^-]$
 $\text{H}_2\text{O} \rightleftharpoons [\text{OH}^-] + [\text{H}^+]$
 $(1 - \alpha)C \quad \quad \alpha \cdot C \quad \quad \alpha \cdot C$
 $\alpha = 1.9 \times 10^{-9}$; density of water = 1 g/cc
 $\therefore C = \frac{1}{18} \times 1000 = 55.56 \text{ moles / L}$

$$[\text{OH}^-] = [\text{H}^+] = 55.56 \times 1.9 \times 10^{-9} = 1.055 \times 10^{-7}$$

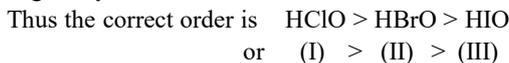
$$\text{Hence } K_w = [\text{H}^+][\text{OH}^-] = (1.055 \times 10^{-7})^2 = 1.1 \times 10^{-14}$$

26. (c): AlCl_3 gets hydrolysed to form an acidic solution



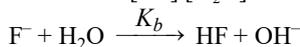
$$[\text{H}^+] > [\text{OH}^-], \text{ so acidic.}$$

27. (a): The strength increases with increase in electro negativity of central metal atom.



28. (c): $\text{HF} + \text{H}_2\text{O} \xrightarrow{K_a} \text{H}_3\text{O}^+ + \text{F}^-$

$$\text{or } K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}][\text{H}_2\text{O}]}$$



$$\text{or } K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-][\text{H}_2\text{O}]}$$

$$\therefore K_a \times K_b = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 10^{-14}$$

$$\text{Given } \text{p}K_b = 10.83, \therefore K_b = 1.48 \times 10^{-11} (\text{p}K_b = -\log K_b)$$

$$\therefore K_a = \frac{10^{-14}}{1.48 \times 10^{-11}} = 6.75 \times 10^{-4}$$

29. (d): $A_2X_3 \rightleftharpoons 2A^{3+} + 3X^{2-}$

$$K_{sp} = [A^{3+}]^2 [X^{2-}]^3 = (2y)^2 (3y)^3 = 108y^5$$

30. (b): Aqueous solution of NaCl is neutral, $\text{pH} = 7$. Aqueous solution of NH_4Cl is slightly acidic because HCl is a strong acid and NH_4OH is a weak base so its pH is slightly acidic *i.e.* slightly less than 7.

Aqueous solution of NaCN is slightly basic because NaOH is strong base and HCN is a weak acid *i.e.* its pH is slightly more than 7.

The aqueous solution of HCl is highly acidic. The pH is 1 or 2.

Thus increasing order of pH is $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$

31. (a): The reaction will be exothermic because of the formation of three $x-y$ bonds from the gaseous atoms. In this case Δn is also negative so the reaction will be affected both by temperature and pressure.

Catalyst has no effect on equilibrium concentrations of various species.

32. (d): $K_p = K_c \cdot RT^{\Delta n}$

$$\text{or } K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$$

33. (d): In the initial stages of reaction, there is an increase in the concentration of each one of the products and therefore Q will increase.

34. (a): Higher is the oxidation state of Cl , higher is the acidity.

35. (a): $A_p B_{q(s)} \rightleftharpoons pA^{+q} + qB^{-p}$

$$L_s = (p \cdot S)^p \cdot (q \cdot S)^q$$

$$= p^p \cdot S^p \cdot q^q \cdot S^q \text{ or } p^p \cdot q^q \cdot S^{(p+q)}$$

36. (d): When pressure is changed, x changes in such a way so that there is no change in K_p because temperature remains constant so K_p remains unchanged.

37. (d): $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$; $K_p = K_c$ ($\therefore \Delta n = 1$)
Because temperature is constant so there is no change in K_p or K_c .

Since volume is halved so the pressure gets doubled and thus α will decrease to keep K_c or K_p constant.



$$\text{Initial } a \quad 0$$

$$\text{Equi. } (a-x) \quad 2x$$

Let the total pressure = P

$$\text{then } P_{\text{NO}_2} = \frac{2x}{(a+x)} \times P \text{ and } P_{\text{N}_2\text{O}_4} = \frac{(a-x)}{(a+x)} \times P$$

$$\text{Hence } K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{4x^2 P^2}{(a+x)^2} \times \frac{(a+x)}{P(a-x)} = \frac{4x^2 P}{(a^2 - x^2)}$$

Since K_p is constant, so $x \propto \frac{1}{\sqrt{P}}$

So when volume is halved, pressure gets doubled.

Hence α will decrease.

38. (b): $h = \sqrt{\frac{K_w}{K_a \times C}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 0.1}} = 10^{-4}$

$$\text{Hence \% age hydrolysis} = 10^{-4} \times 100 = 0.01$$

39. (c): $\text{NaSO}_4 \rightleftharpoons 2\text{Na}^+ + \text{SO}_4^{2-}$ Total
(0.004 - x) 2x x 0.004 - x + 2x + x
= (0.004 + 2x)

Since both solutions are isotonic, so $0.004 + 2x = 0.01$ or $x = 3 \times 10^{-3}$

$$\% \text{ dissociation} = \frac{3 \times 10^{-3}}{0.004} \times 100 = 75\%$$

40. (b): $\text{CH}_3\text{NH}_2 + \text{HCl} \longrightarrow \text{CH}_3\text{NH}_3^+\text{Cl}^-$

$$\text{Initial } 0.1 \quad 0.08 \quad 0$$

$$\text{Equi. } 0.02 \quad 0 \quad 0.08$$

Since it is a basic buffer, so

$$\text{pOH} = \text{p}K_b + \log \frac{0.08}{0.02} = -\log 5 \times 10^{-4} + \log 4$$

$$= 3.30 + 0.602 = 3.902$$

$$\text{pH} = 14 - \text{pOH} = 14 - 3.902 = 10.09$$

$$[\text{H}^+] = 7.99 \times 10^{-11} \text{ M} = 8 \times 10^{-11} \text{ M}$$

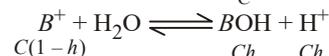
41. (b): As the reaction takes place in two steps

$$k = k_1 \times k_2 = 6.8 \times 10^{-3} \times 1.6 \times 10^{-3} = 10.8 \times 10^{-6}$$

$$= 1.08 \times 10^{-5}$$

42. (b): At equilibrium, at a particular temperature the concentrations of reactants and products will be same (not equal) whether the reaction is carried out in presence or absence of catalyst. A catalyst simply helps to attain the equilibrium quickly by lowering the activation energy. At equilibrium, $\Delta G = 0$ thus, $\Delta G_{\text{N}_2} + 3G_{\text{H}_2} = 2G_{\text{NH}_3}$

43. (c): $\text{BOH} + \text{HCl} \longrightarrow \text{BCl} + \text{H}_2\text{O}$



$$C(1-h) \quad Ch \quad Ch$$

For titration, $N_{\text{acid}} \times V_{\text{acid}} = N_{\text{base}} \times V_{\text{base}}$.

$$\frac{2}{15} \times V = 2.5 \times \frac{2}{5}$$

Equilibrium

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$\therefore V = \text{volume of HCl used} = 7.5 \text{ mL}$

In resulting solution, concentration of salt

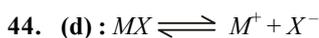
$$[BCl] = \frac{2/5 \times 2.5}{10} = \frac{2}{20} = 0.1$$

$$\therefore \frac{Ch^2}{1-h} = \frac{K_w}{K_b} \quad \text{or} \quad h = \sqrt{\frac{K_w}{K_b \times C}} = \sqrt{\frac{10^{-14}}{10^{-12} \times 0.1}}$$

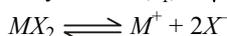
$$\Rightarrow h = \sqrt{\frac{1}{10}}$$

$$\text{Now, } [H^+] = Ch = 0.1 \times \sqrt{\frac{1}{10}} = 0.1 \times 0.316 = 3.16 \times 10^{-2} \text{ M}$$

$$[H^+] \approx 3.2 \times 10^{-2} \text{ M}$$

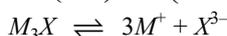


$$\text{Solubility of } MX(x_1) = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$$



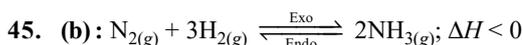
$$\text{Solubility of } MX_2(x_2) = 4x_2^3 = K_{sp}$$

$$\therefore x_2 = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{3.2 \times 10^{-14}}{4}\right)^{1/3} = 2 \times 10^{-5}$$



$$\text{Solubility of } M_3X(x_3) = 27x_3^4 = 2.7 \times 10^{-15} = x_3 = 10^{-4}$$

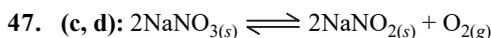
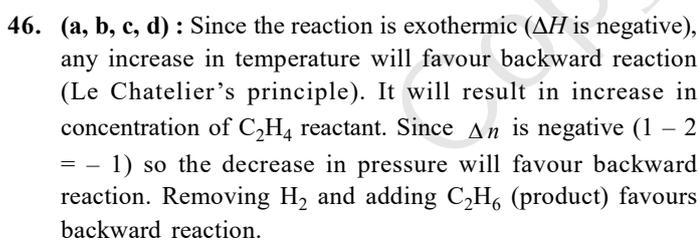
$$\therefore x_1 > x_3 > x_2 \quad \Rightarrow MX > M_3X > MX_2$$



Initially, with increase in temperature ($T_2 > T_1$)

% yield increases.

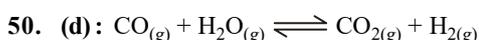
Afterwards, equilibrium is reached and if the temperature is increased, *i.e.*, heat is supplied to the system, then according to Le Chatelier's principle, the equilibrium will shift in the backward direction, where the heat is absorbed. Hence, the % yield decreases.



In this case Δn is positive ($1 - 0 = 1$) so increase in pressure favours backward reaction. Since heat is added so the reaction is endothermic so increase in temperature will favour the forward reaction.

48. (a) : There is no change in concentrations at constant volume.

49. (b, c, d) : If we introduce an inert gas at constant pressure then the equilibrium is shifted in the direction in which the number of moles increases. In this case the forward reaction is accelerated by increase in quantity of PCl_5 (a reactant) and also by increase of space (*i.e.* volume of container).



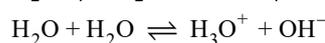
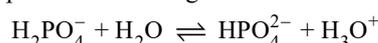
$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

Catalyst has no effect on point of equilibrium. Addition of inert gas has no effect on equilibrium because $\Delta n = 0$ ($2 - 2 = 0$)

Since $\Delta n = 0$ so the equilibrium is not affected by change in volume.

If the amount of $CO_{(g)}$ is increased, K_c will decrease, but since temperature is constant and so the value of K_c remains unchanged. To maintain constancy of K_c the amount of CO_2 will increase if we increase the amount of CO .

51. (b, c) : pH of $1 \times 10^{-8} \text{ M HCl}$ will be less than 7 because acidic pH lies in the range 0-7.



The value of ionic product of water (K_w) increases with increase in temperature. For half-neutralisation of a weak acid

$$\text{by a strong base, } pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Since $[\text{salt}] = [\text{acid}]$, $\therefore pH = pK_a$

52. (a, c) : A buffer solution can be prepared by mixing a weak acid with salt of its conjugate base (acidic buffer) or a weak base with salt of its conjugate acid (basic buffer).

53. (d) : Buffer solution is one, where pH is not altered to any great extent by the addition of small quantities of either an acid or a base. Buffer solutions can be obtained by mixing :

- a weak acid with its salt with a strong base
- a weak base with its salt with a strong acid.

Thus, option (d) CH_3COOH and CH_3COONa is the only buffer solution among the given options.

54. (a) : Rate with respect to weak acid

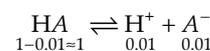
$$R_1 = k[H^+]_{\text{weak acid}}$$

and rate with respect to strong acid

$$R_2 = k[H^+]_{\text{strong acid}}$$

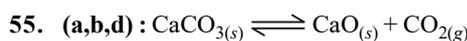
$$\therefore \frac{R_1}{R_2} = \frac{k[H^+]_{\text{weak acid}}}{k[H^+]_{\text{strong acid}}} = \frac{1}{100}$$

$$\therefore [H^+]_{\text{weak acid}} = \frac{1}{100} = 0.01 \text{ M}$$

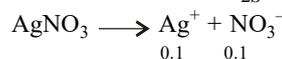
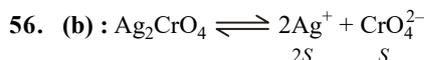


$$1-0.01=1 \quad 0.01 \quad 0.01$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{0.01 \times 0.01}{1} = 1 \times 10^{-4}$$



The equilibrium constant (K) is independent of the initial amount of $CaCO_3$ whereas at a given temperature, it is independent of pressure of CO_2 . ΔH is independent of catalyst and it depends on temperature.



$$[CrO_4^{2-}] = S, [Ag^+] = [2S + 0.1] \approx 0.1 \text{ M}$$

$$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$$

$$[\text{CrO}_4^{2-}] = \frac{K_{sp}}{[\text{Ag}^+]^2} = \frac{1.1 \times 10^{-12}}{(0.1)^2} = 1.1 \times 10^{-10} \text{ mol L}^{-1}$$

$$S = 1.1 \times 10^{-10} \text{ mol L}^{-1}$$

57. SO_4^{2-}

58. Amphoteric

59. $K_p = K_c(RT)^{\Delta n}$; [Δn = number of moles of gaseous products – number of moles of gaseous reactants]60. No change; [K_p is constant at any constant temperature]

61. More; [Conjugate base of a weaker acid is stronger]

62. Less; [$K_p = K_c(RT)^{\Delta n}$; Here $\Delta n = (1 - 2) = -1$]63. I_2 64. **False** : AlCl_3 is a Lewis acid but the Lewis acid character is due to its tendency to accept electrons.65. **False** : K' for backward reaction *i.e.* $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$ is

$$K' = \frac{[A_2]^{1/2}[B_2]^{1/2}}{[AB]}$$

$$\text{or } (K')^2 = \frac{[A_2][B_2]}{[AB]^2} = \frac{1}{K} \text{ or } K' = \sqrt{\frac{1}{K}}$$

66. **True** : Lower the pressure, lower is the boiling point. The cooling occurs due to evaporation.67. **False** : In case of sodium hydroxide solubility decreases with increase in temperature.68. Let the number of moles of sodium propionate = x

$$\text{Then pH} = \text{p}K_a + \frac{[\text{Salt}]}{[\text{Acid}]} = -\log(1.34 \times 10^{-5}) + \log\left[\frac{x}{0.02}\right]$$

$$\text{or } 4.75 = -\log(1.34 \times 10^{-5}) + \log\left[\frac{x}{0.02}\right]$$

$$\text{or } 4.75 = 4.8729 + \log\left[\frac{x}{0.02}\right]$$

$$\text{or } \log\left[\frac{x}{0.02}\right] = 4.75 - 4.8729 = -0.1229$$

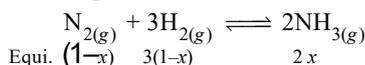
$$\text{or } x = 1.5 \times 10^{-2} \text{ moles}$$

∴ Amount of sodium propionate = 1.5×10^{-2} moles

When 0.01 moles of HCl is added, 0.03 moles (0.01 + 0.02) propionic acid and 0.005 moles (0.015 – 0.010) of sodium propionate are formed.

$$\therefore \text{pH} = -\log(1.34 \times 10^{-5}) + \log\frac{0.005}{0.03}$$

$$= 4.87 - 0.78 = 4.09$$

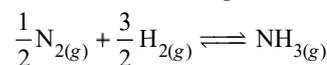
For HCl in water, $\text{pH} = -\log 10^{-2} = 2$ 69. Let x represents the reacted concentration in molesEqui. $(1-x)$ $3(1-x)$ $2x$

$$\therefore K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3-3x}{V}\right)^3}$$

$$= \frac{4x^2V^2}{(1-x)^4 \times 27} = \frac{4 \times (0.0025)^2 \times 16}{27}$$

$$= 1.48 \times 10^{-5} \text{ litre}^2 \text{ mol}^{-2} \quad [(1-x) \approx 1]$$

Again, for the second equation



$$K'_C = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} = \sqrt{K_C}$$

$$= \sqrt{1.48 \times 10^{-5}} = 3.82 \times 10^{-3} \text{ litre mol}^{-1}$$

70. The pH of solution is given by

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

It is given that 20 ml of 0.2 M sodium hydroxide is added to 50 ml of 0.2 M acetic acid to give 70 ml of solution.

$$[\text{Acid}] = \frac{30 \times 0.2}{70}$$

$$[\text{Salt}] = \frac{20 \times 0.2}{70}$$

$$\text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\therefore \text{pH} = 4.74 + \log\left[\frac{20 \times 0.2}{70} \times \frac{70}{30 \times 0.2}\right]$$

$$= 4.74 - 0.18 = 4.56$$

Additional volume of 0.2 M NaOH required to make pH of solution 4.74

$$\text{pH} = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } 4.74 = -\log 1.8 \times 10^{-5} + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } 4.74 = 4.7447 + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } \log\left(\frac{[\text{Salt}]}{[\text{Acid}]}\right) = -0.0047 \text{ or } \frac{[\text{Salt}]}{[\text{Acid}]} = 0.99$$

Let the volume of 0.2 M NaOH added such that the pH of solution is 4.74 be x ml, then it will further neutralize x ml of 0.2 M acetic acid to produce x ml of 0.2 M sodium acetate and so the resulting solution will contain(30 – x) ml of 0.2 M acetic acid(20 + x) ml of 0.2 M sodium acetate∴ Number of moles of acetic acid in (70 + x) ml solution

$$= \frac{0.2}{1000} \times (30 - x) = 2 \times 10^{-4} \times (30 - x)$$

Number of moles of CH_3COONa in (70 + x) ml of solution

$$= \frac{0.2}{1000} \times (20 + x) = 2 \times 10^{-4} (20 + x)$$

$$\therefore \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{2 \times 10^{-4} \times (20 + x)}{2 \times 10^{-4} (30 - x)} = \frac{20 + x}{30 - x}$$

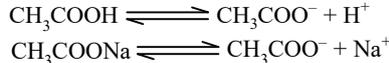
$$\text{or } 0.99 = \frac{20 + x}{30 - x} \text{ or } x = 4.87$$

Hence additional volume of 0.2 M NaOH required to make the pH of solution 4.74 is 4.87 ml.

Equilibrium

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71. (i) Aqueous solution of CH_3COONa is basic because on hydrolysis it gives a weak acid (CH_3COOH) and a strong base (NaOH)



- (ii) Acetate ions generated from sodium acetate, suppress the ionisation of acetic acid due to common ion effect. Hence its acidity decreases.
- (iii) Due to completely filled outermost shell, Na^+ cannot accept lone pair of electrons, whereas due to incompletely filled outermost shell Ag^+ can accept lone pair of electrons. Hence Ag^+ is a stronger Lewis acid than Na^+ .
- (iv) The product of concentration of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water (K_w). The value of K_w changes with temperature *i.e.* the concentration of H^+ (hence pH) and OH^- ions (hence pOH) also changes with temperature.

$$72. \alpha = \sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{\left(\frac{4.9 \times 10^{-8}}{1/10}\right)} \quad \left(\because C = 1/10 \text{ N or M}\right)$$

$$= 7 \times 10^{-4} = 0.07\%$$

$$[\text{H}^+] = C \cdot \alpha = \frac{1}{10} \times 7 \times 10^{-4} = 7 \times 10^{-5} \text{ mol litre}^{-1}$$

$$\therefore \text{pH} = 4.15$$

$$\therefore [\text{OH}^-][\text{H}^+] = 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{10^{-14}}{7 \times 10^{-5}} = 1.43 \times 10^{-10} \text{ mol litre}^{-1}$$

73. Given: K_{sp} for $\text{AgI} = 8.5 \times 10^{-17}$

$$K_{sp} \text{ for } \text{Hg}_2\text{I}_2 = 2.5 \times 10^{-26}$$

Since the mixture contains Ag^+ (0.1M) and H_2^{2+} (0.1 M), therefore $[\text{I}^-]$ required for fully precipitating as AgI

$$= \frac{8.5 \times 10^{-17}}{0.1} = 8.5 \times 10^{-16} \text{ M}$$

Again the $[\text{I}^-]$ required to completely precipitate Hg_2I_2

$$= \sqrt{\frac{2.5 \times 10^{-26}}{0.1}} = 5 \times 10^{-13} \text{ M}$$

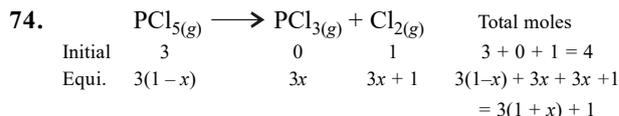
Since $[\text{I}^-]$ needed to precipitate AgI is smaller than that needed to precipitate Hg_2I_2 so first of all AgI will start to get precipitated and larger precipitation of AgI can be obtained if more of I^- is added, but along with AgI , Hg_2I_2 will also be precipitated from the mixture only when the molar concentration of iodide ion, $[\text{I}^-]$ approaches $5.0 \times 10^{-13} \text{ M}$. The molar concentration of $[\text{Ag}^+]$, left when Hg_2I_2 begins to precipitate, is given as

$$\frac{8.5 \times 10^{-17}}{5.0 \times 10^{-13}} = 1.7 \times 10^{-4} \text{ M}$$

Thus % age of $[\text{Ag}^+]$ left unprecipitated

$$= \frac{1.7 \times 10^{-4}}{0.1} \times 100 = 0.17\%$$

Hence % age of Ag^+ precipitated = $(100 - 0.17)\% = 99.83\%$



Where x is the degree of dissociation of PCl_5

$$\therefore \text{Total number of moles at equilibrium} = 3(1+x) + 1 \dots(i)$$

$$PV = nRT \quad (\text{For } n \text{ moles})$$

$$\therefore n = \frac{PV}{RT} = \frac{2.05 \times 100}{0.082 \times 500} = 5 \dots(ii)$$

Comparing (i) and (ii)

$$3(1+x) + 1 = 5$$

$$\text{or } 3x = 4 - 3$$

$$\text{or } x = \frac{1}{3} \text{ or } 0.333$$

Thus % age of dissociation of PCl_5 is 33.3%

Now

$$K_p = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\left[\frac{3xp}{3(1+x)+1}\right] \left[\frac{(3x+1)p}{3(1+x)+1}\right]}{\left[\frac{3(1-x)p}{3(1+x)+1}\right]}$$

$$= \frac{3xp^2(3x+1)}{(3+3x+1)^2} \times \frac{(3+3x+1)}{3p(1-x)} = \frac{xp(3x+1)}{(3+3x+1)(1-x)}$$

$$= \frac{x(3x+1)p}{(4+3x)(1-x)}$$

Substituting $x = 1/3$ and $p = 2.05 \text{ atm}$, we get

$$K_p = \frac{\frac{1}{3} \left(3 \times \frac{1}{3} + 1\right) \times 2.05}{\left(4 + 3 \times \frac{1}{3}\right) \times \left(1 - \frac{1}{3}\right)}$$

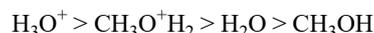
$$= \frac{\frac{1}{3} \times 2 \times 2.05}{5 \times \frac{2}{3}} = \frac{2 \times 2.05}{10} = \frac{4.1}{10} = 0.41$$

75. (i) Among oxyacids of the same element there is an increase in acidic nature with increase in oxidation number of the element. Thus we have



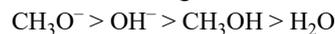
$$\text{O. No. of Cl} \quad +1 \quad +3 \quad +5 \quad +7$$

- (ii) The conjugate acids of weaker bases are stronger. Thus we have



(decreasing acidic order of conjugate bases).

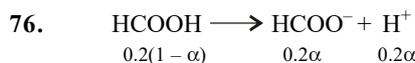
Hence increasing order of basicity is



- (iii) $\text{BaO} > \text{B}_2\text{O}_3 > \text{CO}_2 > \text{SO}_3 > \text{Cl}_2\text{O}_7$

Basicity increases with increase in oxidation number.

Here Ba (+2), B (+3), C (+4), S (+6), Cl (+7)



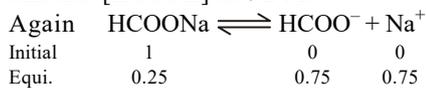
$$0.2(1-\alpha) \quad 0.2\alpha \quad 0.2\alpha$$

$$\therefore [\text{H}^+] = 0.2\alpha$$

$$\text{or } \alpha = \frac{[\text{H}^+]}{0.2} = \frac{6.4 \times 10^{-3}}{0.2} \text{ or } 3.2 \times 10^{-2}$$

So we find that α (degree of dissociation) of HCOOH is very low, on addition of sodium formate the dissociation of HCOOH (weak electrolyte) will be suppressed due to common ion effect.

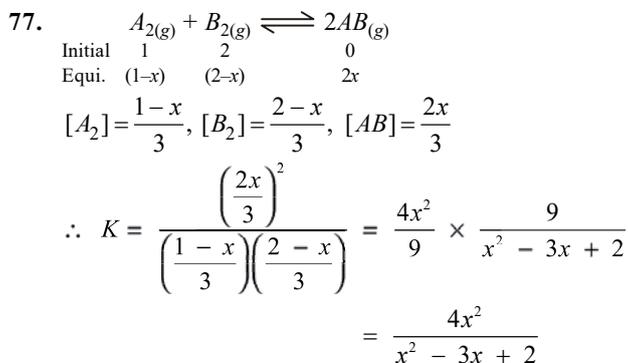
Since degree of dissociation is very low which has been further suppressed and so we can now neglect it and can take the [HCOOH] as 0.2 M.



$$\therefore [\text{HCOO}^-] = 0.75$$

It is an acidic buffer containing formic acid (HCOOH) and its salt (HCOONa) so its pH is given by

$$\begin{aligned} \text{pH} &= -\text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} \\ &= -\log (2.4 \times 10^{-4}) + \log \frac{0.75}{0.20} = 4.19 \end{aligned}$$



But K is 50, so $\frac{4x^2}{x^2 - 3x + 2} = 50$

or $4x^2 = 50x^2 - 150x + 100$

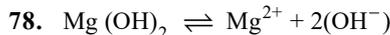
or $46x^2 - 150x + 100 = 0$

or $23x^2 - 75x + 50 = 0$

or $x = \frac{75 \pm \sqrt{75 \times 75 - 4 \times 23 \times 50}}{2 \times 23} = 0.93 \text{ and } 2.326$

The value 2.326 is not valid since $x < 2$.

Mole of $\text{AB} = 2x = 2 \times 0.93 = 1.86$



If S is the solubility then

$$K_{sp} = S \times (2S)^2 = 4S^3$$

Here S is given as 9.57×10^{-3} g/litre

$$\text{or } S = \frac{9.57 \times 10^{-3}}{58} \text{ moles/litre} = 1.65 \times 10^{-4} \text{ moles/litre}$$

$$\therefore K_{sp} = 4 \times (1.65 \times 10^{-4})^3 = 1.8 \times 10^{-11}$$

Calculation of solubility of $\text{Mg}(\text{OH})_2$ in $\text{Mg}(\text{NO}_3)_2$

Let the solubility of $\text{Mg}(\text{OH})_2$ be x , then

$$[\text{Mg}^{2+}] = x + 0.02$$

$$[\text{OH}^-] = 2x$$

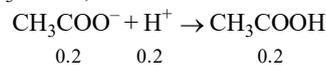
Hence $K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$

or $1.8 \times 10^{-11} = (x + 0.02)(2x)^2$

or $\frac{1.8 \times 10^{-11}}{0.02} = 4x^2$ [neglecting x in comparison to 0.02]

or $x = 1.5 \times 10^{-5}$ moles/litre = $1.5 \times 10^{-5} \times 58$ g/litre = 8.7×10^{-4} g/litre

79. (i) Amount of HCl added = 0.20 mole
Added H^+ ions will combine with acetate (CH_3COO^-) ions to yield acetic acid (CH_3COOH) and it will result in the decrease of concentration of acetate ions (CH_3COO^-) and an increase in the concentration of acetic acid (CH_3COOH).

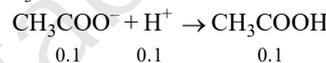


The $[\text{CH}_3\text{COO}^-]$ after addition of 0.2 moles of HCl
= $1.0 - 0.2 = 0.8$ mole

$[\text{CH}_3\text{COOH}]$ after addition of 0.2 moles of HCl
= $1.0 + 0.2 = 1.2$ moles

$$\begin{aligned} \therefore \text{pH} &= -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad [\text{it is acidic buffer}] \\ &= -\log 1.8 \times 10^{-5} + \log \frac{0.8}{1.2} \quad \text{or } \text{pH} = 4.5686 \end{aligned}$$

- (ii) Amount of HCl added = 0.20 mole. Out of this 0.1 mole will combine with 0.1 mole of CH_3COO^- to form 0.1 mole of CH_3COOH



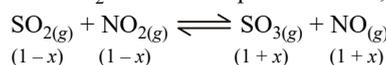
Now total concentration of $\text{CH}_3\text{COOH} = 0.1 + 0.1$
= 0.2 moles

In presence of H^+ ions, the CH_3COOH will remain almost unionised. Therefore pH of the solution will be due to presence of H^+ ions of HCl *i.e.*

$$0.2 - 0.1 = 0.1 \text{ mole of HCl}$$

$$\text{pH} = -\log (\text{H}^+) = -\log (0.1) = 1$$

80. Initial concentration of each gas = 1 mole. Let the number of moles of NO_2 reacted at equilibrium = x , then



$$\therefore K_C = \frac{(1+x)(1+x)}{(1-x)(1-x)} = 16 \text{ (given)}$$

$$\therefore \frac{(1+x)^2}{(1-x)^2} = 4^2 \quad \text{or} \quad \frac{1+x}{1-x} = 4$$

or $x = 0.6$

Thus the concentration of NO at equilibrium = $1 + x$

$$= (1 + 0.6) \text{ moles} = 1.6 \text{ moles}$$

and the concentration of NO_2 at equilibrium = $1 - x$

$$= (1 - 0.6) \text{ moles} = 0.4 \text{ moles}$$

81. (i) $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ Total number of moles
Equi. $(1-\alpha)$ 2α $1-\alpha+2\alpha=1+\alpha$

$$\begin{aligned} \therefore K_p &= \frac{\left[\left(\frac{2\alpha}{1+\alpha}\right)P\right]^2}{\left[\left(\frac{1-\alpha}{1+\alpha}\right)P\right]} \quad [P = \text{Total pressure}] \\ &= \frac{\left[\frac{2 \times 0.25 \times 1}{1+0.25}\right]^2}{\left[\frac{1-0.25}{1+0.25} \times 1\right]} = 0.266 \text{ atm} \end{aligned}$$

Equilibrium

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$$(ii) K_p = \frac{4\alpha^2 P^2(1+\alpha)}{(1+\alpha)^2(1-\alpha) \times P} = \frac{4\alpha^2 P}{(1+\alpha)(1-\alpha)}$$

$$\text{or } 0.266 = \frac{4\alpha^2 P}{1-\alpha^2} \text{ or } \alpha = 0.63$$

Hence % age dissociation = 63%

$$82. \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

If we add x moles of HCl and it will combine with NaCN to form x moles of HCN (a weak acid)



At Equi. $0.01 - x$ x x x

Since it is an acidic buffer, so

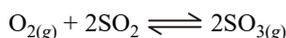
$$\therefore \text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } 8.5 = 10 - \log(4.1) + \log \left(\frac{0.01 - x}{x} \right)$$

$$\text{or } \frac{0.01 - x}{x} = 0.1296 \quad (\text{Taking antilog})$$

$$\text{or } x = 8.85 \times 10^{-3} \text{ M}$$

83. Since the reaction is being carried out at constant volume so the change in partial pressure of a species will be directly proportional to the change in amount of the species.



Initial P: 2 atm 0 1 atm

Equi P: (2 atm + x) 2 x (1 atm - 2 x)

Where 2 x is the change in partial pressure of SO_2 at equilibrium.

$$\therefore K_p = \frac{(P_{\text{SO}_3})^2}{(P_{\text{O}_2})(P_{\text{SO}_2})^2} \text{ or } 900 \text{ atm}^{-1} = \frac{(1 - 2x)^2}{(2x)^2 (2 + x)}$$

If we assume x to be very small in comparison to 1, we have

$$900 = \frac{1}{4x^2 \times 2} \quad [\text{neglecting } x \text{ terms}]$$

$$\text{or } 4x^2 = \frac{1}{2} \times \frac{1}{900}$$

$$\text{or } x^2 = \frac{1}{2} \times \frac{1}{900} \times \frac{1}{4} \text{ or } x = 0.0118 \text{ atm}$$

Thus $P_{\text{SO}_2} = 2x = 2 \times 0.0118 = 0.0236 \text{ atm}$

$$P_{\text{O}_2} = (2 + x) = 2 + 0.0118 = 2.0118 \text{ atm}$$

$$P_{\text{SO}_3} = (1 - 2x) = 1 - 0.0236 = 0.976 \text{ atm}$$

$$84. \text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]} = -\log 1.8 \times 10^{-5} + \log \frac{0.25}{0.05}$$

$$\text{or pOH} = 5 - \log 1.8 + \log 5 = 5.6989 - 0.2552 = 5.4437$$

$$\therefore -\log [\text{OH}^-] = 5.4437$$

$$\text{or } \log [\text{OH}^-] = -5.4437$$

$$\text{or } [\text{OH}^-] = 3.5999 \times 10^{-6} \quad (\text{Taking antilog})$$

$$K_{sp} \text{ for Mg(OH)}_2 = [\text{Mg}^{2+}] [\text{OH}^-]^2$$

$$\therefore 6 \times 10^{-10} = [\text{Mg}^{2+}] [3.5999 \times 10^{-6}]^2$$

$$\text{or } [\text{Mg}^{2+}] = \frac{6 \times 10^{-10}}{12.95928 \times 10^{-12}} = 0.4629 \times 10^2 = 46.29 \text{ mol/L}$$

$$K_{sp} \text{ for Al(OH)}_3 = [\text{Al}^{3+}] [\text{OH}^-]^3$$

$$\text{or } 6 \times 10^{-32} = [\text{Al}^{3+}] [3.5999 \times 10^{-6}]^3$$

$$\text{or } [\text{Al}^{3+}] = \frac{6 \times 10^{-32}}{(3.5999 \times 10^{-6})^3} = 1.286 \times 10^{-15} \text{ mol/L}$$

85. Suppose the total number of moles of all gases at equilibrium is n .

Then using the gas equation, $PV = nRT$ (For n moles)

$$n = \frac{PV}{RT} = \frac{4.92 \times 5}{0.0821 \times 600} \text{ or } 0.5 \text{ moles}$$

At equilibrium the number of moles of various gases are:

Number of moles of $\text{CH}_3\text{OH} = 0.1$ (given)

Number of moles of $\text{CO} = 0.1$

$$\text{Hence number of moles of } \text{H}_2 = 0.5 - (0.1 + 0.1) \\ = 0.5 - 0.2 = 0.3 \text{ moles}$$

Molar concentration of $\text{CH}_3\text{OH} =$ Molar concentration of CO

$$= \frac{0.1}{5} \text{ or } 0.02$$

$$\text{Molar concentration of } \text{H}_2 = \frac{0.3}{5} \text{ or } 0.06$$

$$\therefore K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}] [\text{H}_2]^2} = \frac{0.02}{0.02 \times (0.06)^2} = 277.78 \text{ mol}^{-2} \text{ L}^2$$

$$\text{Since } K_p = K_c \times (RT)^{\Delta n}$$

$$\text{or } K_p = 277.78 \times (0.082 \times 600)^{-2} = 0.115 \text{ atm}^{-2}$$

86. **Case I.** $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

Initial C 0 0
Equi. $C(1 - \alpha)$ $C\alpha$ $C\alpha$

$$\therefore [\text{H}^+] = C\alpha = C \times \sqrt{\frac{K_a}{C}} = \sqrt{K_a C}$$

$$\text{or } [\text{H}^+] = \sqrt{1.8 \times 10^{-5} \times 1} = 4.24 \times 10^{-3} \text{ M}$$

$$\text{Hence } \text{pH} = -\log \text{H}^+ = -\log 4.24 \times 10^{-3} = 2.3724$$

Case II. pH after dilution = $2 \times 2.3724 = 4.7448$

If concentration after dilution is C_1

and degree of dissociation is α_1

$$\text{Then } \text{pH} = -\log [\text{H}^+] \text{ or } 4.7448 = -\log [\text{H}^+]$$

$$\text{or } [\text{H}^+] = 1.8 \times 10^{-5} = C_1 \times \alpha_1$$

The dissociation constant K_a is given by

$$K_a = \frac{[\text{CH}_3\text{COO}^-] [\text{H}^+]}{[\text{CH}_3\text{COOH}]} \\ = \frac{(C_1 \times \alpha_1) (C_1 \times \alpha_1)}{C_1(1 - \alpha_1)} = \frac{C_1 \alpha_1^2}{(1 - \alpha_1)}$$

$$\text{or } 1.8 \times 10^{-5} = \frac{1.8 \times 10^{-5} \times \alpha_1}{1 - \alpha_1}$$

$$\left[\because C_1 \times \alpha_1 = 1.8 \times 10^{-5} \right]$$

$$\text{or } 1 - \alpha_1 = \alpha_1 \text{ or } \alpha_1 = 0.5$$

Since $[\text{H}^+] = C_1 \times \alpha_1$, we get $1.8 \times 10^{-5} = C_1 \times 0.5$

$$\text{or } C_1 = \frac{1.8 \times 10^{-5}}{0.5} \text{ or } 3.6 \times 10^{-5} \text{ M}$$

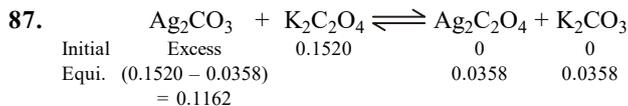
Since number of moles of CH_3COOH before and after dilution will be same,

\therefore Moles of CH_3COOH before dilution =

Number of moles of CH_3COOH after dilution

$$\text{or } 1 \times 1 = 3.6 \times 10^{-5} \times V \quad [\because \text{Mole} = M \times V \text{ in litres}]$$

$$\text{or } V = 2.78 \times 10^4 \text{ L}$$



$$\text{At equilibrium, } [\text{C}_2\text{O}_4]^{2-} = \frac{0.1162}{0.5} = 0.2324 \text{ mol L}^{-1}$$

$$[\text{K}_2\text{CO}_3]_{\text{eq}} = [\text{CO}_3^{2-}]_{\text{eq}} = \frac{0.0358}{0.5} = 0.0716 \text{ mol L}^{-1}$$

Since K_{sp} for $\text{Ag}_2\text{C}_2\text{O}_4 = 1.29 \times 10^{-11} \text{ mol}^3 \text{ L}^{-3}$ at 25°C (given)

$$\therefore [\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}] = 1.29 \times 10^{-11}$$

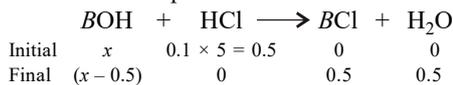
$$\text{or } [\text{Ag}^+]^2 \times 0.2324 = 1.29 \times 10^{-11}$$

$$\text{or } [\text{Ag}^+]^2 = \frac{1.29 \times 10^{-11}}{0.2324}$$

$$\text{Hence } K_{sp} \text{ for } \text{Ag}_2\text{CO}_3 = [\text{Ag}^+]^2 [\text{CO}_3^{2-}]$$

$$= \frac{1.29 \times 10^{-11}}{0.2324} \times 0.0716 = 3.9 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3}$$

88. **Case I.** The equation for concerned reaction is



$$\text{Molar concentration of BOH} = \frac{x - 0.5}{V}$$

$$\text{Molar concentration of BCl} = \frac{0.5}{V}$$

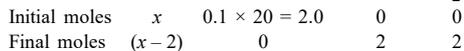
$$\text{Molar concentration of H}_2\text{O} = \frac{0.5}{V}$$

The pOH of this basic buffer is given by

$$\text{pOH} = -\log K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{or } 14 - 10.04 = -\log K_b + \log \frac{0.5}{(x - 0.5)} \quad \dots(i)$$

Case II. $\text{BOH} + \text{HCl} \longrightarrow \text{BCl} + \text{H}_2\text{O}$



$$\text{Molar concentration of BOH} = \frac{x - 2}{V_1}$$

$$\text{Molar concentration of BCl} = \frac{2}{V_1}$$

$$\text{Molar concentration of H}_2\text{O} = \frac{2}{V_1}$$

Since this solution is also a buffer, so

$$\text{p(OH)} = -\log K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$14.0 - 9.14 = -\log K_b + \log \frac{2}{(x - 2)} \quad \dots(ii)$$

From (i) - (ii), we get

$$3.96 - 4.86 = -0.90$$

$$\text{or } -0.90 = \frac{0.25x - 0.5}{x - 0.5}$$

$$\text{or } 0.25x - 0.5 = -0.90x + 0.45$$

$$\text{or } 0.25x + 0.90x = 0.5 + 0.45$$

$$\text{or } 1.15x = 0.95 \quad \text{or } x = \frac{0.95}{1.15} = 0.8$$

Substituting x in (i) we get

$$3.96 = -\log K_b + \log \frac{0.5}{0.8 - 0.5}$$

$$\text{or } \log K_b = -3.96 + \log \frac{5}{3}$$

$$\text{or } \log K_b = -3.96 + \log 5 - \log 3$$

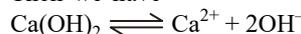
$$\text{or } \log K_b = -3.96 + 0.6990 - 0.4771$$

$$\text{or } \log K_b = -3.7381$$

$$\text{or } K_b = 1.828 \times 10^{-4}$$

89. Let the solubility of Ca(OH)_2 in water be S moles L^{-1}

Then we have



$$K_{sp} = S \times (2S)^2 = 4S^3$$

$$\text{or } S = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}} = \left(\frac{4.42 \times 10^{-5}}{4}\right)^{\frac{1}{3}} = 2.227 \times 10^{-2} \text{ mol L}^{-1}$$

\therefore Amount of Ca(OH)_2 in 500 ml of saturated solution

$$= \frac{2.227 \times 10^{-2}}{2} \times 74 \quad [\text{Molar mass of } \text{Ca(OH)}_2 = 74]$$

$$= 82.39 \times 10^{-2} \text{ g or } 823.9 \text{ mg}$$

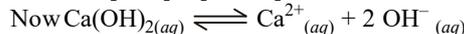
Amount of Ca(OH)_2 in solution after mixing :

As equal volumes of (500 ml) both Ca(OH)_2 and 0.4 M NaOH have been mixed.

$$\therefore \text{Concentration of NaOH in 500 ml of solution} = \frac{0.4}{2} = 0.2 \text{ M}$$

Since NaOH is a strong base

therefore $[\text{OH}^-] = [\text{NaOH}] = 0.2 \text{ M}$



$$K_{sp} = [\text{Ca}^{2+}_{(aq)}] [\text{OH}^-_{(aq)}]^2$$

$$\text{or } [\text{Ca}^{2+}_{(aq)}] = \frac{K_{sp}}{[\text{OH}^-_{(aq)}]^2} = \frac{4.42 \times 10^{-5}}{(0.2)^2} = 1.105 \times 10^{-3}$$

So amount of Ca(OH)_2 in mixture solution

$$= 1.105 \times 10^{-3} \times 74 = 0.0818 \text{ g or } 81.8 \text{ mg}$$

Amount of Ca(OH)_2 precipitated :

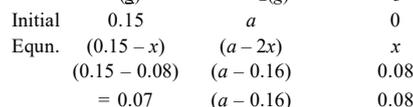
Amount of Ca(OH)_2 initially present = 823.9 mg

Amount of Ca(OH)_2 left in solution = 81.8 mg

$$\therefore \text{Amount of } \text{Ca(OH)}_2 \text{ precipitated} = (823.9 - 81.8) \text{ mg}$$

$$= 742.1 \text{ mg}$$

90. (i) $\text{CO}_{(g)} + 2\text{H}_{2(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$



Total moles at equilibrium = 0.07 + a - 0.16 + 0.08

$$= (a - 0.01)$$

Using gas equation, assuming that total number of moles at equilibrium is n , we get

$$PV = nRT \quad (\text{For } n \text{ moles})$$

$$\text{or } n = \frac{PV}{RT} = \frac{8.5 \times 2.5}{0.082 \times 750} = 0.345$$

Equilibrium

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$$\therefore 0.345 = a - 0.01 \text{ or } a = 0.355$$

$$\therefore \text{Moles of CO at equilibrium} = 0.15 - 0.08 = 0.07$$

$$\text{Moles of H}_2 \text{ at equilibrium} = 0.355 - 0.16 = 0.195$$

$$\text{Moles of CH}_3\text{OH at equilibrium} = 0.08$$

$$\text{Also } K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{\frac{0.08}{2.5}}{\left(\frac{0.07}{2.5}\right)\left(\frac{0.195}{2.5}\right)^2}$$

$$= 188.23 \text{ mol}^{-2} \text{ litre}^2$$

$$\text{Since } K_p = K_c \times (RT)^{\Delta n}$$

$$\therefore K_p = 188.23 \times (0.082 \times 750)^{-2} \quad [\therefore \Delta n = -2]$$

$$= 0.05 \text{ atm}^{-2}$$

Final pressure when there is no reaction

$$\text{Moles of CO} = 0.15$$

$$\text{Moles of H}_2 = 0.355$$

$$\text{Total moles} = 0.15 + 0.355 = 0.505$$

$$\text{Now using } PV = nRT, \text{ we get } P \times 2.5 = 0.505 \times 0.082 \times 750$$

$$\text{or } P = 12.438 \text{ atm}$$

91. Let the volume of NaHCO₃ solution mixed = x ml

Then the number of moles of NaHCO₃ in x ml of 5 M

$$\text{NaHCO}_3 \text{ solution} = \frac{5 \times x}{1000} = 0.005x \text{ mol}$$

Number of moles of H₂CO₃ in 10 ml of 2 M

$$\text{H}_2\text{CO}_3 \text{ solution} = \frac{2 \times 10}{1000} = 0.02 \text{ mol}$$

$$\text{Given, pH of solution} = 7.4 \quad K_a \text{ for H}_2\text{CO}_3 = 7.8 \times 10^{-7}$$

Using the reaction

$$\text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad (\text{For acidic buffer})$$

we get,

$$7.4 = -\log (7.8 \times 10^{-7}) + \log \frac{0.005x}{0.02}$$

$$\text{or } 7.4 = 7 - \log 7.8 + \log \frac{0.005x}{0.02}$$

$$\text{or } 7.4 = 7 - 0.892 + \log (0.25x)$$

$$\text{or } 7.4 = 6.108 + \log (0.25x)$$

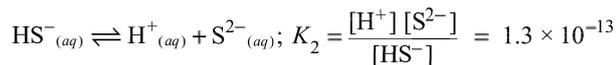
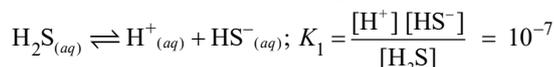
$$\text{or } \log (0.25x) = 7.4 - 6.108 = 1.292$$

$$\text{or } 0.25x = 19.59 \quad \text{or } x = 78.36$$

Thus the volume of 5 M NaHCO₃ solution to be mixed = 78.36 ml

92. **Ionisation constant (K) for H₂S**

In water H₂S ionises in two steps as follows :



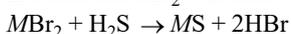
$$\text{The ionisation constant } K \text{ for H}_2\text{S} = K_1 \times K_2$$

$$= 10^{-7} \times 1.3 \times 10^{-13}$$

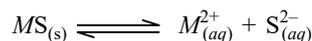
$$= 1.3 \times 10^{-20}$$

S²⁻ ion concentration in solution

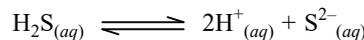
In solution MBr₂ will react with H₂S to form MS.



For metal sulphide MS



$$K_{sp} = [\text{M}^{2+}][\text{S}^{2-}] \Rightarrow [\text{S}^{2-}] = \frac{6 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19} \text{ M}$$

Concentration of H⁺ ion in solution

$$\therefore K = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$\text{or } [\text{H}^+]^2 = \frac{K \times [\text{H}_2\text{S}]}{[\text{S}^{2-}]} = \frac{1.3 \times 10^{-20} \times 0.1}{1.2 \times 10^{-19}}$$

$$= 1.08 \times 10^{-2} \text{ M}$$

$$\text{or } [\text{H}^+] = (1.08 \times 10^{-2})^{1/2} = 1.04 \times 10^{-1} \text{ M}$$

pH of solution

$$\text{pH} = -\log [\text{H}^+] = -\log (1.04 \times 10^{-1})$$

$$= 1 - \log 1.04 = 1 - 0.0170 = 0.983$$

93. $2\text{AB}_2(g) \rightleftharpoons 2\text{AB}(g) + \text{B}_2(g)$

$$\text{Initial} \quad 1 \quad 0 \quad 0$$

$$\text{Equi.} \quad (1-x) \quad x \quad x/2$$

Total number of moles at equilibrium

$$= 1 - x + x + \frac{x}{2} = \frac{2+x}{2}$$

Total equilibrium pressure = P

$$P_{\text{AB}_2(g)} = \frac{(1-x)}{\left(\frac{2+x}{2}\right)} \times P = \frac{2(1-x)}{(2+x)} \times P$$

$$P_{\text{AB}(g)} = \frac{x}{\left(\frac{2+x}{2}\right)} \times P = \frac{2x}{(2+x)} \times P$$

$$P_{\text{B}_2(g)} = \frac{x/2}{\left(\frac{2+x}{2}\right)} \times P = \frac{x}{(2+x)} \times P$$

$$\therefore K_p = \frac{(P_{\text{AB}})^2 (P_{\text{B}_2})}{(P_{\text{AB}_2})^2} = \frac{\left(\frac{2x}{2+x} \times P\right)^2 \left(\frac{x}{2+x} \times P\right)}{\left(\frac{2(1-x)}{2+x} \times P\right)^2}$$

$$\text{or } K_p = \frac{x^3 P}{2} \quad [\therefore 2+x \approx 2, 1-x \approx 1]$$

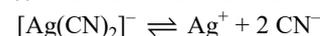
$$\text{or } x = \left(\frac{2K_p}{P}\right)^{1/3}$$

94. Conc. of Ag⁺ ions = Conc. of AgNO₃ = 0.03 M

Most of these Ag⁺ ions will be present in the form of [Ag(CN)₂]⁻

0.03 M AgNO₃ requires 2 × 0.03 M or 0.06 M CN⁻ to form [Ag(CN)₂]⁻

∴ Concentration of free CN⁻ at equi. = 0.1 - 0.06 = 0.04 M



$$\therefore K = \frac{[\text{Ag}^+][\text{CN}^-]^2}{[\text{Ag}(\text{CN})_2]^-}$$

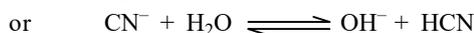
$$\text{or } 4.0 \times 10^{-19} = \frac{[\text{Ag}^+][0.04]^2}{0.03}$$

$$\text{or } [\text{Ag}^+] = \frac{4 \times 10^{-19} \times 0.03}{0.04 \times 0.04} = 7.5 \times 10^{-18} \text{ M}$$

95. Ammonium formate (HCOONH_4) is the salt of a weak acid and a weak base, so pH of its aqueous solution is given by

$$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a - \text{p}K_b] = \frac{1}{2}[14 + 3.8 - 4.8] = 6.5$$

96. $\text{NaCN} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{HCN}$



At Equi. $C(1-h)$

$C.h$

$C.h$

Thus $[\text{OH}^-] = C.h$, where h is the degree of hydrolysis and C is the concentration of salt

From the above ionic equation

$$K_b = \frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]} = \frac{[\text{OH}^-]^2}{[\text{CN}^-]}$$

$$\text{or } \log K_b = 2 \log [\text{OH}^-] - \log [\text{CN}^-]$$

$$\text{or } -\log K_b = -2 \log [\text{OH}^-] + \log [\text{CN}^-]$$

$$\text{or } \text{p}K_b = -2 \log [\text{OH}^-] + \log [\text{CN}^-]$$

$$\text{or } 4.70 = -2 \log [\text{OH}^-] + \log (0.5)$$

$$[\text{p}K_b = 4.70; [\text{CN}^-] = 0.5 \text{ M}]$$

$$\text{or } 4.70 = -2 \log [\text{OH}^-] - 0.30$$

$$\text{or } 4.70 + 0.30 = -2 \log [\text{OH}^-]$$

$$\text{or } \log [\text{OH}^-] = -\frac{5.0}{2} = -2.50$$

$$\text{or } [\text{OH}^-] = 10^{-2.5} \quad (\text{Taking antilog})$$

$$\text{or } [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-2.5}} \text{ or } 10^{-11.5}$$

$$\therefore \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 10^{-11.5} = 11.5$$

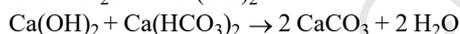
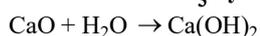
97. Amount of HCO_3^- in the given sample = 183 ppm

$$= 183 \times 10^{-6} \times 1000 \text{ kg}$$

$$= 183 \times 10^{-6} \times 1000 \times 1000 \text{ g} = 183 \text{ g}$$

$$\therefore \text{Number of moles of } \text{HCO}_3^- \text{ in the given sample} = \frac{183}{61} = 3 \text{ moles}$$

Removal of HCO_3^- by CaO :



From the above equations, it is evident that 2 moles of HCO_3^- are removed by 1 mole of CaO

\therefore 3 Moles of HCO_3^- will be removed by $\frac{1}{2} \times 3$ moles of CaO or 1.5 moles of CaO .

After complete removal of HCO_3^- from the sample we have 96 ppm of CaSO_4 in it.

Thus the remaining sample contains Ca^{2+} ions = 96 ppm

$$= 96 \times 10^{-6} \times 1000 \text{ kg}$$

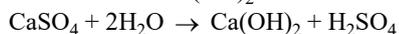
$$= 96 \times 10^{-6} \times 1000 \times 1000 \text{ g} = 96 \text{ g}$$

Hence number of moles of Ca^{2+} present

$$= \frac{96}{40} \text{ or } 2.4 \text{ moles in } 1000 \text{ kg of water}$$

$$= 2.4 \text{ moles in } 1000 \text{ L} = 2.4 \times 10^{-3} \text{ moles/L}$$

Since CaSO_4 is a salt of weak base and strong acid. It is 100% dissociable to Ca(OH)_2

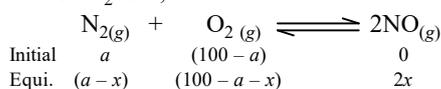


$$[\text{H}^+] = \text{Conc. of } \text{Ca}^{2+} = 2.4 \times 10^{-3}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (2.4 \times 10^{-3}) = 2.62$$

98. $\text{N}_2 + \text{O}_2 \rightleftharpoons 2 \text{NO}$

If the total number of moles of O_2 and N_2 initially is 100 and that of N_2 is a , then we have



$$\therefore \frac{2x}{100} = \frac{1.8}{100} \quad (\text{given})$$

$$\text{or } x = 0.9$$

$$\text{Hence } K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$\begin{aligned} \text{or } 2.1 \times 10^{-3} &= \frac{(2x)^2}{(a-x)(100-a-x)} \\ &= \frac{(2 \times 0.9)^2}{(a-0.9)(100-a-0.9)} \end{aligned}$$

$$\text{or } a = 79$$

$$\therefore \% \text{ N}_2 \text{ in air} = 79\%$$

$$\% \text{ O}_2 \text{ in air} = 100 - 79 = 21\%$$

99. $\text{Ag}_2\text{CO}_3(s) \rightleftharpoons 2\text{Ag}^+_{(aq)} + \text{CO}_3^{2-}_{(aq)}$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}]$$

$$\text{or } 8.2 \times 10^{-12} = [\text{Ag}^+]^2 \times 1.5$$

$$(\because K_{sp} = 8.2 \times 10^{-12}; [\text{CO}_3^{2-}] = 1.5 \text{ M})$$

$$\text{or } [\text{Ag}^+] = \left(\frac{8.2 \times 10^{-12}}{1.5} \right)^{\frac{1}{2}} = 2.34 \times 10^{-6} \text{ M}$$

To calculate K_{sp} of AgCl :

$$[\text{Ag}^+] = 2.34 \times 10^{-6} \text{ M}$$

$$\therefore [\text{Cl}^-] = \frac{0.0026 \text{ g L}^{-1}}{35.5 \text{ g mol}^{-1}} = 7.32 \times 10^{-5} \text{ M}$$

$$\therefore K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 2.34 \times 10^{-6} \times 7.32 \times 10^{-5} = 1.71 \times 10^{-10}$$

100. The condition for visibility of colour of indicator can be derived by using the relation

$$\text{pH} = \text{p}K_b + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$(i) \text{pH} = 5 + \log 10 \quad (ii) \text{pH} = 5 + \log 0.1$$

$$= 5 + 1 = 6$$

$$= 5 - 1 = 4$$

$$\text{Thus minimum change in pH} = 6 - 4 = 2$$

101. $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

$$\text{Given: } [\text{Ag}(\text{NH}_3)_2]^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3; K_c = 6.2 \times 10^{-8}$$

$$\text{or } \text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$$

$$K_f = \frac{1}{6.2 \times 10^{-8}} = \frac{10^8}{6.2}$$

$$\text{or } K_f = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2}$$

$$\text{or } \frac{10^8}{6.2} = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]^2} \quad \text{or } [\text{Ag}^+] = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{\frac{10^8}{6.2} \times [\text{NH}_3]^2}$$

Equilibrium

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Since the formation constant (K_f) of the complex $[\text{Ag}(\text{NH}_3)_2]^+$ is very high, so most of Ag^+ which dissolves must get converted to the complex. For dissolution of each Ag^+ we have one Cl^-

$$\therefore [\text{Cl}^-] = [\text{Ag}(\text{NH}_3)_2]^+$$

Let the concentration of (Cl^-) be C M.

Then, we have

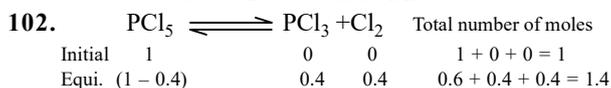
$$K_{sp} = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{\frac{10^8}{6.2} \times [\text{NH}_3]^2} \times C$$

$$\text{or } K_{sp} = \frac{C}{\frac{10^8}{6.2} \times (1)^2} \times C$$

$$\text{or } C^2 = K_{sp} \times \frac{10^8}{6.2} \times (1)^2$$

$$\text{or } C^2 = 1.8 \times 10^{-10} \times \frac{10^8}{6.2} \times (1)^2$$

$$\text{or } C = (0.29 \times 10^{-2})^{1/2} = 0.538 \times 10^{-1} = 0.0538 \text{ M.}$$



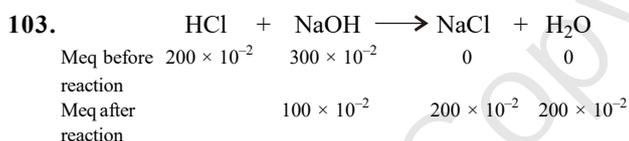
Average molecular mass of the mixture

$$= \frac{0.6 \times 208.5 + 0.4 \times 137.5 + 0.4 \times 71}{1.4} = 148.92$$

For an ideal gas, we have

$$PV = nRT = \frac{W}{M}RT \quad \text{or} \quad PM = \frac{W}{V}RT = dRT$$

$$\text{or } d = \frac{PM}{RT} = \frac{(1 \text{ atm}) \times (148.92 \text{ g mol}^{-1})}{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}) (400 \text{ K})} = 4.54 \text{ g L}^{-1}$$



$$\therefore [\text{OH}^-] = \frac{100 \times 10^{-2}}{500} = 2 \times 10^{-3}$$

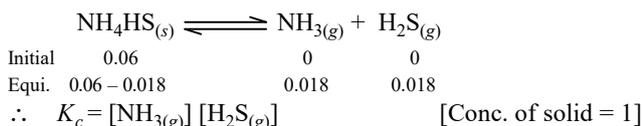
$$\text{or } \text{pOH} = -\log[\text{OH}^-] = -\log(2 \times 10^{-3}) = 3 - 0.3010 = 2.6990$$

$$\text{or } \text{pH} = 14 - \text{pOH} = 14 - 2.6990 = 11.3010$$

104. Moles of NH_4HS introduced = $\frac{\text{Weight of } \text{NH}_4\text{HS}}{\text{Mol. Wt. of } \text{NH}_4\text{HS}} = \frac{3.06}{51} = 0.06 \text{ mol}$

Degree of dissociation of $\text{NH}_4\text{HS} = 30\%$

$$\text{So, moles of } \text{NH}_4\text{HS} \text{ dissociated} = \frac{0.06 \times 30}{100} = 0.018 \text{ mol}$$

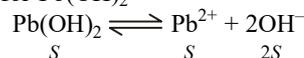


$$= \frac{0.018}{2} \times \frac{0.018}{2} = 8.1 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2}$$

$$K_p = K_c \times (RT)^{\Delta n} = 8.1 \times 10^{-5} \times (0.082 \times 300)^2 \quad [\because \Delta n_g = 2 - 0 = 2] = 4.9 \times 10^{-2} \text{ atm}^2$$

Addition of more NH_4HS will have no effect on this equilibrium because concentration of NH_4HS (solid) is not involved in the formula of K_p or K_c .

105. K_{sp} for $\text{Pb}(\text{OH})_2$



$$\therefore K_{sp} = S \times (2S)^2 = 4S^3 \quad [S \text{ is the solubility of } \text{Pb}(\text{OH})_2]$$

$$\text{Hence } K_{sp} = 4S^3 = 4 \times (6.7 \times 10^{-6})^3 = 1.203 \times 10^{-15}$$

The pH of buffer solution = 8

$$\therefore \text{pOH} = 14 - 8 = 6 \quad \text{or } [\text{OH}^-] = 10^{-6}$$

$$\text{Thus, } [\text{Pb}^{2+}] \times [10^{-6}]^2 = 1.203 \times 10^{-15}$$

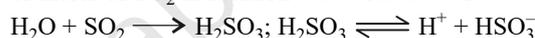
$$\text{or } [\text{Pb}^{2+}] = \frac{1.203 \times 10^{-15}}{10^{-12}} = 1.203 \times 10^{-3} \text{ mol litre}^{-1}$$

106. Solubility of SO_2 in water at 298 K = $1.3653 \text{ mol L}^{-1}$

$$\text{Average conc. of } \text{SO}_2 = 10 \text{ ppm} = 10 \times 10^{-6} \text{ or } 10^{-5} \text{ mol L}^{-1}$$

$$\text{or } 10^{-5} = \frac{\text{Moles of } \text{SO}_2 \text{ in solution}}{1.3653}$$

$$\text{or moles of } \text{SO}_2 \text{ in solution} = C = 1.3653 \times 10^{-5}$$



$$\therefore \text{pH} = \frac{1}{2}[\text{p}K_a - \log(C)]$$

$$= \frac{1}{2}[1.92 - \log(1.3653 \times 10^{-5})]$$

$$= \frac{1}{2}[1.92 + 5 - 0.1351] = 3.39$$

107. (i) By mixing the two solution volume is doubled and so the molarity of each component is halved.

$$[\text{CH}_3\text{COOH}] = 0.1 \text{ M} \quad \text{and} \quad [\text{HCl}] = 0.1 \text{ M}$$

HCl being a strong acid is completely ionised and so $[\text{H}^+]$ ion due to $\text{HCl} = 0.1 \text{ M}$

Due to common ion effect the ionisation of CH_3COOH will be suppressed because of presence of H^+ (from HCl)



Initial	C	0	0
Equi.	$C(1 - \alpha)$	$C\alpha$	$C\alpha + 0.1$

$$\text{Thus } K_a = \frac{C\alpha(C\alpha + 0.1)}{C(1 - \alpha)} = \frac{C\alpha^2 + 0.1\alpha}{(1 - \alpha)}$$

Since α is very small, $C\alpha^2$ can be neglected and $1 - \alpha \approx 1$.

$$\therefore K_a = \frac{0.1\alpha}{1}$$

$$\text{or } \alpha = \frac{K_a}{0.1} = \frac{1.75 \times 10^{-5}}{0.1} = 1.75 \times 10^{-4}$$

$$[\text{H}^+]_{\text{Total}} = 0.1 + C\alpha \approx 0.1 \quad [\because C\alpha \text{ is negligible}]$$

$$\text{or } \text{pH} = 1$$

(ii) $6 \text{ g NaOH} = \frac{6}{40}$ or 0.15 mol

0.1 mol of NaOH will be consumed by 0.1 mole of HCl .

Thus 0.05 mole of NaOH will react with acetic acid as follows:



Initial	0.05	0.1	0	0
Equi.	0	$0.1 - 0.05 = 0.05$	0.05	0.05

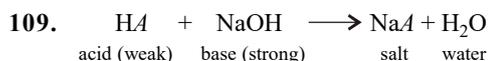
It will be a buffer solution containing acetic acid and sodium acetate (acidic buffer). Its pH will be given by

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log(1.75 \times 10^{-5}) + \log \frac{0.05}{0.05}$$

$$= -\log(1.75 \times 10^{-5}) + \log 1 = 4.75$$

- 108.** A higher value of K_b of a solvent indicates that the polarity of solvent molecules is quite large and so it has a higher value of dipole-dipole interaction. Due to high value of dipole-dipole interaction the solvent has a high b.p. Therefore the correct order of K_b values of given solvent is

Solvent	B. P.	K_b
X	100°C	0.68
Y	27°C	0.53
Z	235°C	0.98



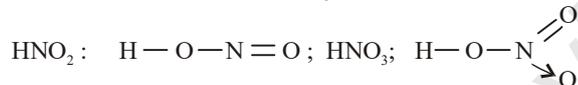
At the end point the solution contains only NaA. The concentration of NaA is $\frac{0.1}{2}$ or 0.05 M.

Since the salt (NaA) is a salt of strong base and weak acid which is likely to have a low value of K_a , its pH is given by

$$\text{pH} = -\log \sqrt{\frac{K_w \cdot K_a}{C}} = -\log \sqrt{\frac{10^{-14} \times 5 \times 10^{-6}}{0.05}} = 9$$

- 110. (c):** In case of oxyacids the acidic strength increases with increase in oxidation state of the central atom so the assertion is correct.

Structures of HNO_2 and HNO_3 are as follows



As is evident from above structures statement-1 is true but statement-2 is wrong.

- 111. (d):** In this case statement-1 is wrong because endothermic reactions are favoured at higher temperature and exothermic reactions are favoured at lower temperature in accordance with Le Chatelier's principle.

Statement-2 is correct as it is in accordance with Le Chatelier's principle.

- 112. (8):** Given, $K_a = 1 \times 10^{-4}$.

$$\therefore \text{p}K_a = -\log(1 \times 10^{-4}) = 4$$

$$c = 0.01 \text{ M}$$

Since the solution contains a salt of weak acid and strong base,

$$\therefore \text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c$$

$$= 7 + \frac{1}{2} \times 4 + \frac{1}{2} \times \log(0.01) = 9 + \frac{1}{2} \times (-2) = 8$$

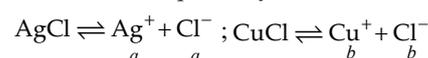
\therefore pH of solution = 8.

- 113. (3):** In aqueous solution,



Basic solutions turn red litmus blue.

- 114. (7):** Let the solubility of AgCl and CuCl be a mol litre⁻¹ and b mol litre⁻¹ respectively.



$$\therefore K_{sp} \text{ of AgCl} = [\text{Ag}^+][\text{Cl}^-]$$

$$1.6 \times 10^{-10} = a(a+b) \quad \dots(i)$$

$$\text{Similarly } K_{sp} \text{ of CuCl} = [\text{Cu}^+][\text{Cl}^-]$$

$$1.0 \times 10^{-6} = b(a+b) \quad \dots(ii)$$

On solving (i) and (ii)

$$\text{or } a = 1.6 \times 10^{-4} \times b$$

Substituting the value of a in eqn. (i),

$$1.6 \times 10^{-10} = 1.6 \times 10^{-4} b (1.6 \times 10^{-4} b + b)$$

$$\Rightarrow 10^{-6} = b^2 (1.6 \times 10^{-4} + 1) \Rightarrow b = 10^{-3} \Rightarrow a = 1.6 \times 10^{-7}$$

$$[\text{Ag}^+] = 1.6 \times 10^{-7}; \therefore x = 7$$

- 115. (3):** Given:

$$\Lambda_m^c(\text{HX}) = \frac{\Lambda_m^c(\text{HY})}{10}$$

$$\Lambda_m^{\circ}(\text{HX}) = \Lambda_m^{\circ}(\text{HY}) \quad (\because \lambda_{X^-}^{\circ} \approx \lambda_{Y^-}^{\circ})$$

$$K_a(\text{HX}) = \left(\frac{C\alpha^2}{1-\alpha} \right)_{\text{HX}}$$

$$K_a(\text{HX}) = 0.01(\alpha_{\text{HX}})^2 \quad (\because \alpha \ll 1) \quad \dots(i)$$

$$\text{Similarly, } K_a(\text{HY}) = 0.10(\alpha_{\text{HY}})^2 \quad \dots(ii)$$

On dividing equation (i) by (ii), we get

$$\frac{K_a(\text{HX})}{K_a(\text{HY})} = \frac{0.01 \left(\frac{\alpha_{\text{HX}}}{\alpha_{\text{HY}}} \right)^2}{0.10} \quad \dots(iii)$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^{\circ}}$$

$$\frac{\alpha_{\text{HX}}}{\alpha_{\text{HY}}} = \frac{(\Lambda_m^c / \Lambda_m^{\circ})_{\text{HX}}}{(\Lambda_m^c / \Lambda_m^{\circ})_{\text{HY}}} = \left(\frac{1}{10} \Lambda_m^c(\text{HY}) \right) \times \frac{1}{\Lambda_m^c(\text{HY})} = \frac{1}{10}$$

Substituting above value in equation (iii),

$$\frac{K_a(\text{HX})}{K_a(\text{HY})} = \frac{0.01 \left(\frac{1}{10} \right)^2}{0.10} = 1 \times 10^{-3}$$

$$\log K_a(\text{HX}) - \log K_a(\text{HY}) = \log(1 \times 10^{-3})$$

$$-\log K_a(\text{HX}) - (-\log K_a(\text{HY})) = -\log(1 \times 10^{-3})$$

$$\text{p}K_a(\text{HX}) - \text{p}K_a(\text{HY}) = 3$$



10

Redox Reactions and Electrochemistry

Multiple Choice Questions with ONE Correct Answer

1. One mole of N_2H_4 loses ten moles of electrons to form a new compound Y . Assuming that all the nitrogen appears in the new compound, what is the oxidation state of nitrogen in Y ? (There is no change in the oxidation state of hydrogen).
(a) -1 (b) -3 (c) +3 (d) +5
(1981)
2. Molten sodium chloride conducts electricity due to the presence of
(a) free electrons (b) free ions
(c) free molecules
(d) atoms of sodium and chlorine. (1981)
3. The standard reduction potentials at 298 K for the following half reactions are given against each
- | | |
|---|---------|
| $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ | - 0.762 |
| $Cr^{3+}_{(aq)} + 2e^- \rightleftharpoons Cr_{(s)}$ | - 0.740 |
| $2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$ | 0.000 |
| $Fe^{3+}_{(aq)} + 2e^- \rightleftharpoons Fe^{2+}_{(aq)}$ | 0.770 |
- Which is the strongest reducing agent?
(a) $Zn_{(s)}$ (b) $Cr_{(s)}$ (c) $H_{2(g)}$ (d) $Fe^{2+}_{(aq)}$
(1981)
4. The oxidation number of carbon in CH_2O is
(a) -2 (b) +2 (c) 0 (d) +4
(1982)
5. Faraday's laws of electrolysis are related to the
(a) atomic number of the reaction
(b) atomic number of the anion
(c) equivalent weight of the electrolyte
(d) speed of the cation (1983)
6. A solution containing one mole per litre of each $Cu(NO_3)_2$; $AgNO_3$; $Hg_2(NO_3)_2$; is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are
 $Ag/Ag^+ = +0.80$, $2Hg/Hg_2^{++} = +0.79$
 $Cu/Cu^{++} = +0.34$, $Mg/Mg^{++} = -2.37$
- With increasing voltage, the sequence of deposition of metals on the cathode will be
(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag
(c) Ag, Hg, Cu (d) Cu, Hg, Ag
(1984)
7. The electric charge for electrode deposition of one gram equivalent of a substance is
(a) one ampere per second
(b) 96,500 coulombs per second
(c) one ampere for one hour
(d) charge on one mole of electrons (1984)
8. The reaction:
 $\frac{1}{2} H_{2(g)} + AgCl_{(s)} = H^+_{(aq)} + Cl^-_{(aq)} + Ag_{(s)}$
occurs in the galvanic cell
(a) $Ag | AgCl_{(s)} | KCl_{(soln)} | AgNO_3_{(soln)} | Ag$
(b) $Pt | H_{2(g)} | HCl_{(soln)} | AgNO_3_{(soln)} | Ag$
(c) $Pt | H_{2(g)} | HCl_{(soln)} | AgCl_{(s)} | Ag$
(d) $Pt | H_{2(g)} | KCl_{(soln)} | AgCl_{(s)} | Ag$ (1985)
9. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively
(a) H_2, O_2 (b) O_2, H_2 (c) O_2, Na (d) O_2, SO_2
(1987)
10. The brown ring complex compound is formulated as $[Fe(H_2O)_5(NO)]SO_4$. The oxidation state of iron is:
(a) 1 (b) 2 (c) 3 (d) 0
(1987)
11. The standard oxidation potentials, E° , for the half reactions are as
 $Zn = Zn^{2+} + 2e^-$; $E^\circ = +0.76 V$
 $Fe = Fe^{2+} + 2e^-$; $E^\circ = +0.41 V$
The EMF for the cell oxidation:
 $Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$
(a) -0.35 V (b) +0.35 V
(c) +1.17 V (d) - 1.17 V
(1988)

12. The oxidation number of phosphorus in $\text{Ba}(\text{H}_2\text{PO}_2)_2$ is
 (a) +3 (b) +2 (c) +1 (d) -1 (1990)
13. The oxidation states of the most electronegative element in the products of the reaction, BaO_2 with dil. H_2SO_4 is
 (a) 0 and -1 (b) -1 and +2
 (c) -2 and 0 (d) -2 and -1 (1991)
14. For the redox reaction:

$$\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \longrightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$$
 the correct coefficients of the reactants for the balanced reaction are:

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

 (1992)
15. A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode are:
 (a) O_2 , H_2 (b) $\text{S}_2\text{O}_8^{2-}$, Na
 (c) O_2 , Na (d) $\text{S}_2\text{O}_8^{2-}$, H_2 (1996)
16. A standard hydrogen electrode has zero electrode potential because
 (a) hydrogen is easiest to oxidise
 (b) this electrode potential is assumed to be zero
 (c) hydrogen atom has only one electron
 (d) hydrogen is the lightest element (1997)
17. The standard reduction potentials of Cu^{2+}/Cu and $\text{Cu}^{+}/\text{Cu}^0$ are 0.337 V and 0.153 V respectively. The standard electrode potential of Cu^{+}/Cu half cell is
 (a) 0.184 V (b) 0.827 V
 (c) 0.521 V (d) 0.490 V (1997)
18. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential of $\text{Z} > \text{Y} > \text{X}$, then,
 (a) Y will oxidize X and not Z
 (b) Y will oxidize Z and not X
 (c) Y will oxidize both X and Z
 (d) Y will reduce both X and Z (1999)
19. The oxidation number of sulphur in S_8 , S_2F_2 , H_2S respectively, are
 (a) 0, +1 and -2 (b) +2, +1 and -2
 (c) 0, +1 and +2 (d) -2, +1 and +2 (1999)
20. Amongst the following identify the species with an atom in +6 oxidation state.
 (a) MnO_4^- (b) $\text{Cr}(\text{CN})_6^{3-}$ (c) NiF_6^{2-} (d) CrO_2Cl_2 (2000)
21. For the electrochemical cell, $M|M^+ || X^-|X$, $E^\circ(M^+/M) = 0.44$ V and $E^\circ(X/X^-) = 0.33$ V.
 From this data one can deduce that
 (a) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction
 (b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction
 (c) $E_{\text{cell}} = 0.77$ V
 (d) $E_{\text{cell}} = -0.77$ V (2000)
22. Saturated solution of KNO_3 is used to make 'salt-bridge' because
 (a) velocity of K^+ is greater than that of NO_3^-
 (b) velocity of NO_3^- is greater than that of K^+
 (c) velocities of both K^+ and NO_3^- are nearly the same
 (d) KNO_3 is highly soluble in water (2001)
23. The correct order of equivalent conductance at infinite dilution of LiCl , NaCl and KCl is
 (a) $\text{LiCl} > \text{NaCl} > \text{KCl}$ (b) $\text{KCl} > \text{NaCl} > \text{LiCl}$
 (c) $\text{NaCl} > \text{KCl} > \text{LiCl}$ (d) $\text{LiCl} > \text{KCl} > \text{NaCl}$ (2001)
24. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:

$$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \quad E^\circ = 1.51 \text{ V}$$

$$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O} \quad E^\circ = 1.38 \text{ V}$$

$$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq}) \quad E^\circ = 0.77 \text{ V}$$

$$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq}) \quad E^\circ = 1.40 \text{ V}$$
 Identify the only incorrect statement regarding the quantitative estimation of aqueous $\text{Fe}(\text{NO}_3)_2$.
 (a) MnO_4^- can be used in aqueous HCl
 (b) $\text{Cr}_2\text{O}_7^{2-}$ can be used in aqueous HCl
 (c) MnO_4^- can be used in aqueous H_2SO_4
 (d) $\text{Cr}_2\text{O}_7^{2-}$ can be used in aqueous H_2SO_4 (2002)
25. In the electrolytic cell, flow of electrons is from
 (a) cathode to anode in solution
 (b) cathode to anode through external supply
 (c) cathode to anode through internal supply
 (d) anode to cathode through internal supply (2003)

Redox Reactions and Electrochemistry

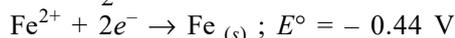
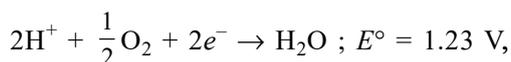
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26. The EMF of the cell

$\text{Zn} | \text{Zn}^{2+} (0.01 \text{ M}) || \text{Fe}^{2+} (0.001 \text{ M}) | \text{Fe}$
at 298 K is 0.2905 then the value of equilibrium constant for the cell reaction is

- (a) $e^{\frac{0.32}{0.0295}}$ (b) $10^{\frac{0.32}{0.0295}}$
(c) $10^{\frac{0.26}{0.0295}}$ (d) $10^{\frac{0.32}{0.0591}}$ (2004)

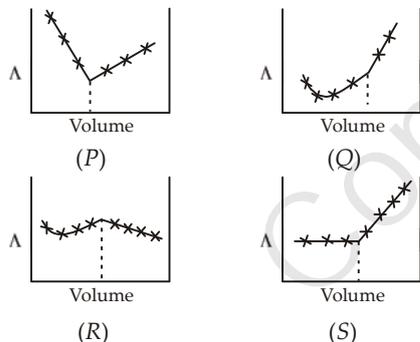
27. The half-cell reaction for the corrosion

find the ΔG° (in kJ) for the overall reaction.

- (a) -76 (b) -322
(c) -161 (d) -152 (2005)

28. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of H_2 gas at the cathode is (1 Faraday = 96500 C mol^{-1})

- (a) $9.65 \times 10^4 \text{ sec}$ (b) $19.3 \times 10^4 \text{ sec}$
(c) $28.95 \times 10^4 \text{ sec}$ (d) $38.6 \times 10^4 \text{ sec}$ (2008)

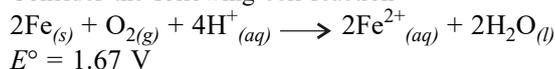
29. $\text{AgNO}_3(aq.)$ was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) versus the volume of AgNO_3 is

- (a) P (b) Q (c) R (d) S (2011)

30. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are

- (a) II, III haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III in magnetite
(d) III in haematite and II, III in magnetite (2011)

31. Consider the following cell reaction

At $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$, $P(\text{O}_2) = 0.1 \text{ atm}$ and $\text{pH} = 3$, the cell potential at 25°C is

- (a) 1.47 V (b) 1.77 V
(c) 1.87 V (d) 1.57 V (2011)

32. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?

- (a) $\text{HNO}_3, \text{NO}, \text{NH}_4\text{Cl}, \text{N}_2$
(b) $\text{HNO}_3, \text{NO}, \text{N}_2, \text{NH}_4\text{Cl}$
(c) $\text{HNO}_3, \text{NH}_4\text{Cl}, \text{NO}, \text{N}_2$
(d) $\text{NO}, \text{HNO}_3, \text{NH}_4\text{Cl}, \text{N}_2$ (2012)

33. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively

- (a) redox reaction; -3 and -5
(b) redox reaction; +3 and +5
(c) disproportionation reaction; -3 and +5
(d) disproportionation reaction; -3 and +3 (2012)

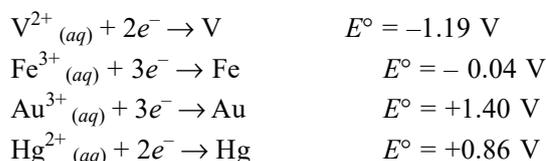
34. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a

- (a) reducing agent, oxidising agent
(b) reducing agent, reducing agent
(c) oxidising agent, oxidising agent
(d) oxidising agent, reducing agent. (2014)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

35. The standard reduction potential values of three metallic cations, X, Y and Z are 0.52, -3.03 and -1.18 V respectively. The order of reducing power of the corresponding metals is

- (a) $Y > Z > X$ (b) $X > Y > Z$
(c) $Z > Y > X$ (d) $Z > X > Y$ (1998)

36. For the reduction of NO_3^- ion in an aqueous solution, E° is +0.96 V. Values of E° for some metal ions are given belowThe pair(s) of metals that is(are) oxidised by NO_3^- in aqueous solution is(are)

- (a) V and Hg (b) Hg and Fe
(c) Fe and Au (d) Fe and V. (2009)

37. Among the following, the intensive property is (properties are)

- (a) molar conductivity (b) electromotive force
(c) resistance (d) heat capacity (2010)

38. In a galvanic cell, the salt bridge
 (a) does not participate chemically in the cell reaction
 (b) stops the diffusion of ions from one electrode to another
 (c) is necessary for the occurrence of the cell reaction
 (d) ensures mixing of the two electrolytic solutions. (2014)

39. For the reaction :
 $\Gamma + \text{ClO}_3^- + \text{H}_2\text{SO}_4 \rightarrow \text{Cl}^- + \text{HSO}_4^- + \text{I}_2$
 The correct statement(s) in the balanced equation is/are
 (a) stoichiometric coefficient of HSO_4^- is 6
 (b) iodide is oxidized
 (c) sulphur is reduced
 (d) H_2O is one of the products. (2014)

40. Fe^{3+} is reduced to Fe^{2+} by using
 (a) H_2O_2 in presence of NaOH
 (b) Na_2O_2 in water
 (c) H_2O_2 in presence of H_2SO_4
 (d) Na_2O_2 in presence of H_2SO_4 (2015)

Fill in the Blanks

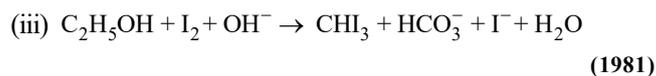
41. The more the standard reduction potential, the is its ability to displace hydrogen from acids. (1986)
42. The electrical conductivity of a solution of acetic acid will be if a solution of sodium hydroxide is added. (1987)

True / False

43. The dependence of electrode potential for the electrode M^{n+}/M with concentration under STP conditions is given by the expression: $E = E^\circ + \frac{0.0591}{n} \log_{10} [M^{n+}]$ (1993)

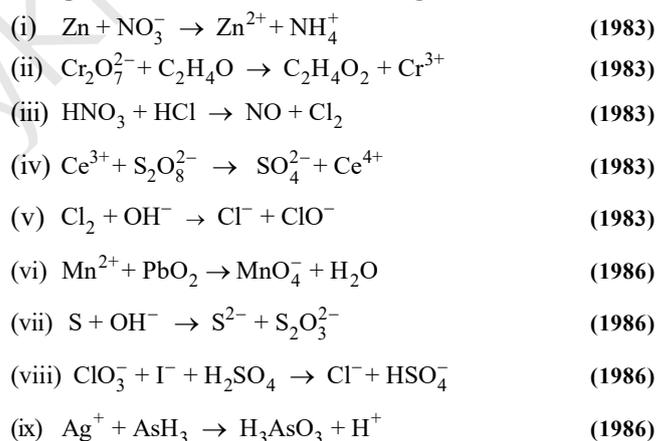
Subjective Problems

44. A current of 3.7 ampere is passed for 6 hours between nickel electrodes in 0.5 litre of a 2M solution of $\text{Ni}(\text{NO}_3)_2$. What will be molarity of solution at the end of the electrolysis? (1978)
45. The density of copper is 8.94 g/ml. Find out the number of coulombs needed to plate an area of $10 \text{ cm} \times 10 \text{ cm}$ to a thickness 10^{-2} cm using CuSO_4 solution as electrolyte. (1979)
46. Balance the following equations.
 (i) $\text{Cu}_2\text{O} + \text{H}^+ + \text{NO}_3^- \rightarrow \text{Cu}^{2+} + \text{NO} + \text{H}_2\text{O}$ (1981)
 (ii) $\text{K}_4[\text{Fe}(\text{CN})_6] + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + \text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{CO}$ (1981)



47. Consider the cell
 $\text{Zn} | \text{Zn}^{2+}_{(aq)} (1.0 \text{ M}) || \text{Cu}^{2+}_{(aq)} (1.0 \text{ M}) | \text{Cu}$
 The standard reduction potentials are:
 $+0.350 \text{ volts for } 2e^- + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Cu}$ and
 $-0.763 \text{ volts for } 2e^- + \text{Zn}^{2+}_{(aq)} \rightarrow \text{Zn}$
 (i) Write down the cell reaction.
 (ii) Calculate the EMF of the cell.
 (iii) Is the cell reaction spontaneous or not? (1982)
48. In an electrolysis experiment current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold and the second contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode of the second cell. Also calculate the magnitude of the current in amperes. (1 Faraday = 96500 coulombs) (1983)

49. Complete and balance the following reactions:



50. How long a current of 3 ampere has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer? Density of silver is 10.5 g/cm^3 . (1985)
51. The EMF of a cell corresponding to the reaction:
 $\text{Zn}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Zn}^{2+}(0.1 \text{ M}) + \text{H}_{2(g)} (1 \text{ atm})$
 is 0.28 volt at 15°C .
 Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.
 $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ volt}; E^\circ_{\text{H}^+/\text{H}_2} = 0$ (1986)
52. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g/mL . Sulphuric acid of density 1.294 g/mL is 39% by weight and that of 1.139 g/mL is 20% H_2SO_4 by weight. The battery holds

Redox Reactions and Electrochemistry

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- 3.5 litres of the acid and the volume remained practically constant during the discharge.
Calculate the number of ampere-hours for which the battery must have been used. The charging and discharging reactions are:

$$\text{Pb} + \text{SO}_4^{2-} = \text{PbSO}_4 + 2e^- \quad (\text{charging})$$

$$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2e^- = \text{PbSO}_4 + 2\text{H}_2\text{O} \quad (\text{discharging})$$
(1986)
- 53.** Arrange the following in increasing oxidation number of iodine.
 I_2 , HI, HIO_4 , ICl **(1986)**
- 54.** A 100 watt, 110 volt incandescent lamp is connected in series with an electrolyte cell containing cadmium sulphate solution. What weight of cadmium will be deposited by the current flowing for 10 hours? **(1987)**
- 55.** A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The EMF of the cell is 0.118 V at 25°C . Calculate the concentration of hydrogen ions at the positive electrode. **(1988)**
- 56.** In a fuel cell hydrogen and oxygen react to produce electricity. In the process hydrogen gas is oxidised at the anode and oxygen at the cathode. If 67.2 litre of H_2 at STP react in 15 minutes, what is the average current produced? If the entire current is used for electrodeposition of copper from copper (II) solution, how many grams of copper will be deposited?
 Anode reaction: $\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2e^-$
 Cathode reaction : $\text{O}_2 + 2\text{H}_2\text{O} + 2e^- \rightarrow 4\text{OH}^-$. **(1988)**
- 57.** An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 mL and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis. **(1989)**
- 58.** The standard reduction potential at 25°C of the reaction, $2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$ is -0.8277 V. Calculate the equilibrium constant for the reaction $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ at 25°C . **(1989)**
- 59.** The standard reduction potential of Cu^{++}/Cu and Ag^+/Ag electrodes are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard EMF is positive. For what concentration of Ag^+ with the EMF of the cell, at 25°C , be zero if the concentration of Cu^{2+} is 0.01 M? **(1990)**
- 60.** Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 per cent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed? **(1990)**
- 61.** Zinc granules are added in excess to a 500 mL. of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of $\text{Zn}^{2+} | \text{Zn}$ and $\text{Ni}^{2+} | \text{Ni}$ are -0.75 V and -0.24 V respectively, find out the concentration of Ni^{2+} in solution at equilibrium. **(1991)**
- 62.** A current of 1.70 A is passed through 300.0 ml of 0.160 M solution of a ZnSO_4 for 230 sec. with a current efficiency of 90%. Find out the molarity of Zn^{2+} after the deposition of Zn. Assume the volume of the solution to remain constant during the electrolysis. **(1991)**
- 63.** For the galvanic cell
 $\text{Ag} | \text{AgCl}_{(s)}, \text{KCl} (0.2 \text{ M}) || \text{KBr} (0.001 \text{ M}), \text{AgBr}_{(s)} | \text{Ag}$
 calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C .
 $[K_{sp}(\text{AgCl}) = 2.8 \times 10^{-10}; K_{sp}(\text{AgBr}) = 3.3 \times 10^{-13}]$ **(1992)**
- 64.** An aqueous solution of NaCl on electrolysis gives $\text{H}_{2(g)}$, $\text{Cl}_{2(g)}$ and NaOH according to the reaction
 $2\text{Cl}^-_{(aq)} + 2\text{H}_2\text{O} \rightarrow 2\text{OH}^-_{(aq)} + \text{H}_{2(g)} + \text{Cl}_{2(g)}$.
 A direct current of 25 amperes with a current efficiency of 62% is passed through 20 litres of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the cathode. How long will it take to produce 1 Kg of Cl_2 ? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation). **(1992)**
- 65.** The standard reduction potential for the half-cell
 $\text{NO}_3^-_{(aq)} + 2\text{H}^+_{(aq)} + e^- \rightarrow \text{NO}_{2(g)} + \text{H}_2\text{O}$ is 0.78 V.
 (i) Calculate the reduction potential in 8M H^+ .
 (ii) What will be the reduction potential of the half-cell in a neutral solution? Assume all the other species to be at unit concentration. **(1993)**
- 66.** Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation.
 $\text{CrO}_{3(aq)} + 6\text{H}^+_{(aq)} + 6e^- \rightarrow \text{Cr}_{(s)} + 3\text{H}_2\text{O}$
 Calculate (i) how many grams of chromium will be plated out by 24,000 coulombs and (ii) how long will it take to the plate out 1.5 g of chromium by using 12.5 amp current. **(1993)**

67. The standard reduction potential of the Ag^+/Ag electrode at 298 K is 0.799 V. Given that for AgI , $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI . Also calculate the standard reduction potential of the $\text{I}^-/\text{AgI}/\text{Ag}$ electrode. (1994)
68. The Edison storage cells is represented as
 $\text{Fe}_{(s)} | \text{FeO}_{(s)} | \text{KOH}_{(aq)} | \text{Ni}_2\text{O}_{3(s)} | \text{Ni}_{(s)}$
 The half-cell reactions are:
 $\text{Ni}_2\text{O}_{3(s)} + \text{H}_2\text{O}_{(l)} + 2e^- \rightleftharpoons 2\text{NiO}_{(s)} + 2\text{OH}^-; E^\circ = +0.40 \text{ V}$
 $\text{FeO}_{(s)} + \text{H}_2\text{O}_{(l)} + 2e^- \rightleftharpoons \text{Fe}_{(s)} + 2\text{OH}^-; E^\circ = -0.87 \text{ V}$
 (i) What is the cell reaction?
 (ii) What is the cell EMF? How does it depend on the concentration of KOH ?
 (iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ? (1994)
69. Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. Explain. (1994)
70. An excess of liquid mercury is added to an acidified solution of $1.0 \times 10^{-3} \text{ M Fe}^{3+}$. It is found that 5% of Fe^{3+} remains at equilibrium at 25°C . Calculate $E^\circ_{\text{Hg}_2^{2+}/\text{Hg}}$, assuming that the only reaction that occurs is $2\text{Hg} + 2\text{Fe}^{3+} \longrightarrow \text{Hg}_2^{2+} + 2\text{Fe}^{2+}$.
 (Given $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$) (1995)
71. The standard reduction potential for Cu^{2+}/Cu is + 0.34 V. Calculate the reduction potential at $\text{pH} = 14$ for the above couple. K_{sp} of $\text{Cu}(\text{OH})_2$ is 1.0×10^{-19} . (1996)
72. Electrolysis of a solution of MnSO_4 in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the reaction:
 $\text{Mn}^{2+}_{(aq)} + 2\text{H}_2\text{O} \longrightarrow \text{MnO}_{2(s)} + 2\text{H}^+_{(aq)} + \text{H}_{2(g)}$
 Passing a current of 27 A for 2 hours gives only 1 kg of MnO_2 . What is the value of current efficiency? Write the reactions taking place at the cathode and at the anode. (1997)
73. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 amperes? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3 . (1997)
74. Calculate the equilibrium constant for the reaction
 $\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$
 (Given $E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44 \text{ V}$ and $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 \text{ V}$) (1997)
75. Calculate the equilibrium constant for the reaction, $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and I_3^-/I^- couples. (1998)
76. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the EMF of the cell $\text{Ag} | \text{Ag}^+ (\text{satd. Ag}_2\text{CrO}_4) || \text{Ag}^+ (0.1 \text{ M}) | \text{Ag}$ is 0.164 V at 298 K. (1998)
77. A cell, $\text{Ag} | \text{Ag}^+ || \text{Cu}^{2+} | \text{Cu}$, initially contains 1 M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 h. (1999)
78. Copper sulphate solution (250 ml) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to be with. (2000)
79. The following electrochemical cell has been set up.
 $\text{Pt}(1) | \text{Fe}^{3+}, \text{Fe}^{2+} (a = 1) | \text{Ce}^{4+}, \text{Ce}^{3+} (a = 1) | \text{Pt}(2)$
 $E^\circ (\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.77 \text{ V} ; E^\circ (\text{Ce}^{4+}/\text{Ce}^{3+}) = 1.61 \text{ V}$
 If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time? (2000)
80. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 35°C .
 $\text{Pt} | \text{H}_{2(g)} | \text{HCl}_{(aq)} | \text{AgCl}_{(s)} | \text{Ag}_{(s)}$
 (i) Write the cell reaction.
 (ii) Calculate ΔH° and ΔS° for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C .
 (iii) Calculate the solubility of AgCl in water at 25°C .
 Given: The standard reduction potential of the $\text{Ag}^+_{(aq)}/\text{Ag}_{(s)}$ couple is 0.80 V at 25°C . (2001)
81. Two students use same stock solution of ZnSO_4 and a solution of CuSO_4 . The EMF of one cell is 0.03 V higher than the other. The concentration of CuSO_4 in the cell with higher EMF value is 0.5 M. Find out the conc. of CuSO_4 in the other cell ($2.303 RT/F = 0.06$) (2003)
82. Find the equilibrium constant for the reaction,
 $\text{In}^{2+} + \text{Cu}^{2+} \longrightarrow \text{In}^{3+} + \text{Cu}^+$ at 298 K
 Given: $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15 \text{ V}; E^\circ_{\text{In}^{2+}/\text{In}^+} = -0.40 \text{ V}$
 $E^\circ_{\text{In}^{3+}/\text{In}^+} = -0.42 \text{ V}$ (2004)

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83. (a) For the reaction $\text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)} \rightleftharpoons \text{AgCl}_{(s)}$

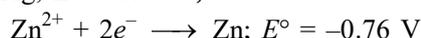
Species	ΔG_f° (kJ/mol)
$\text{Ag}^+_{(aq)}$	+77
$\text{Cl}^-_{(aq)}$	-129
$\text{AgCl}_{(s)}$	-109

Write the cell representation of above reaction and calculate E°_{cell} at 298 K.

Also find the solubility product of AgCl.

(b) If 6.539×10^{-2} g of metallic zinc is added to 100 ml saturated solution of AgCl. Find the value of $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$

How many moles of Ag will be precipitated in the above reaction. Given that



(It was given that Atomic mass of Zn = 65.39)

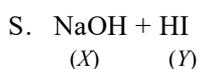
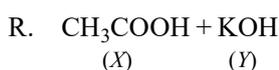
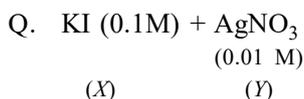
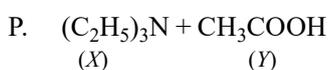
(2005)

84. We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14} . If 10^{-7} mole of AgNO_3 are added to 1 litre of this solution. Find conductivity (specific conductance) of this solution in terms of 10^{-7} Sm^{-1} units. Given, $\lambda^\circ_{(\text{Ag}^+)} = 6 \times 10^{-3} \text{ Sm}^2/\text{mol}$, $\lambda^\circ_{(\text{Br}^-)} = 8 \times 10^{-3} \text{ Sm}^2/\text{mol}$, $\lambda^\circ_{(\text{NO}_3^-)} = 7 \times 10^{-3} \text{ Sm}^2/\text{mol}$. (2006)

Matrix Match Type

85. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List I. The variation in conductivity of these reactions is given in List II. Match List I with List II and select the correct answer using the code given below the lists :

List I



List II

1. Conductivity decreases and then increases

2. Conductivity decreases and then does not change much

3. Conductivity increases and then does not change much

4. Conductivity does not change much and then increases

P Q R S

(a) 3 4 2 1

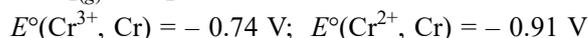
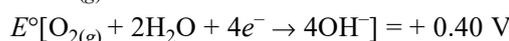
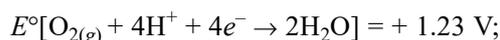
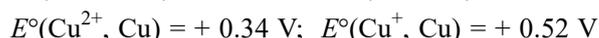
(b) 4 3 2 1

(c) 2 3 4 1

(d) 1 4 3 2

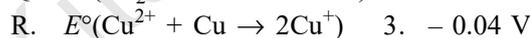
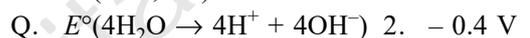
(2013)

86. The standard reduction potential data at 25°C is given below.



Match E° of the redox pair in List I with the values given in List II and select the correct answer using the code given below the lists:

List I



List II

1. -0.18 V

2. -0.4 V

3. -0.04 V

4. -0.83 V

P Q R S

(a) 4 1 2 3

(b) 2 3 4 1

(c) 1 2 3 4

(d) 3 4 1 2

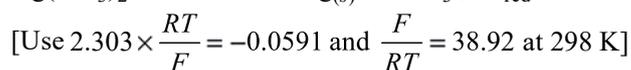
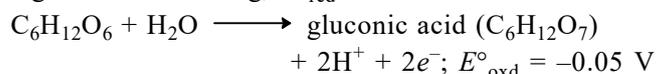
(2013)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension - 1

Tollen's reagent is used for the detection of aldehyde when a solution of AgNO_3 is added to glucose with NH_4OH then gluconic acid is formed.



87. $2\text{Ag}^+ + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \longrightarrow 2\text{Ag}_{(s)} + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+$
Find $\ln K$ of this reaction.

(a) 66.13

(b) 58.45

(c) 28.30

(d) 46.29

88. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?

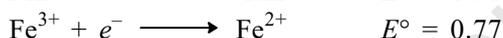
- (a) E_{oxd} will increase by a factor of 0.65 from E_{oxd}°
 (b) E_{oxd} will decrease by a factor of 0.65 from E_{oxd}°
 (c) E_{red} will increase by a factor of 0.65 from E_{red}°
 (d) E_{red} will decrease by a factor of 0.65 from E_{red}°

89. Ammonia is always added in this reaction. Which of the following must be incorrect?

- (a) NH_3 combines with Ag^+ to form a complex
 (b) $\text{Ag}(\text{NH}_3)_2^+$ is a stronger oxidising agent than Ag^+
 (c) In absence of NH_3 silver salt of gluconic acid is formed
 (d) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode. (2006)

Comprehension - 2

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential (E°) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to questions 14 to 16.



90. Among the following, identify the correct statement.

- (a) Chloride ion is oxidised by O_2
 (b) Fe^{2+} is oxidised by iodine
 (c) Iodide ion is oxidised by chlorine
 (d) Mn^{2+} is oxidised by chlorine.

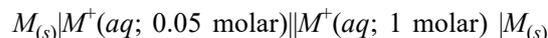
91. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because

- (a) O_2 oxidises Mn^{2+} to Mn^{3+}
 (b) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
 (c) Fe^{3+} oxidises H_2O to O_2
 (d) Mn^{3+} oxidises H_2O to O_2 . (2007)

Comprehension - 3

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting

potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is:



For the above electrolytic cell the magnitude of the cell potential $|E_{\text{cell}}| = 70 \text{ mV}$.

92. For the above cell

- (a) $E_{\text{cell}} < 0$; $\Delta G > 0$ (b) $E_{\text{cell}} > 0$; $\Delta G < 0$
 (c) $E_{\text{cell}} < 0$; $\Delta G^{\circ} > 0$ (d) $E_{\text{cell}} > 0$; $\Delta G^{\circ} < 0$

93. If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be

- (a) 35 mV (b) 70 mV
 (c) 140 mV (d) 700 mV (2010)

Comprehension - 4

The electrochemical cell shown below is a concentration cell.
 $M | M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2) || M^{2+} (0.001 mol dm⁻³) | M

The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

94. The value of ΔG (kJ mol⁻¹) for the given cell is (take 1 F = 96500 C mol⁻¹)

- (a) -5.7 (b) 5.7
 (c) 11.4 (d) -11.4

95. The solubility product (K_{sp} ; mol³ dm⁻⁹) of MX_2 at 298 K based on the information available for the given concentration cell is (take $2.303 \times R \times 298/F = 0.059 \text{ V}$)

- (a) 1×10^{-15} (b) 4×10^{-15}
 (c) 1×10^{-12} (d) 4×10^{-12} (2012)

Integer Answer Type

96. The difference in the oxidation numbers of the two types of sulphur atoms in $\text{Na}_2\text{S}_4\text{O}_6$ is (2011)

97. All the energy released from the reaction $X \rightarrow Y$, $\Delta_r G^{\circ} = -193 \text{ kJ mol}^{-1}$ is used for oxidizing M^+ as $M^+ \rightarrow M^{3+} + 2e^-$, $E^{\circ} = -0.25 \text{ V}$.

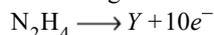
Under standard conditions, the number of moles of M^+ oxidized when one mole of X is converted to Y is $[F = 96500 \text{ C mol}^{-1}]$ (2015)

ANSWER KEY

1. (c) 2. (b) 3. (a) 4. (c) 5. (c) 6. (c)
 7. (d) 8. (c) 9. (a) 10. (b) 11. (a) 12. (c)
 13. (d) 14. (a) 15. (a) 16. (b) 17. (c) 18. (a)
 19. (a) 20. (d) 21. (b) 22. (c) 23. (b) 24. (a)
 25. (c) 26. (b) 27. (b) 28. (b) 29. (d) 30. (d)
 31. (d) 32. (b) 33. (None) 34. (a) 35. (a) 36. (a, b, d)
 37. (a, b) 38. (a, b) 39. (a, b, d) 40. (a, b) 41. Negative; greater
 42. Increased 43. False 44. 1.172 M 45. 27172 coulombs
46. (i) $3\text{Cu}_2\text{O} + 2\text{NO}_3^- + 14\text{H}^+ \longrightarrow 6\text{Cu}^{2+} + 2\text{NO} + 7\text{H}_2\text{O}$;
 (ii) $\text{K}_4\text{Fe}(\text{CN})_6 + 6\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} \longrightarrow 2\text{K}_2\text{SO}_4 + \text{FeSO}_4 + 3(\text{NH}_4)_2\text{SO}_4 + 6\text{CO}$
 (iii) $\text{C}_2\text{H}_5\text{OH} + 4\text{I}_2 + 6\text{OH}^- \longrightarrow \text{CHI}_3 + \text{HCOO}^- + 5\text{I}^- + 5\text{H}_2\text{O}$
48. 0.8042 A 50. 125.1 sec 51. 8.62 52. 265.03 ampere - hours. 54. 19.05 g
 55. 10^{-4} M 56. 190.5 g 57. 58.49 ml 58. 9.33×10^{-15} 59. 1.479×10^{-9} M
 60. 347.4 kJ 61. 5.128×10^{-18} mol L⁻¹ 62. 0.154 M 64. 48.71 hrs; 1.408 M
 65. 0.886 V; -0.046 V 66. 2.1554 g; 22.27 min 67. -0.148 V
 70. 0.7926 V 71. -0.22 V 72. $\text{Mn}^{2+} \longrightarrow \text{Mn}^{4+} + 2e^-$ (anode)
 $2\text{H}^+ + 2e^- \longrightarrow \text{H}_{2(\text{g})}$ (cathode) 73. 272.18 g; 1.02×10^4 cm²
74. 7.6×10^{12} 75. 6.25×10^7 76. 2.287×10^{-12} mol³ litre⁻³ 77. E_{cell} will increase by 0.01 V
 78. 7.95×10^{-5} mole⁻¹ 81. 0.05 M 82. 10^{10} 83. 10^{-10} ; 52.88; 10^{-5}
 84. 55 Sm⁻¹ 85. (a) 86. (d) 87. (b) 88. (c) 89. (d)
 90. (c) 91. (d) 92. (b) 93. (c) 94. (d) 95. (b)
 96. (5) 97. (4)

Explanations

- 1 (c): From the given information, we have



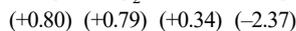
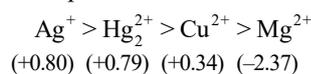
The oxidation state of N in $\text{N}_2\text{H}_4 = -2$ $\{\because 2x + 4 = 0 \text{ or } x = -2\}$
The two nitrogen atoms in Y (product) will balance the charge of $10e^-$. Hence the oxidation state of N will increase by +5 *i.e.* from -2 to +3.

2. (b): Current is carried by the movement of ions; cation towards the negative electrode (cathode) and anion towards the positive electrode (anode).
3. (a): More negative the value of reduction potential, stronger is the reducing property *i.e.* power to accept electrons.

4. (c): Let oxidation state of C in CH_2O be x , then we have
 $x + 2 + (-2) = 0$ or $x = 0$

5. (c): $\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1 \cdot I \cdot t}{Z_2 \cdot I \cdot t}$ or $\frac{Z_1}{Z_2} = \frac{E_1}{E_2}$

6. (c): The ions can be arranged as under on the basis of their reduction potential values

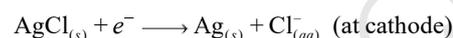


Mg^{2+} will not be reduced as its reduction potential value is much lower.

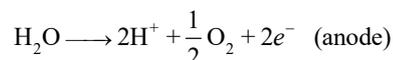
On the basis of above reduction potential values we can easily conclude that the deposition of metals will be in the order Ag, Hg, Cu.

7. (d): Charge of one mole (6.023×10^{23}) electrons = 96500 C.

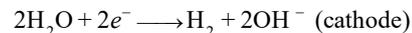
8. (c): $\text{H}_{2(g)} \longrightarrow 2\text{H}^+_{(aq)} + 2e^-$ (at anode)



9. (a): At anode water is oxidised instead of SO_4^{2-} .



At cathode water is reduced instead of Na^+



10. (b): Let the oxidation state of iron in $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}] \text{SO}_4$ be x .

The complex ion is $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{+2}$. In it we have

$$x + 5 \times 0 + 1 \times 0 = 2$$

$$\text{or } x = +2$$

11. (a): We know $E^\circ_{\text{cell}} = E^\circ_{\text{red (cathode)}} - E^\circ_{\text{red (anode)}}$
 $= -0.41 - (-0.76) = -0.41 + 0.76$
 $= 0.35 \text{ V}$

[Electrode with higher oxidation potential acts as anode]

12. (c): In $\text{Ba}(\text{H}_2\text{PO}_4)_2$, we have $2 + 2(2 + x - 4) = 0$

$$\text{or } 2 + 4 + 2x - 8 = 0$$

$$\text{or } 2x = 8 - 4 - 2 \quad \text{or } x = 2/2 = +1$$

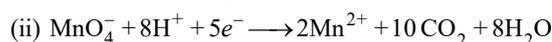
13. (d): The reaction can be represented as



In the products the most electronegative element is oxygen.

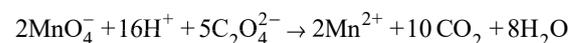
The oxidation state of oxygen is -1 in H_2O_2 which is a peroxide and -2 in BaSO_4 .

14. (a): To get the balanced reaction, we write two half reactions.



(Reduction)

To get balanced net reaction multiply (i) by 5 and (ii) by 2 and add, we get

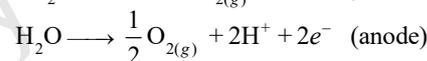
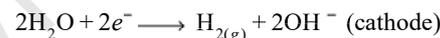


From this balanced equation we get various coefficients as 2, 5 and 16 for MnO_4^- , $\text{C}_2\text{O}_4^{2-}$ and H^+ respectively.

15. (a): At cathode, water is more easily reduced in comparison to Na^+ .

At anode, water is more easily oxidised in comparison to SO_4^{2-} .

The electrode reactions are:



16. (b): By convention the standard electrode potential (E°) for hydrogen electrode is taken as zero.

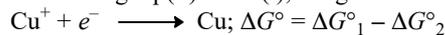
17. (c): (i) $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$;

$$\Delta G^\circ_1 = -nFE^\circ_1 = -2F \times 0.337$$



$$\Delta G^\circ_2 = -nFE^\circ_2 = -1F \times 0.153$$

Subtracting eq (ii) from (i), we get



$$= -2F \times 0.337 - (-1F \times 0.153)$$

$$= -0.674 F + 0.153 F = -0.521 F$$

$$E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{0.521F}{1 \times F} = 0.521 \text{ V}$$

18. (a): From the given data, we have following information

Z is reduced and Y is oxidized

Z is reduced and X is oxidized

Y is reduced and X is oxidized

Thus 'Y' will oxidize 'X' and it will not oxidize 'Z'.

19. (a): Oxidation number of S in S_8 is zero, in S_2F_2 it is +1 ($2x - 2 = 0$ or $x = +1$) and in H_2S it is

$$-2 \quad (+2 + x = 0 \text{ or } x = -2)$$

20. (d): Oxidation numbers are

Mn in MnO_4^- is +7

Cr in $[\text{Cr}(\text{CN})_6]^{3-}$ is +3 $(x - 6 = -3 \text{ or } x = +3)$

Ni in NiF_6^{2-} is +4 $(x - 6 = -2 \text{ or } x = +4)$

and Cr in CrO_2Cl_2 is +6 $(x + 2 \times (-2) + 2 \times (-1) = 0$

or $x - 4 - 2 = 0$ or $x = +6$).

Redox Reactions and Electrochemistry

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21. (b): $M^+ + X^- \longrightarrow M + X$ is spontaneous because for the cell represented by $M/M^+ \parallel X/X^-$, the value of E° is positive i.e. $(0.44 - 0.33) \text{ V} = 0.11 \text{ V}$.

22. (c): The ionic mobilities of K^+ and NO_3^- ions are nearly the same. It helps to keep the cathode and anode half-cells neutral at all times.

23. (b): On moving down in group 1 (i.e. from Li^+ to K^+), the ionic radii increases and so the degree of solvation decreases. It results in decrease in the effective size of the ion and so the ionic mobility increases. Therefore equivalent conductance at infinite dilution increases on moving down. Hence the correct order is



24. (a): The oxidation of Cl^- ion by MnO_4^- can be represented as $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{Cl}_{2(g)}$

The cell corresponding to the above equation is



$$E_{\text{cell}}^\circ = (1.51 - 1.40) \text{ V} = 0.11 \text{ V}$$

Since E_{cell}° is positive so ΔG° ($\Delta G^\circ = -nFE^\circ$) must be negative and so this cell is feasible.

MnO_4^- will oxidise both Fe^{2+} ions and Cl^- ions simultaneously and so it cannot be used for the quantitative estimation of aq. $\text{Fe}(\text{NO}_3)_2$.

25. (c): In an electrolytic cell, the electrons do not flow themselves. The migration of ions towards oppositely charged electrodes, indirectly constitutes the flow of electrons from cathode to anode through internal supply.

26. (b): Cell reaction is, $\text{Zn} + \text{Fe}^{2+} \rightarrow \text{Zn}^{2+} + \text{Fe}$

$$\text{Using, } E = E^\circ - \frac{0.059}{2} \log \frac{10^{-2}}{10^{-3}}$$

$$(n = 2, [\text{Zn}^{2+}] = 10^{-2}, [\text{Fe}^{2+}] = 10^{-3})$$

Since $E = 0.2905$

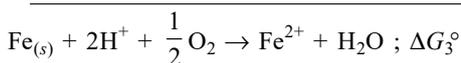
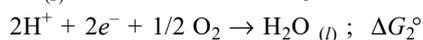
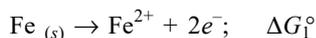
$$\therefore 0.2905 = E^\circ - 0.0295$$

$$\text{or } E^\circ = 0.2905 + 0.0295 = 0.3200 \text{ V}$$

$$\text{Again } E^\circ = \frac{0.059}{2} \log K_{\text{eq}}$$

$$\therefore 0.32 = \frac{0.059}{2} \log K_{\text{eq}} \quad \text{or } K_{\text{eq}} = 10^{0.0295}$$

27. (b): Applying $\Delta G^\circ = -nFE^\circ$.



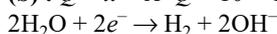
Applying $\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$

$$\Delta G_3^\circ = (-2F \times 0.44) + (-2F \times 1.23)$$

$$= -(2 \times 96500 \times 0.44 + 2 \times 96500 \times 1.23) = -322310 \text{ J}$$

$$\therefore \Delta G_3^\circ = -322 \text{ kJ}$$

28. (b): $Q = it$ or $Q = 10 \times 10^{-3} \times t$... (i)



0.01 mole of H_2 is liberated by 0.02 Faraday of charge.

i.e., $Q = 0.02 \times 96500$... (ii)

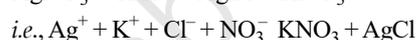
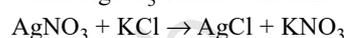
from (i) and (ii), $10 \times 10^{-3} \times t = 0.02 \times 96500$

$$\therefore t = \frac{0.02 \times 96500}{10 \times 10^{-3}} = 19.3 \times 10^4 \text{ sec}$$

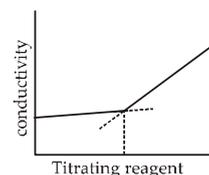
29. (d): Precipitation titration can be effectively followed by conductometric methods, though not so well as acid-base titrations which are characterised by sharp breaks because both the hydrogen ion and hydroxyl ion have very high equivalent ionic conductances.

In precipitation titrations, one pair of ions is substituted for another and as one experimenter has a choice of reagents, good results can usually be obtained. If a cation is to be precipitated, titrant whose cation has the smallest possible mobility is selected and if an anion is to be precipitated, a titrant whose anion has as small mobility as possible, in this way the maximum, possible change in conductance during a titration is assured.

When AgNO_3 reacts with KCl



In this titration, in the early stages of the titration, addition of silver nitrate, the conductance does not change very much because the Cl^- ions are replaced by NO_3^- ions; both have almost same ionic conductances. After the end point is passed, the excess of the added (i.e., addition of volume of reagent) salt causes a sharp increase in conductance.



30. (d): In haematite (Fe_2O_3) oxidation number of iron

$$2x + 3 \times (-2) = 0, x = 3$$

Magnetite (Fe_3O_4) is an equimolar mixture of FeO and Fe_2O_3

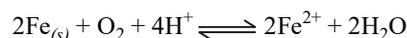
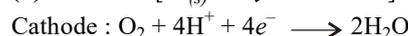
Therefore, oxidation number of iron in FeO

$$\text{FeO} : x - 2 = 0 \Rightarrow x = 2$$

Oxidation number of iron in Fe_2O_3

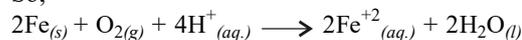
$$2x + 3 \times (-2) = 0; x = 3$$

31. (d): Anode: $[\text{Fe}_{(s)} \longrightarrow \text{Fe}^{2+} + 2e^-] \times 2$



$$Q = \frac{[\text{Fe}^{2+}]^2}{[\text{H}^+]^4 \times \text{P}_{\text{O}_2}} = \frac{[10^{-3}]^2}{[10^{-3}]^4 \times 0.1}$$

So,



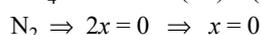
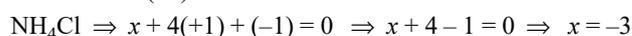
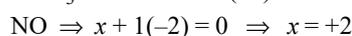
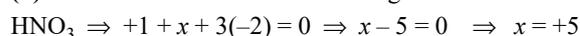
$n = 4$ (no. of electrons involved)

From Nernst's equation,

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q = 1.67 - \frac{0.0591}{4} \log \frac{(10^{-3})^2}{(10^{-3})^4 \times 0.1}$$

$$\{\therefore [\text{H}^+] = 10^{-\text{pH}}\} = 1.67 - 0.1034 = 1.57 \text{ V}$$

32. (b): Let the oxidation state of nitrogen be x .

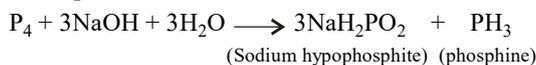


Decreasing order of oxidation state is

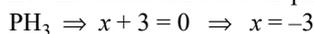


33. None is correct.

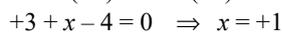
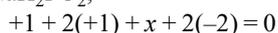
White phosphorus dissolved in NaOH on boiling in inert atmosphere.



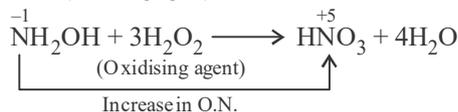
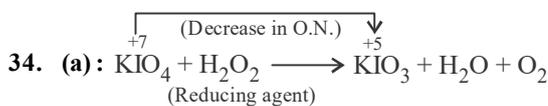
Let the oxidation state of phosphorus be x .



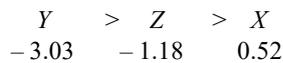
In NaH_2PO_2 ,



Thus the given reaction is disproportionation as oxidation state changes from 0 to -3 and $+1$. But none of the given option is correct.



35. (a): Lower the reduction potential stronger is the reducing nature. Thus the correct order is



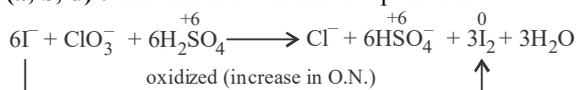
36. (a, b, d): The substances which have lower reduction potentials are strong reducing agents while those which have higher reduction potentials are stronger oxidising agents.

$\therefore E_{M^{n+}/M}^0$ for V, Fe and Hg are lower than that of NO_3^- , so NO_3^- will oxidise V, Fe and Hg.

37. (a, b): Molar conductivity and electromotive forces are intensive properties.

38. (a, b): Salt bridge keeps the solutions in two half-cells electrically neutral. It prevents transference or diffusion of the ions from one half-cell to the other.

39. (a, b, d): The balanced chemical equation is



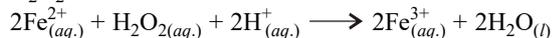
40. (a, b): (a) H_2O_2 in alkaline medium reduces Fe^{3+} to Fe^{2+} ,
 $2\text{Fe}_{(aq)}^{3+} + \text{H}_2\text{O}_{2(aq)} + 2\text{OH}_{(aq)}^- \longrightarrow 2\text{Fe}_{(aq)}^{2+} + \text{O}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$

(b) Na_2O_2 in water,

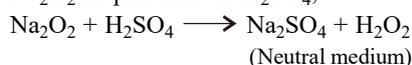


(H_2O_2 in alkaline medium reduces Fe^{3+} to Fe^{2+})

(c) H_2O_2 in acidic medium oxidises Fe^{2+} to Fe^{3+} .



(d) Na_2O_2 in presence of H_2SO_4 ,



In alkaline medium, reducing action of H_2O_2 is more effective.

41. Negative, greater

42. Increased

43. **False**: At 273 K the value of E is 0.0541 (by calculation) and not 0.0591 which is the value at 298 K. In the formula the value of T is different in two cases.

44. Calculation of g eq. of nickel deposited

Here, $I = 3.7 \text{ A}$, $t = 6 \times 60 \times 60$ seconds

\therefore Total quantity of electricity flown, $Q = It$

$Q = 3.7 \times 6 \times 60 \times 60$ coulombs = 79920 coulombs

Since 96500 coulombs of electricity deposits 1 g-eq. of Ni.

$$79920 \text{ coulombs of electricity} = \frac{1}{96500} \times 79920 \text{ g-eq.}$$

$$= 0.828 \text{ g-eq. of Ni}$$

Calculation of molarity of the solution

No. of moles of Ni in 0.828 gm eq. = $\frac{\text{gm eq. of Ni}}{\text{valency}}$

$$\frac{0.828}{2} [\text{valency of Ni in } \text{Ni}(\text{NO}_3)_2 = 2] = 0.414 \text{ mole}$$

$$\text{No. of moles of Ni in 0.5 litre of the original solution} = \frac{2 \times 0.5}{1}$$

$$= 1.0 \text{ mole}$$

Since nickel deposited = 0.414 mole

Nickel left in 0.5 litre of solution = $1.0 - 0.414 = 0.586$ mole

$$\therefore \text{Molarity of nickel} = \frac{0.586 \times 1}{0.5} \text{ M} = 1.172 \text{ M}$$

45. Equivalent of $\text{Cu} = \frac{63.5}{2} = 31.75$

Area to be plated = $10 \times 10 = 100$ sq. cm.

Thickness of layer = 10^{-2} cm

\therefore Volume of copper required = $100 \times 10^{-2} \text{ cm}^3 = 1 \text{ c.c.}$

Weight of 1 c.c. of Cu = 8.94 g

According to Faradays Law of Electrolysis

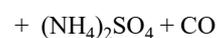
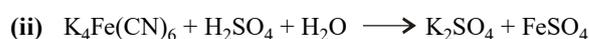
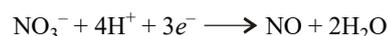
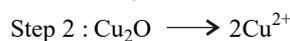
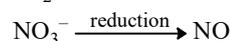
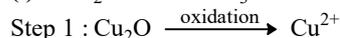
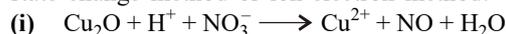
To deposit 31.75 g Cu electricity needed = 96500 coulombs

To deposit 8.94 g Cu electricity needed

$$= \frac{96500}{31.75} \times 8.94 \text{ Coulombs}$$

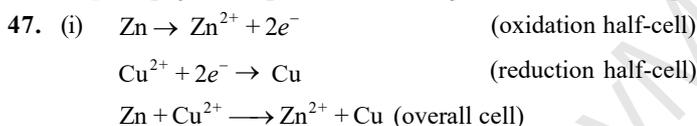
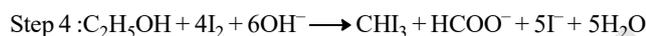
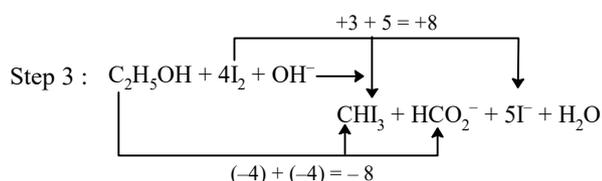
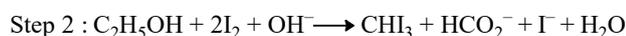
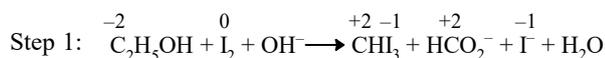
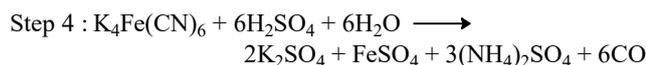
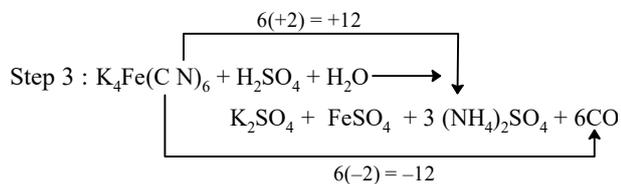
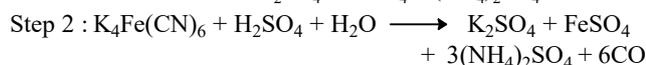
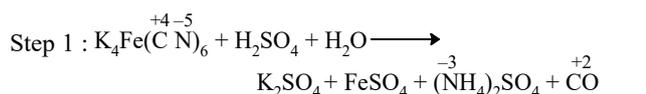
$$= 27172 \text{ coulombs.}$$

46. The equations may be balanced following either oxidation-state change method or ion-electron method.



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(ii) E. M. F. of the cells :

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.350 - (-0.763) = 0.350 + 0.763 = 1.113 \text{ V.}$$

(iii) Since E_{cell}° is positive so the ΔG value is negative and thus the reaction is spontaneous.

48. Weight of gold deposited in first cell = 9.85 g

Atomic weight of gold = 197

Oxidation number of gold = +3

$$\therefore \text{Equivalent weight of gold} = \frac{197}{3}$$

Using the relation, $W = z. i. t.$ we get

$$\begin{aligned} \text{Charge required to deposit 1g eq. (197/3) of gold} \\ = 1F = 96500 \text{ coulombs} \end{aligned}$$

$$\begin{aligned} \therefore \text{Charge required to deposit 9.85 g of gold} &= \frac{1}{197/3} \times 9.85 F \\ &= \frac{3 \times 9.85}{197} \times 96500 \text{ C} = 14475 \text{ C} \end{aligned}$$

Amount of copper deposited at cathode in second cell

From Faraday's second law, we have

$$\frac{\text{Weight of Cu}}{\text{Weight of Au}} = \frac{\text{Eq. wt. of Cu}}{\text{Eq. wt. of Au}}$$

$$\text{or weight of Cu} = \frac{9.85 \times 63.5 \times 3}{197 \times 2} \quad [\text{Eq. wt. of Cu} = 63.5/2,$$

$$\text{Eq. wt. of Au} = 197/3] = 4.7625 \text{ g}$$

$$\text{Since current} = \frac{Q}{T} = \frac{14475}{5 \times 3600} \text{ A} = 0.8042 \text{ A}$$

49. (i) $4\text{Zn} + \text{NO}_3^- + 10\text{H}^+ \longrightarrow 4\text{Zn}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O}$
 (ii) $\text{Cr}_2\text{O}_7^{2-} + 3\text{C}_2\text{H}_4\text{O} + 8\text{H}^+ \longrightarrow 3\text{C}_2\text{H}_4\text{O}_2 + 2\text{Cr}^{3+} + 4\text{H}_2\text{O}$
 (iii) $2\text{HNO}_3 + 6\text{HCl} \longrightarrow 2\text{NO} + 3\text{Cl}_2 + 4\text{H}_2\text{O}$
 (iv) $2\text{Ce}^{3+} + \text{S}_2\text{O}_8^{2-} \longrightarrow 2\text{Ce}^{4+} + 2\text{SO}_4^{2-}$
 (v) $\text{Cl}_2 + 2\text{OH}^- \longrightarrow \text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O}$
 (vi) $2\text{Mn}^{2+} + 5\text{PbO}_2 + 4\text{H}^+ \longrightarrow 2\text{MnO}_4^- + 5\text{Pb}^{2+} + 2\text{H}_2\text{O}$
 (vii) $4\text{S} + 6\text{OH}^- \longrightarrow 2\text{S}^{2-} + \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O}$
 (viii) $\text{ClO}_3^- + 6\text{I}^- + 6\text{H}_2\text{SO}_4 \longrightarrow \text{Cl}^- + 6\text{HSO}_4^- + 3\text{I}_2 + 3\text{H}_2\text{O}$
 (ix) $6\text{Ag}^+ + \text{AsH}_3 + 4\text{H}_2\text{O} \longrightarrow 6\text{Ag} + \text{H}_3\text{AsO}_4 + 8\text{H}^+$

50. Surface volume = area \times thickness
 $= 80 \text{ cm}^2 \times 0.005/10 \text{ cm} = 0.04 \text{ cm}^3$
 Mass of silver (Ag) deposited = volume \times density
 $= 0.04 \times 10.5 = 0.42 \text{ g}$

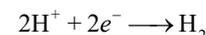
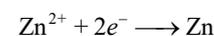
The cell reaction is : $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$

$$\text{Since } \frac{W}{E} = \frac{Q}{F} = \frac{I.t.}{F}$$

$$\therefore \frac{0.42}{108} = \frac{i \times t}{96500} \quad [\text{eq. wt. of Ag, } E = 108, 1F = 96500 \text{ C}]$$

$$\text{or } \frac{0.42}{108} = \frac{3 \times t}{96500} \quad \text{or } t = 125.1 \text{ sec.}$$

51. The half-cell reactions are



We know that

$$E_{\text{Zn/Zn}^{2+}} = E_{\text{Zn/Zn}^{2+}}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Zn}]}$$

$$\begin{aligned} \therefore E_{\text{Zn/Zn}^{2+}} &= 0.76 - \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log \frac{0.1}{1} \\ &= 0.76 - (-0.03) = 0.79 \text{ V} \end{aligned}$$

Also

$$\begin{aligned} E_{\text{H}^+/\text{H}_2} &= E_{\text{H}^+/\text{H}_2}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{H}_2]}{[\text{H}^+]^2} \\ &= 0 - \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log \frac{1}{[\text{H}^+]^2} \\ &= 0.0591 \log [\text{H}^+] = -0.0591 \text{ pH} \end{aligned}$$

$$\text{Since } E_{\text{cell}} = E_{\text{Zn/Zn}^{2+}} + E_{\text{H}^+/\text{H}_2}$$

$$\text{or } 0.28 = 0.79 - 0.0591 \text{ pH}$$

$$\text{or } \text{pH} = \frac{0.79 - 0.28}{0.0591} = \frac{0.51}{0.0591} = 8.62$$

52. Density of 39% H_2SO_4 before discharge = 1.294 g/ml

So, amount of H_2SO_4 in solution before discharge

$$= \frac{3500 \times 1.294 \times 39}{100} \text{ g} = 1766.3 \text{ g}$$

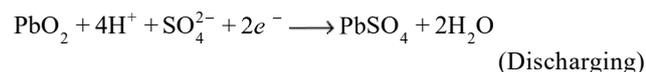
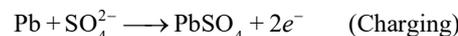
Density of 20% H_2SO_4 after discharge = 1.139 g/ml

So, amount of H_2SO_4 in solution after discharge

$$= \frac{3500 \times 1.139 \times 20}{100} \text{ g} = 797.3 \text{ g}$$

Amount of H_2SO_4 consumed by battery = $(1766.3 - 797.3) \text{ g}$
 $= 969 \text{ g} = 9.887 \text{ moles}$

The reaction that takes place during charging and discharging of a battery are



Adding the above two reactions, we get



From this it is evident that 2 moles of H_2SO_4 are consumed to give 2 moles of electrons *i.e.* 2 Faraday of current.

1 mole of $\text{H}_2\text{SO}_4 = 1\text{F}$ of current = 96500 coulombs

Thus the number of ampere-hours

$$= \frac{96500 \times 9.887}{60 \times 60} = 265.03 \text{ ampere-hours.}$$

53. Oxidation number of iodine in various species:

Species	O.N.
I_2	0
HI	-1
ICl	+1
HIO_4	+7

Thus the arrangement in increasing order of O.N. of iodine is $\text{HI} < \text{I}_2 < \text{ICl} < \text{HIO}_4$.

54. Current = $\frac{\text{Watt}}{\text{Volt}} = \frac{100}{110} = 0.91 \text{ amp.}$

Since $Q = I \times t$

$$\therefore Q = 0.91 \times 10 \times 3600 \text{ coulomb}$$

$$= 32760 \times \frac{1}{96500} \text{ Faraday} = 0.339 \text{ Faraday}$$

Hence weight of cadmium deposited

$$= \frac{0.339 \times 112.4}{2} = 19.05 \text{ g}$$

55. $E_{\text{cell}} = 0.059/n \log C_2/C_1$ [For a concentration cell]
 The given cell is a concentration cell because in it both electrodes are of the same element.

$$\text{or } 0.118 = \frac{0.059}{1} \log \frac{C_{\text{H}^+}}{10^{-6}} \quad \text{or } \log \frac{C_{\text{H}^+}}{10^{-6}} = \frac{0.118}{0.059}$$

$$\text{or } C_{\text{H}^+} = 10^{-4} \text{ M}$$

56. It is evident that for 22.4 L of H_2 gas we need 2 Faraday electricity.

\therefore For 67.2 L of H_2 gas the electricity required

$$= \frac{2}{22.4} \times 67.2 \text{ F} = 6\text{F}$$

Using the relation, $Q = I \times t$, we get

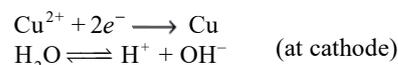
$$6 \times 96500 = I \times 15 \times 60$$

$$\text{or } I = \frac{6 \times 96500}{15 \times 60} = 643.3 \text{ ampere}$$

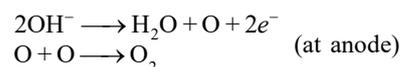
Since amount of copper deposited by 1F = g-eq. wt. of copper = 63.5/2 g

$$\therefore \text{Amount of copper deposited by } 6\text{F} = \frac{63.5}{2} \times 6 = 190.5 \text{ g}$$

57. The following reactions occur at the electrodes:



At this electrode Cu^{2+} ions will be discharged as long as such ions are present in solution. Only after that H^+ ions will get discharged.



So O_2 gas will be obtained at anode.

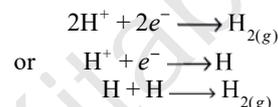
From Faraday's second law

31.75 g of Cu = 8 g of oxygen = 5.6 L of oxygen at NTP

$$\text{or } 0.4 \text{ g of Cu} = \frac{5.6}{31.75} \times 0.4 \text{ L of O}_2 \text{ at NTP}$$

$$= 0.07055 \text{ L or } 70.55 \text{ ml}$$

When all Cu^{2+} ions get discharged, H^+ will start getting discharged to liberate H_2 gas at cathode.



During this period O_2 is being discharged at anode.

In this case, we should calculate the amount of H_2 collected at cathode.

8 g of $\text{O}_2 \equiv 1 \text{ g of H}_2$

5.6 L of O_2 at NTP = 11.2 L of H_2 at NTP

Quantity of electricity passed after 1st electrolysis,

$$Q = I \times t = 1.2 \times 7 \times 60 = 504 \text{ Coulombs}$$

\therefore Volume of O_2 liberated by 504 C (at anode)

$$= \frac{5.6}{96500} \times 504 \text{ L} = 0.02924 \text{ L} = 29.24 \text{ ml}$$

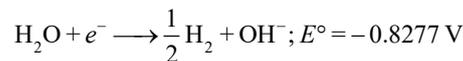
Volume of H_2 liberated by 504 C (at cathode)

$$= \frac{11.2}{96500} \times 504 \text{ ml} = 0.05849 \text{ L} = 58.49 \text{ ml}$$

Hence total volume of O_2 liberated = 70.55 + 29.24 = 99.79 ml

Volume of H_2 liberated = 58.49 ml

58. $\text{H}_2\text{O} + \frac{1}{2}\text{H}_{2(g)} \rightleftharpoons \text{H}_3\text{O}^+ + e^-; E^\circ = 0.00\text{V}$
 [Oxidation Half - cell]



[Reduction Half - cell]

From the above two, we get net reactions as:



Thus $n = 1$ [number of electrons involved = 1]

using the relation,

$$E = \frac{0.059}{n} \log K_c$$

$$\text{or } \log K_c = \frac{n}{0.059} \times E^\circ_{\text{cell}} = \frac{-0.8277}{0.059} \quad [\because n = 1]$$

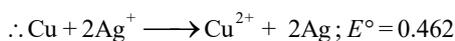
$$\text{or } \log K_c = -14.03 \quad \text{or } K_c = 9.33 \times 10^{-15}$$

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59. Given: $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.337 \text{ V}$; $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.799$

$$E^\circ_{\text{Ag}^+/\text{Ag}} + E^\circ_{\text{Cu}/\text{Cu}^{2+}} = 0.799 - 0.337 = 0.462$$



Thus the cell will work if we have copper anode and silver cathode.

We know that

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$\text{or } E_{\text{cell}} = 0 - \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \quad [\because E^\circ = 0]$$

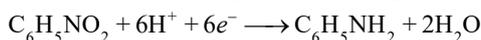
$$\text{or } 0.462 = \frac{0.059}{2} \log \frac{0.01}{[\text{Ag}^+]^2}$$

$$\text{or } \frac{462 \times 2}{59} = \log 10^{-2} - \log [\text{Ag}^+]^2$$

$$\text{or } \log [\text{Ag}^+]^2 = -17.66$$

$$\therefore [\text{Ag}^+]^2 = 2.188 \times 10^{-18} \quad \text{or } [\text{Ag}^+] = 1.479 \times 10^{-9} \text{ M}$$

60. The reactions taking place can be represented as



Thus 123 g of $\text{C}_6\text{H}_5\text{NO}_2$ (Nitrobenzene) requires hydrogen = 6g

$$\begin{aligned} \therefore \text{Hydrogen required by 12.3 g of } \text{C}_6\text{H}_5\text{NO}_2 \\ = \frac{6}{123} \times 12.3 = 0.6 \text{ g} \end{aligned}$$

Since 1 g of hydrogen is liberated by 1 Faraday (96500 C)

$$\begin{aligned} \therefore 0.6 \text{ g of hydrogen will be liberated by} \\ = \frac{96500}{1} \times 0.6 \text{ C} = 57900 \text{ C} \end{aligned}$$

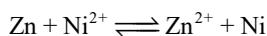
As the current efficiency is only 50%

$$\therefore \text{Quantity of electricity required} = \frac{100}{50} \times 57900 \text{ C} = 115800 \text{ C}$$

$$\begin{aligned} \text{Energy consumed} &= 3 \times 115800 \text{ volt coulombs} \\ &= 347400 \text{ J} = 347.4 \text{ kJ} \end{aligned}$$

61. The cell may be represented as $\text{Zn}/\text{Zn}^{2+} \parallel \text{Ni}^{2+}/\text{Ni}$

Net cell reaction is



$$\text{EMF of cell: } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} \quad [\because n = 2]$$

$$= E^\circ_{\text{Ni}^{2+}/\text{Ni}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]}$$

$$\text{or } E_{\text{cell}} = -0.24 - (-0.75) - 0.0295 \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]}$$

$$\text{or } E_{\text{cell}} = 0.51 - 0.0295 \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} \quad \dots(i)$$

At equilibrium $E_{\text{cell}} = 0$

Let the $[\text{Ni}^{2+}]$ at equilibrium be x mol/litre.

Then $[\text{Zn}^{2+}] = (1-x)$ $[\because 1 \text{ mole } \text{Ni}^{2+} \text{ gives } 1 \text{ mole } \text{Zn}^{2+}]$

$$\therefore 0.0295 \log \frac{(1-x)}{x} = 0.51$$

$$\text{or } \log \frac{(1-x)}{x} = \frac{0.51}{0.0295} = 17.29 \quad \text{or } \frac{(1-x)}{x} = 1.95 \times 10^{17}$$

$$\begin{aligned} \text{or } x &= \frac{1}{1.95 \times 10^{17}} \quad [(1-x) \approx 1] \\ &= 5.128 \times 10^{-18} \text{ mol L}^{-1} \end{aligned}$$

62. $I = \frac{1.70 \times 90}{100}$ ampere

$$\therefore \text{Eq. of } \text{Zn}^{2+} \text{ lost} = \frac{I \cdot t}{96500} = \frac{1.70 \times 90 \times 230}{100 \times 96500} = 3.646 \times 10^{-3}$$

$$\therefore \text{Meq. of } \text{Zn}^{2+} \text{ lost} = 3.646$$

$$\text{Initial Meq. of } \text{Zn}^{2+} = 300 \times 0.160 \times 2$$

$$(\text{For } \text{Zn}^{2+}, \text{Meq.} = M \times 2 \times V_{(\text{in ml})})$$

$$48 \times 2 = 96$$

$$\therefore \text{Meq. of } \text{Zn}^{2+} \text{ left in solution} = 96 - 3.646 = 92.354$$

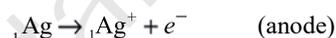
$$\therefore \text{Concentration of } \text{ZnSO}_4 \text{ solution} = \frac{92.354}{2 \times 300} = 0.154 \text{ M}$$

63. The given cell is

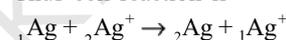


Anode Cathode

The reaction of the electrodes are



Thus cell reaction is



[Note: subscript 1 is for anode and 2 is for cathode species]

$$\text{EMF of cell, } E_{\text{cell}} = E^\circ - \frac{0.059}{1} \log \frac{[{}_1\text{Ag}^+]}{[{}_2\text{Ag}^+]} \quad (\because n = 1)$$

$$\text{Now } K_{sp} (\text{AgCl}) = [\text{Ag}^+][\text{Cl}^-]$$

$$\text{or } 2.8 \times 10^{-10} = [\text{Ag}^+] (0.2)$$

$$\text{or } [{}_1\text{Ag}^+] = \frac{2.8 \times 10^{-10}}{0.2} = 1.4 \times 10^{-9} \text{ M}$$

$$\text{For } \text{AgBr}, K_{sp} (\text{AgBr}) = [\text{Ag}^+][\text{Br}^-]$$

$$\text{or } 3.3 \times 10^{-13} = [\text{Ag}^+] (0.001)$$

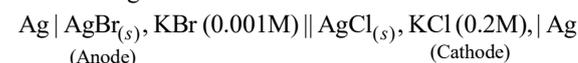
$$\text{or } [{}_2\text{Ag}^+] = \frac{3.3 \times 10^{-13}}{0.001} = 3.3 \times 10^{-10}$$

$$\text{or } E = E^\circ - \frac{0.059}{1} \log \frac{(1.4 \times 10^{-9})}{(3.3 \times 10^{-10})}$$

$$= 0 - 0.059 \log 14/3.3 = -0.037 \text{ V}$$

The negative value of E_{cell} indicates that the reaction as written is not spontaneous. For the reaction to be spontaneous EMF should be positive and thus the above reaction be reversed (*i.e.* the polarities be reversed).

Hence the galvanic cell is



(Anode)

(Cathode)

Thus $\text{Ag}|\text{AgBr}_{(s)}$ acts as anode and $\text{AgCl}|\text{Ag}$ acts as cathode.

64. $2\text{Cl}^-_{(aq)} + 2\text{H}_2\text{O} \longrightarrow 2\text{OH}^-_{(aq)} + \text{H}_{2(g)} + \text{Cl}_{2(g)}$

The electrode reactions are



Current, $I = \frac{62}{100} \times 25 = 15.5$ amperes (62% efficiency)

Weight of Cl_2 evolved = 1 kg or 1000 g

$$= \frac{1000}{71} \text{ moles} = 14.08 \text{ moles}$$

Using the relation, $W = \frac{E.I.t.}{96500}$ we get,

$$1000 = \frac{35.5 \times 15.5 \times t}{96500}$$

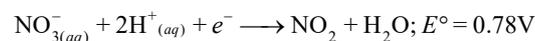
or $t = 175374.83$ sec = 48.71 hrs.

Since number of moles of Cl_2 produced = 14.08 moles

$\therefore \text{OH}^-$ released in electrolysis = 2×14.08 moles

Hence molarity of $\text{OH}^- = \frac{2 \times 14.08}{20} = 1.408 \text{ M}$

65. (i) The half-cell reaction is



According to Nernst equation

$$E = E^\circ - \frac{0.59}{1} \log \frac{[\text{NO}_2][\text{H}_2\text{O}]}{[\text{NO}_3^-][\text{H}^+]^2} \quad [:\because n=1]$$

$$= 0.78 - 0.59 \log 1/(8)^2$$

$$= 0.78 - (-0.106) = 0.886 \text{ V}$$

(ii) In neutral solution $[\text{H}^+] = 10^{-7}$

$$\therefore E = 0.78 - \frac{0.059}{1} \log \frac{1}{(10^{-7})^2}$$

$$= 0.78 - 0.059 \times 14 = 0.78 - 0.826 = -0.046 \text{ V}$$

66. $\text{CrO}_3 + 6\text{H}^+ + 6e^- \longrightarrow \text{Cr} + 3\text{H}_2\text{O}$

From the above equation we find the 6 mol of electrons are required to deposit 1 mol of Cr.

(i) Weight of Cr deposited by $6 \times 96500 \text{ C} = 52 \text{ g}$

$\therefore 24000 \text{ C}$ of electricity will deposit

$$\text{Cr} = \frac{52}{6 \times 96500} \times 24000 \text{ g} = 2.1554 \text{ g}$$

(ii) Amount of electricity required for depositing 1 mol of Cr (or 52 g of Cr) = $6 \times 96500 \text{ C}$

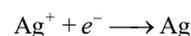
$$\therefore \text{Amount of electricity required to deposit 1.5 g}$$

$$= \frac{6 \times 96500}{52} \times 1.5 \text{ C} = 16071.9 \text{ C}$$

Using the relation $Q = It$. we get

$$\text{or } t = \frac{16071.9}{12.5} = 1336.15 \text{ s} = 22.27 \text{ min}$$

67. The electrode reaction is



Using Nernst equation,

$$E = E^\circ - \frac{0.059}{1} \log \frac{1}{[\text{Ag}^+]} \quad [:\because n=1]$$

In saturated solution of AgI,



$$[\text{Ag}^+] = [\text{I}^-]; K_{sp} = 8.7 \times 10^{-17}$$

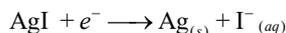
$$\therefore [\text{Ag}^+][\text{I}^-] = 8.7 \times 10^{-17} \text{ or } [\text{Ag}^+] = \sqrt{8.7 \times 10^{-17}}$$

$$(\therefore [\text{Ag}^+] = [\text{I}^-])$$

or $[\text{Ag}^+] = 9.327 \times 10^{-4} \text{ M}$

$$\therefore E = 0.799 - 0.059 \log \frac{1}{9.327 \times 10^{-4}} = 0.325 \text{ V}$$

The standard reduction potential for the electrode $\text{I}^-/\text{AgI}/\text{Ag}$ is



$$\therefore E = E^\circ - \frac{0.059}{1} \log \frac{[\text{Ag}][\text{I}^-]}{[\text{AgI}]} \quad [:\because n=1]$$

$$\text{or } E = E^\circ - \frac{0.059}{1} \log [\text{I}^-] \quad [:\because [\text{Ag}] = [\text{AgI}] = 1, \text{ both solids}]$$

$$\text{or } 0.325 = E^\circ - \frac{0.059}{1} \log (9.327 \times 10^{-9})$$

$$\text{or } E^\circ = 0.325 + 0.059 \log (9.327 \times 10^{-9})$$

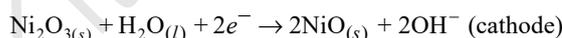
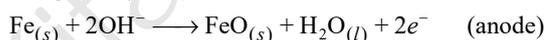
$$= 0.325 + 0.059 (-9 + 0.9697) = 0.325 - 0.059 \times 8.0303$$

$$= 0.325 - 0.4737877 = -0.148 \text{ V}$$

68. (i) $E^\circ_{\text{Ni}_2\text{O}_3/\text{NiO}} = +0.40 \text{ V}; E^\circ_{\text{FeO}/\text{Fe}} = -0.87 \text{ V}$

$$\therefore E^\circ_{\text{NiO}/\text{Ni}_2\text{O}_3} = -0.40 \text{ V}; E^\circ_{\text{Fe}/\text{FeO}} = +0.87 \text{ V}$$

Since $E^\circ_{\text{Ox.pot.}}$ for $\text{Fe}|\text{FeO} > E^\circ_{\text{Ox.pot.}}$ for $\text{NiO}/\text{Ni}_2\text{O}_3$, so the redox changes may be written as follows:



Net reaction : $\text{Fe}_{(s)} + \text{Ni}_2\text{O}_{3(s)} \rightarrow \text{FeO}_{(s)} + 2\text{NiO}_{(s)}$

$$(ii) E_{\text{cell}} = E^\circ_{\text{ox.pot.}} (\text{Fe}/\text{FeO}) + E^\circ_{\text{ox.pot.}} (\text{Ni}_2\text{O}_3/\text{NiO})$$

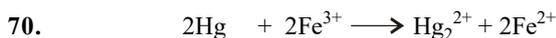
$$= 0.87 + 0.40 = 1.27 \text{ V}$$

It does not depend on concentration of OH^- .

$$(iii) \text{Electrical energy, } \Delta G = nFE_{\text{cell}} = 2 \times 96500 \times 1.27$$

$$= 2.45 \times 10^5 \text{ J} = 245 \text{ kJ}$$

69. The thin protective layer of aluminium oxide is formed on the surface and it protects the metal from attack of water and air and makes it stable.



Initial moles	1.0×10^{-3}	0	0
Eqm.	$\frac{5 \times 1.0 \times 10^{-3}}{100}$	$\frac{95 \times 1 \times 10^{-3}}{100 \times 2}$	$\frac{95 \times 10^{-3}}{100}$
moles	$= 0.05 \times 10^{-3}$	$= 0.475 \times 10^{-3}$	$= 0.95 \times 10^{-3}$

$$\text{Now } E = E^\circ - \frac{0.059}{n} \log \frac{[\text{Hg}_2^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

At equilibrium $E = 0$

$$\therefore 0 = E^\circ - \frac{0.059}{2} \log \frac{(0.475 \times 10^{-3})(0.95 \times 10^{-3})^2}{(0.05 \times 10^{-3})^2}$$

$$\text{or } E^\circ_{\text{cell}} = \frac{0.059}{2} \times (-0.766) = -0.0226 \text{ V}$$

$$\text{Also } E^\circ_{\text{cell}} = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^\circ_{\text{Hg}_2^{2+}/\text{Hg}}$$

$$\therefore -0.0226 = 0.77 - E^\circ_{\text{Hg}_2^{2+}/\text{Hg}}$$

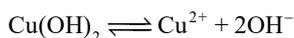
$$\text{or } E^\circ_{\text{Hg}_2^{2+}/\text{Hg}} = 0.77 + 0.0226 = 0.7926 \text{ V}$$

71. At pH = 14, $[\text{H}^+] = 1 \times 10^{-14} \text{ M}; [\text{OH}^-] = 10^0 = 1 \text{ M}$
 $[\therefore [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}]$

Redox Reactions and Electrochemistry

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Cu(OH)₂ ionises as follows:

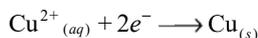


$$\therefore K_{sp} \text{ of Cu(OH)}_2 = [\text{Cu}^{2+}][\text{OH}^-]^2$$

$$\text{or } 1.0 \times 10^{-19} = [\text{Cu}^{2+}](1)^2$$

$$\text{or } [\text{Cu}^{2+}] = 1.0 \times 10^{-19} \text{ M}$$

The standard electrode potential of Cu²⁺/Cu is represented as follows:



Using Nernst equation

$$E = E^\circ - \frac{0.059}{n} \log \frac{1}{[\text{Cu}^{2+}]}$$

$$= 0.34 - \frac{0.059}{2} \log \frac{1}{1 \times 10^{-19}} \quad [n = 2]$$

$$= 0.34 - \frac{0.059}{2} \log(10^{19}) = 0.34 - 0.0295 \times 19$$

$$= (0.34 - 0.56) = -0.22 \text{ V}$$

72. Using the relation, $W = \frac{E.I.t.}{96500}$, we get

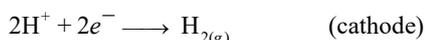
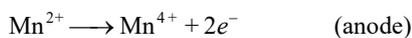
$$1000 = \frac{87}{2} \times \frac{I \times 24 \times 60 \times 60}{96500}$$

$$\left[\text{Eq. wt. of Mn} = \frac{87}{2} \text{ in case of Mn}^{2+} \right]$$

$$\text{or } I = \frac{1000 \times 96500 \times 2}{87 \times 24 \times 60 \times 60} \text{ amperes} = 25.6 \text{ amperes.}$$

$$\text{Current efficiency} = \frac{25.6}{27} \times 100 = 94.8\%$$

Following reactions are involved:



73. Using $W_{\text{Ag}} = \frac{E.I.t.}{96500}$;

$$\text{we get, } W = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500} = 272.18 \text{ g}$$

$$\text{Volume of Ag} = \frac{272.18}{10.5} = 25.92 \text{ ml}$$

$$\therefore \text{Surface area} = \frac{25.92}{0.00254} = 1.02 \times 10^4 \text{ cm}^2.$$

74. $E^\circ_{\text{cell}} = \frac{0.059}{1} \log K_c \quad [n = 1]$

$$\text{or } E^\circ_{\text{cell}} = E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}} + E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = -0.68 + 1.44 = 0.76 \text{ V}$$

$$\therefore 0.76 = 0.59 \log K_c$$

$$\text{or } \log K_c = \frac{0.76}{0.059} = 12.8814 \quad \text{or } K_c = 7.6 \times 10^{12}$$

75. $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$

For the above change at equilibrium, $E = 0$

Using the relation

$$E = E^\circ - \frac{0.059}{2} \log K_c \quad [n = 2]$$

$$\text{or } 0 = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} + E^\circ_{\text{I}^-/\text{I}_3^-} - \frac{0.059}{2} \log K_c$$

$$\text{or } 0 = 0.77 - 0.54 - \frac{0.059}{2} \log K_c$$

$$\text{or } 0 = 0.23 - \frac{0.059}{2} \log K_c$$

$$\text{or } \frac{0.059}{2} \log K_c = 0.23 \quad \text{or } \log K_c = \frac{0.23 \times 2}{0.059}$$

$$\text{or } \log K_c = 7.796 \quad \text{or } K_c = 6.25 \times 10^7$$

76. $\text{Ag} | \text{Ag}^+ (\text{Ag}_2\text{CrO}_4 \text{ sol. saturated}) || \text{Ag}^+ | \text{Ag};$

0.1 M

$$E_{\text{cell}} = 0.164 \text{ V at 298 K.}$$

$$\text{We have } E_{\text{cell}} = E^\circ_{\text{Ag}/\text{Ag}^+} + E^\circ_{\text{Ag}^+/\text{Ag}} + \frac{0.059}{1} \log_{10} \frac{[\text{Ag}^+]_{\text{R.H.S.}}}{[\text{Ag}^+]_{\text{L.H.S.}}}$$

$$\text{or } 0.164 = 0 + \frac{0.059}{1} \log_{10} \frac{0.1}{[\text{Ag}^+]_{\text{L.H.S.}}}$$

$$\therefore [\text{Ag}^+]_{\text{L.H.S.}} = 1.66 \times 10^{-4} \text{ M}$$

$$\text{Now } K_{sp} \text{ for } \text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$\text{Since } [\text{Ag}^+]_{\text{L.H.S.}} = 1.66 \times 10^{-4} \text{ M}$$

$$\therefore [\text{CrO}_4^{2-}]_{\text{L.H.S.}} = \frac{1.66 \times 10^{-4}}{2} \text{ M}$$

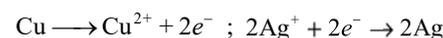
$$\therefore K_{sp} = [1.66 \times 10^{-4}]^2 \left[\frac{1.66 \times 10^{-4}}{2} \right]$$

$$K_{sp} = 2.287 \times 10^{-12} \text{ mol}^3 \text{ litre}^{-3}$$

77. Since $E^\circ_{\text{ox}}(\text{Cu}) > E^\circ_{\text{ox}}(\text{Ag}^+)$

So the given cell will not work [$\therefore E^\circ_{\text{cell}} = \text{negative}$]

The equation for electrochemical cell will be



Thus the *emf* of cell $\text{Cu}|\text{Cu}^{2+}||\text{Ag}^+|\text{Ag}$ will be

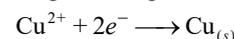
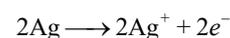
$$E_{\text{cell}} = E^\circ_{\text{cell}} + \frac{0.059}{2} \log \frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]}$$

$$\text{or } E_{\text{cell}} = E^\circ_{\text{ox}}(\text{Cu}) - E^\circ_{\text{Red}}(\text{Ag}) + \frac{0.059}{2} \log \frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]}$$

$$\text{or } E_{\text{cell}} = E^\circ_{\text{cell}} \quad (\because [\text{Ag}^+] = 1\text{M}, [\text{Cu}^{2+}] = 1\text{M})$$

After we have passed 9.65 amperes for a hour (i.e. $9.65 \times 60 \times 60$ coulombs) during which the cell reactions are reversed, the Ag metal passes in solution as Ag⁺ and Cu²⁺ ions get discharged as Cu metal.

Following reactions occur during the period when current is passed.



$$\text{So Ag}^+ \text{ formed} = \frac{9.65 \times 60 \times 60}{96500} = 0.36 \text{ equivalents}$$

$$= 0.36 \text{ mole} \quad [\text{For Ag, Mol. wt.} = \text{Eq. wt.}]$$

$$\text{Cu}^{2+} \text{ ions discharged} = \frac{9.65 \times 60 \times 60}{96500} = 0.36 \text{ equivalents}$$

$$= 0.36/2 \text{ moles} = 0.18 \text{ moles}$$

$$\text{Thus } [\text{Ag}^+] \text{ left} = 1 + 0.36 = 1.36 \text{ mole}$$

$$[\text{Cu}^{2+}] \text{ left} = 1 - 0.18 = 0.18 \text{ mole}$$

The EMF is given by

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.59}{2} \log \frac{(1.36)^2}{0.82} = E_{\text{cell}}^{\circ} + 0.01 \text{ V}$$

Hence E_{cell} will increase by 0.01V.

78. Number of Faradays of electricity passed

$$= \frac{2 \times 10^{-3} \times 16 \times 60}{96500} = 1.989 \times 10^{-5}$$

$$\text{Moles of } \text{Cu}^{2+} \text{ deposited} = \frac{1.989 \times 10^{-5}}{2} = 0.9945 \times 10^{-5}$$

According to Beer's law, Absorbance \propto Concentration

\therefore Reduction of absorption to 50% indicates that the initial moles of Cu^{2+} would be two times of moles of Cu^{2+} reduced.

$$\therefore \text{Initial moles of } \text{Cu}^{2+} = 0.9945 \times 10^{-5} \times 2$$

$$= 1.989 \times 10^{-5}$$

$$\text{Hence concentration of } \text{CuSO}_4 = \frac{1.989 \times 10^{-5} \times 1000}{250}$$

$$= 7.95 \times 10^{-5} \text{ mole}^{-1}$$

79. Given $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} = 1.61 \text{ V}$; $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.77 \text{ V}$

For E_{cell}° to be positive, the following reaction occurs



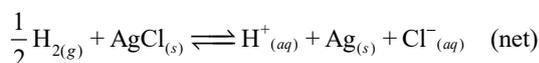
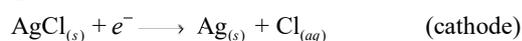
Hence $\text{Ce}^{4+}/\text{Ce}^{3+}$ electrode is cathode.

and $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrode is anode.

In such a case the current will flow from Ce electrode (cathode) to Fe electrode (anode).

The current will decrease with time.

80. (i) The half-cell reaction are



(ii) Since $\Delta S^{\circ} = nF \cdot \frac{dE}{dt}$

$$\therefore \Delta S^{\circ} = 1 \times 96500 \times \left(\frac{-0.02}{20} \right)$$

$$[\therefore n = 1, F = 96500; dt = (35 - 15) = 20^{\circ} \text{ C}]$$

$$dE = (0.21 - 0.23) = -0.02 \text{ V} = -96.5 \text{ J/K mole}$$

$$\text{Since } \Delta G^{\circ} = -nFE^{\circ}$$

$$\text{So } \Delta G^{\circ} = -1 \times 0.23 \times 96500 \text{ J mole} \quad [E_{15^{\circ} \text{ C}}^{\circ} = 0.23 \text{ V}]$$

$$\text{or } \Delta G^{\circ} = -22195 \text{ J mole}$$

$$\text{Again } \Delta H^{\circ} = \Delta G^{\circ} + T\Delta S^{\circ}$$

$$\therefore \Delta H^{\circ} = -22195 + 288 \times (-96.5) = -49.87 \text{ J/mole}$$

(iii) E_{cell}° for $\text{Pt}|\text{H}_{2(g)}|\text{HCl}_{(aq)}|\text{AgCl}_{(s)}|\text{Ag}_{(s)}$ is 0.23 volt at 15° C .

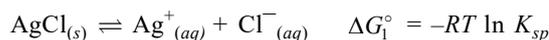
$$\text{Since } \frac{\Delta E}{\Delta T} = \frac{0.02}{20} = 0.001.$$

Therefore E_{cell}° at 25° C

$$E_{\text{cell}}^{\circ} = 0.23 - 0.001 \times 0.23 = 0.22977 \text{ V.}$$

Since E° of anode is zero volt.

$$\therefore E_{\text{Cl}^{-}/\text{AgCl}/\text{Ag}}^{\circ} \text{ at } 25^{\circ} \text{ C} = 0.22977 \text{ V.}$$



$$\Delta G_1^{\circ} + \Delta G_2^{\circ} = \Delta G_3^{\circ}$$

$$\text{Solving, } RT \ln K_{sp} + F \times 0.8 = F \times 0.22977$$

$$\text{or } \frac{2.303RT}{F} \log K_{sp} + 0.8 = 0.22977$$

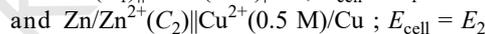
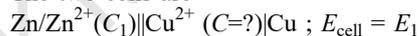
$$0.059 \log K_{sp} + 0.8 = 0.22977; K_{sp} = 2.163 \times 10^{-10}$$

$$\therefore \text{Solubility of AgCl at } 25^{\circ} \text{ C} = 1.47 \times 10^{-5} \text{ M.}$$

81. The cell is represented as:

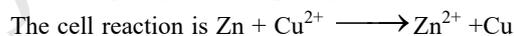


The two cells are



Where $E_2 > E_1$

$$\text{Given, } E_2 - E_1 = 0.03; C_2 = C_1$$



$$\text{So } E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\text{or } E_1 = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{C_1}{C}$$

$$\text{and } E_2 = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{C_2}{0.5}$$

Since same ZnSO_4 solution is used in both cells $C_1 = C_2$

$$\text{Thus } E_2 - E_1 = \frac{0.059}{2} \left[\log \frac{C_1}{C} \times \frac{0.5}{C_1} \right]$$

$$\text{or } 0.03 = \frac{0.06}{2} \log \frac{0.5}{C} \quad [\because E_2 - E_1 = 0.03]$$

$$\text{or } \log \frac{0.5}{C} = \frac{0.03 \times 2}{0.06} = 1$$

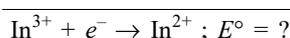
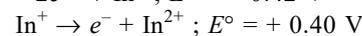
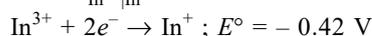
$$\text{or } C = 0.05 \text{ M}$$

82. $\text{Cu}^{2+}_{(aq)} + \text{In}^{2+}_{(aq)} \rightleftharpoons \text{Cu}^{+}_{(aq)} + \text{In}^{3+}_{(aq)}$

$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}^{+}}^{\circ} - E_{\text{In}^{3+}/\text{In}^{2+}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = 0.15 - E_{\text{In}^{3+}/\text{In}^{2+}}^{\circ} \quad \dots (i)$$

For $E_{\text{In}^{3+}/\text{In}^{2+}}^{\circ}$:



$$\text{Applying, } \Delta G^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$$

$$\text{or, } -nFE^{\circ} = -2F(-0.42) - 1F(0.40)$$

Redox Reactions and Electrochemistry

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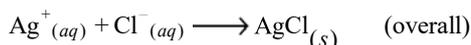
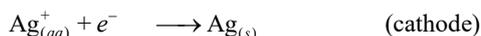
$$\text{or, } -E^\circ = 0.84 - 0.40; \quad E^\circ_{\text{In}^{3+}|\text{In}^{2+}} = -0.44 \text{ V}$$

$$\therefore E^\circ_{\text{cell}} = 0.15 + 0.44 = 0.59 \text{ V}$$

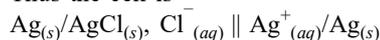
$$\therefore E^\circ = \frac{2.303RT}{nF} \log K_c \quad \therefore 0.59 = \frac{0.059}{1} \log K_c$$

$$\Rightarrow K_c = \text{antilog } 10 = 10^{10}$$

83. (a) From the given data, we can write the following reactions



Thus the cell is



$$\Delta G^\circ_R = \Delta G^\circ(\text{AgCl}) - [\Delta G^\circ(\text{Ag}^+) + \Delta G^\circ(\text{Cl}^-)]$$

$$= -109 - (-129 + 77) = -57 \text{ kJ mol}^{-1} = -57000 \text{ J mol}^{-1}$$

$$\text{Since } \Delta G^\circ_R = -nFE^\circ_{\text{cell}}$$

$$\therefore -57000 = -1 \times 96500 \times E^\circ_{\text{cell}} \quad [\because n = 1]$$

$$\text{or } E_{\text{cell}} = 0.59 \text{ V}$$

$$\text{or } E^\circ_{\text{cell}} = \frac{57000}{96500} \log K_c$$

$$\text{Again } E^\circ_{\text{cell}} = \frac{0.059}{n} \log K_c$$

$$\therefore E^\circ_{\text{cell}} = \frac{0.059}{n} \log \frac{[\text{AgCl}]}{[\text{Ag}^+][\text{Cl}^-]}$$

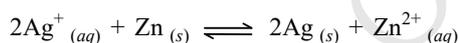
$$\text{or } E^\circ_{\text{cell}} = \frac{0.059}{1} \log \left[\frac{1}{K_{sp}} \right] \quad [K_{sp}(\text{AgCl}) = [\text{Ag}^+][\text{Cl}^-]]$$

$$\text{or } 0.59 = -0.059 \log K_{sp} \quad \text{or } \log K_{sp} = -10$$

$$\text{or } K_{sp} = 10^{-10}$$

$$(b) [\text{Ag}^+]_{\text{sat}} = \sqrt{K_{sp}(\text{AgCl})} = 10^{-5} \text{ M}$$

$$\text{Moles of Zn} = \frac{6.539 \times 10^{-2}}{65.39} = 10^{-3}$$



Applying Nernst equation for the above reaction,

$$E = E^\circ - \frac{0.059}{2} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$\text{At equilibrium, } E_{\text{cell}} = 0; \quad E^\circ_{\text{cell}} = 1.56 \text{ V}$$

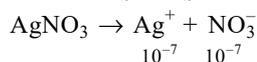
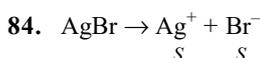
$$0 = 1.56 - \frac{0.059}{2} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$\text{or, } \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{1.56 \times 2}{0.059} = 52.88 = 52.9$$

Since the equilibrium constant K_c for the reaction,



is very high, i.e. $10^{52.88}$, so the reaction will almost go to completion. Therefore, the moles of Ag precipitated is 10^{-5} .



Now the solubility of $\text{Ag}^+ = S + 10^{-7}$

$$K_{sp} = [\text{Ag}^+][\text{Br}^-] = (S + 10^{-7}) \times S$$

$$12 \times 10^{-14} = S^2 + 10^{-7}S$$

$$\Rightarrow S^2 + 10^{-7}S - 12 \times 10^{-14} = 0 \quad \therefore S = 3 \times 10^{-7} \text{ M}$$

$$[\text{Br}^-] = 3 \times 10^{-7} \times 10^3 = 3 \times 10^{-4} \text{ m}^3$$

$$[\text{NO}_3^-] = 10^{-7} \times 10^3 = 10^{-4} \text{ m}^3$$

$$[\text{Ag}^+] = S + 10^{-7} = 3 \times 10^{-7} + 10^{-7}$$

$$= 4 \times 10^{-7} \times 10^3 = 4 \times 10^{-4} \text{ m}^3$$

$$\text{As } \Lambda_m = \frac{\kappa \times 1000}{C}$$

$$\kappa_{\text{Br}^-} = 3 \times 10^{-4} \times 8 \times 10^{-3} = 24 \times 10^{-7}$$

$$\kappa_{\text{Ag}^+} = 4 \times 10^{-4} \times 6 \times 10^{-3} = 24 \times 10^{-7}$$

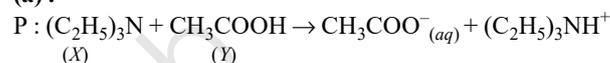
$$\kappa_{\text{NO}_3^-} = 7 \times 10^{-3} \times 10^{-4} = 7 \times 10^{-7}$$

$$\kappa_{\text{Total}} = \kappa_{\text{Br}^-} + \kappa_{\text{Ag}^+} + \kappa_{\text{NO}_3^-}$$

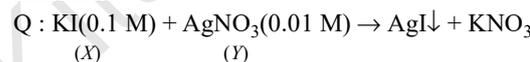
$$= 24 \times 10^{-7} + 24 \times 10^{-7} + 7 \times 10^{-7} = 55 \times 10^{-7} \text{ Sm}^{-1}$$

$$= 55 \text{ Sm}^{-1} \text{ (in terms of } 10^{-7} \text{ Sm}^{-1}\text{)}$$

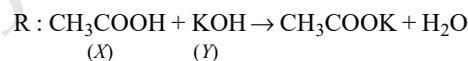
85. (a):



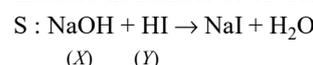
Initially conductivity increases due to ion formation after that it becomes practically constant because X alone cannot form ions.



Number of ions in the solution remains constant until all the AgNO_3 precipitated as AgI . Thereafter conductance increases due to increase in number of ions.

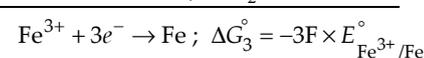
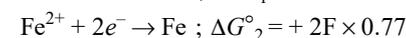
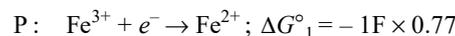


Initially conductance decreases due to the decrease in the number of OH^- ions thereafter it slowly increases due to increase in number of H^+ ions.



Initially it decreases due to decrease in H^+ ions and then increases due to increase in OH^- ions.

86. (d):

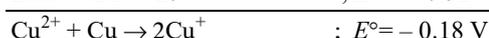
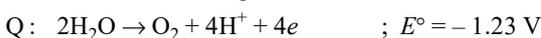


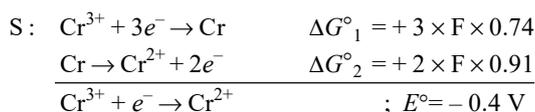
$$\Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2$$

$$-3F \times E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.77F + 0.88F$$

$$-3E^\circ_{\text{Fe}^{3+}/\text{Fe}} = 0.11 \text{ (V)}$$

$$E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -\frac{0.11 \text{ (V)}}{3} = -0.036 \text{ (V)} = 0.04 \text{ V}$$





$$87. \text{ (b): } E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$

$$0.8 - 0.05 = \frac{1 \times 0.0591}{2 \times 2.303} \ln K$$

$$\therefore \ln K = \frac{(0.8 - 0.05) \times 2 \times 2.303}{0.0591} = 58.45$$

88. (c) : On increasing concentration of NH_3 , the concentration of H^+ ion decreases.

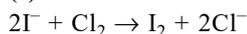
$$E_{\text{red}} = E^\circ_{\text{red}} - \frac{0.0591}{n} \log[\text{H}^+]$$

$$E_{\text{red}} = 0 - \frac{0.0591}{1} \log 10^{-11} = -0.0591 \times (-11) = 0.65$$

89. (d) : NH_3 has no effect on the standard reduction potential.

- The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 25°C is called standard electrode potential.
- The standard reduction potential of an electrode means that reduction reaction is taking place at the electrode.

90. (c) : For the cell reaction,

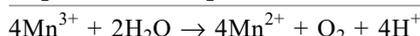
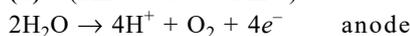


$$E^\circ_{\text{cell}} = E^\circ_{\text{Cl}_2/\text{Cl}^-} + E^\circ_{\text{I}^-/\text{I}_2} = 1.36 - 0.54$$

$$E^\circ = 0.82 \text{ V}$$

E° is positive, so iodide ion is oxidised by chlorine.

91. (d) : $(\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}) \times 4$ cathode



$$E^\circ = E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}} + E^\circ_{\text{H}_2\text{O}/\text{O}_2} = 1.50 + (-1.23) = 0.27 \text{ V}$$

Reaction is feasible.

92. (b) : The net cell reaction is



According to Nernst equation

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[M^+]_{(0.05M)}}{[M^+]_{(1M)}}$$

$$= E^\circ_{\text{cell}} - \frac{0.059}{1} \log(0.05)$$

$$= 0 - 0.059 \log(5 \times 10^{-2}) = -0.059[-2 + \log 5]$$

$\therefore E_{\text{cell}} = +ve$ or $E_{\text{cell}} > 0$ and

hence $\Delta G < 0$ as $\Delta G = -nFE_{\text{cell}}$.

$$93. \text{ (c): } E_{\text{cell}(2)} = E^\circ_{\text{cell}} - \frac{0.0538}{1} \log \left(\frac{0.0025}{1} \right) = -0.0538 \log(0.0025)$$

$$E_{\text{cell}(1)} = 70 \text{ mV}$$

$$\Rightarrow \frac{E_{\text{cell}(2)}}{E_{\text{cell}(1)}} = \frac{\log(0.0025)}{\log(0.05)} = \frac{-2.6}{-1.3} \approx 2$$

$$\Rightarrow E_{\text{cell}(2)} = 70 \times 2 = 140 \text{ mV.}$$

94. (d) : $\Delta G = -nEF$



Thus, $n = 2$

$$\Delta G = -2 \times 0.059 \times 96500 = -11.387 \text{ joule/mol} = -11.4 \text{ kJ/mol}$$

95. (b) : For concentration cell,

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_{2(\text{RHS})}}{C_{1(\text{LHS})}}$$

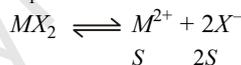
$$E_{\text{cell}} = 0.059 \text{ V}, C_{2(\text{RHS})} = 0.001$$

$$0.059 = \frac{0.0591}{2} \log \frac{0.001}{C_1}$$

$$\Rightarrow \frac{2 \times 0.059}{0.0591} = \log \frac{0.001}{C_1} \Rightarrow \text{antilog } 2 = \frac{0.001}{C_1}$$

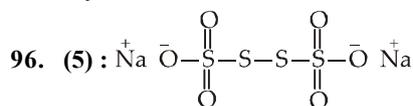
$$\Rightarrow C_1 = \frac{0.001}{100} = 10^{-5}$$

$$C_1 = \text{concentration or solubility of } M^{2+} = 10^{-5}$$



$$K_{sp} = S(2S)^2 = 4S^3$$

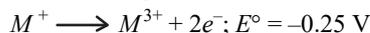
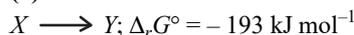
$$K_{sp} = 4 \times (10^{-5})^3 = 4 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$$



S will have oxidation number = +5, 0

Difference in oxidation number = 5

97. (4) : Given :



$$F = 96500 \text{ C mol}^{-1}$$

Let 193 kJ is used for oxidising x moles of M^+ .

For 1 mole of M^+ ,

$$\Delta G^\circ = -nFE^\circ$$

$$= -2 \times 96500 \times (-0.25)$$

$$= 48250 \text{ J mol}^{-1} = 48.25 \text{ kJ mol}^{-1}$$

Thus, no. of moles of M^+ oxidized when one mole of X is

$$\text{converted to } Y = \frac{193}{48.25} = 4.$$



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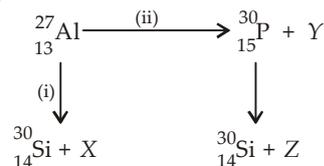
Nuclear Chemistry

Multiple Choice Questions with ONE Correct Answer

1. If uranium (mass number 238 and atomic number 92) emits an α - particle, the product has mass number and atomic number
 (a) 236 and 92 (b) 234 and 90
 (c) 238 and 90 (d) 236 and 90
 (1981)
2. The radiations from a naturally occurring radioactive substance, as seen after deflection by a magnetic field in one direction, are
 (a) definitely alpha rays
 (b) definitely beta rays
 (c) both alpha and beta rays
 (d) either alpha or beta rays
 (1984)
3. The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to
 (a) $\frac{1}{2}$ g (b) $\frac{1}{4}$ g (c) $\frac{1}{8}$ g (d) $\frac{1}{16}$ g
 (1986)
4. $^{27}_{13}\text{Al}$ is a stable isotope, $^{29}_{13}\text{Al}$ is expected to disintegrate by
 (a) α - emission (b) β - emission
 (c) positron emission (d) proton emission
 (1996)
5. The number of neutrons accompanying the formation of $^{139}_{54}\text{Xe}$ and $^{94}_{38}\text{Sr}$ from the absorption of a slow neutron by $^{235}_{92}\text{U}$, followed by nuclear fission is
 (a) 0 (b) 2 (c) 1 (d) 3
 (1999)
6. ^{23}Na is the more stable isotope of Na. Find out the process by which $^{24}_{11}\text{Na}$ can undergo radioactive decay.
 (a) β^- emission (b) α emission
 (c) β^+ emission (d) K electron capture
 (2003)

7. A positron is emitted from $^{23}_{11}\text{Na}$. The ratio of the atomic mass and atomic number of the resulting nuclide is
 (a) $\frac{22}{10}$ (b) $\frac{22}{11}$
 (c) $\frac{23}{10}$ (d) $\frac{23}{12}$
 (2007)

8. Bombardment of aluminium by α -particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Products X, Y and Z respectively are,



- (a) proton, neutron, positron
 (b) neutron, positron, proton
 (c) proton, positron, neutron
 (d) positron, proton, neutron
 (2011)

Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

9. Nuclear reactions accompanied with emission of neutron(s) are
 (a) $^{27}_{13}\text{Al} + ^4_2\text{He} \rightarrow ^{30}_{15}\text{P}$ (b) $^{12}_6\text{C} + ^1_1\text{H} \rightarrow ^{13}_7\text{N}$
 (c) $^{30}_{15}\text{P} \rightarrow ^{30}_{14}\text{Si} + ^0_{-1}\text{e}$
 (d) $^{241}_{96}\text{Am} + ^4_2\text{He} \rightarrow ^{244}_{97}\text{Bk} + ^0_{-1}\text{e}$
 (1988)
10. In the nuclear transmutation,
 $^9_4\text{Be} + \text{X} \rightarrow ^8_4\text{Be} + \text{Y}$
 (X, Y) is(are)
 (a) (γ , n) (b) (p, D)
 (c) (n, D) (d) (γ , p)
 (2013)
11. An element ^A_ZM undergoes an α - emission followed by two successive β -emissions. The element formed is
 (1982)

Fill in the Blanks

12. The number of neutrons in the parent nucleus which gives ${}^1_7\text{N}$ on beta emission is (1985)
13. A radioactive nucleus decays emitting one alpha and two beta particles; the daughter nucleus is of the parent. (1989)

True / False

14. In β^- emission from a nucleus the atomic number of the daughter element decreases by one. (1990)

Subjective Problems

15. Find
- The total number of neutrons and
 - the total mass of neutrons in 7 mg of ${}^{14}\text{C}$. (Assume that mass of neutron = mass of a hydrogen atom) (1980)
16. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half life of 5770 years. What is the rate constant (in years^{-1}) for the decay? What fraction would remain after 11540 years? (1984)
17. ${}^{234}_{90}\text{Th}$ disintegrates to give ${}^{206}_{82}\text{Pb}$ as the final product. How many alpha and beta particles are emitted during this process? (1986)
18. An experiment requires minimum beta activity product at the rate of 346 beta particles per minute. The half-life period of ${}^{99}_{42}\text{Mo}$, which is a beta emitter is 66.6 hours. Find the minimum amount of ${}^{99}_{42}\text{Mo}$, required to carry out the experiment in 6.909 hours. (1989)
19. The nuclidic ratio, ${}^3_1\text{H}$ to ${}^1_1\text{H}$ in a sample of water is $8.0 \times 10^{-18} : 1$. Tritium undergoes decay with a half-life period of 12.3 years. How many tritium atoms would 10.0 g of such a sample contain 40 years after the original sample is collected? (1992)
20. One of the hazards of nuclear explosion is the generation of ${}^{90}\text{Sr}$ and its subsequent incorporation in bones. This nuclide has a half-life of 28.1 years. Suppose one microgram was absorbed by a new-born child, how much ${}^{90}\text{Sr}$ will remain in his bones after 20 years? (1995)
21. ${}^{227}\text{Ac}$ has a half-life of 21.8 years with respect to radioactive decay. The decay follows two parallel paths; one leading to ${}^{227}\text{Th}$ and the other to ${}^{223}\text{Fr}$. The percentage yields of these two daughter nuclides are 2.0 and 98.0 respectively. What are the decay constants (λ) for each of the separate paths? (1996)

22. Write a balanced equation for the reaction of ${}^{14}\text{N}$ with α -particle. (1997)
23. ${}^{238}_{92}\text{U}$ is radioactive and it emits α and β particles to form ${}^{206}_{82}\text{Pb}$. Calculate the number of α and β particles emitted in this conversion. An ore of ${}^{238}_{92}\text{U}$ is found to contain ${}^{238}_{92}\text{U}$ and ${}^{206}_{82}\text{Pb}$ in the weight ratio of 1 : 0.1. The half-life period of ${}^{238}_{92}\text{U}$ is 4.5×10^9 years. Calculate the age of the ore. (2000)
24. ${}^{64}\text{Cu}$ (half-life = 12.8 h) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes. (2002)
25. Complete and balance the following reactions.
- ${}^{234}_{90}\text{Th} \longrightarrow \dots + 7 {}^4_2\text{He} + 6 {}^0_{-1}\beta$ (2004)
 - ${}^{235}_{92}\text{U} + {}^1_0n \longrightarrow \dots + {}^{137}_{52}\text{Te} + {}^{92}_{40}\text{Zr}$ (2005)
 - ${}^{86}_{34}\text{Se} \longrightarrow 2 {}^0_{-1}e + \dots$ (2005)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

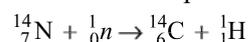
- Statement-1 is true; statement - 2 is true; statement - 2 is a correct explanation for statement - 1.
 - Statement-1 is true; statement - 2 is true; statement - 2 is NOT a correct explanation for statement - 1.
 - Statement - 1 is true, statement - 2 is false.
 - Statement - 1 is false, statement - 2 is true.
26. **Statement-1** : The plot of atomic number (y -axis) versus number of neutrons (x -axis) for stable nuclei shows a curvature towards x -axis from the line of 45° slope as the atomic number is increased.
- Statement-2** : Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides. (2008)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension - 1

Carbon-14 is used to determine the age of organic material. The procedure is based on the formation of ${}^{14}\text{C}$ by neutron capture in the atmosphere.

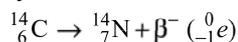


${}^{14}\text{C}$ is absorbed by living organisms during photosynthesis. The ${}^{14}\text{C}$ content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide

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by it ceases and the level of ^{14}C in the dead being falls due to the decay which C^{14} undergoes.



The half-life period of ^{14}C is 5770 years. The decay constant (λ) can be calculated using the formula $\lambda = \frac{0.693}{t_{1/2}}$.

The comparison of the β^- activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method, however, ceases to be accurate over period longer than 30,000 years. The proportion of ^{14}C to ^{12}C in living matter is 1 : 10^{12} .

27. Which of the following options is correct?

- In living organisms, circulation of ^{14}C from atmosphere is high so the carbon content is constant in organism.
- Carbon dating can be used to find out the age of earth crust and rocks.
- Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbon content remains constant in living organism.
- Carbon dating cannot be used to determine concentration of ^{14}C in dead beings.

28. What should be the age of fossil for meaningful determination of its age?

- 6 years
- 6000 years
- 60,000 years
- it can be used to calculate any age.

29. A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the places respectively then

- the age of the fossil will increase at the place where explosion has taken place and $T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$
- the age of the fossil will decrease at the place where explosion has taken place and $T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$
- the age of fossil will be determined to be same
- $\frac{T_1}{T_2} = \frac{C_1}{C_2}$ (2006)

Integer Answer Type

30. The total number of α and β particles emitted in the nuclear reaction $^{238}_{92}\text{U} \longrightarrow ^{214}_{82}\text{Pb}$ is (2009)

31. The number of neutrons emitted when $^{235}_{92}\text{U}$ undergoes controlled nuclear fission to $^{142}_{54}\text{Xe}$ and $^{90}_{38}\text{Sr}$ is (2010)

32. A closed vessel with rigid walls contains 1 mol of $^{238}_{92}\text{U}$ and 1 mol of air at 298 K. Considering complete decay of $^{238}_{92}\text{U}$ to $^{206}_{82}\text{Pb}$, the ratio of the final pressure to the initial pressure of the system at 298 K is (2015)

ANSWER KEY

- | | | | | | |
|---|-----------|--|--------------------------|--------------------------|---------|
| 1. (b) | 2. (d) | 3. (d) | 4. (b) | 5. (d) | 6. (a) |
| 7. (c) | 8. (a) | 9. (a, d) | 10. (a, b) | 11. $\frac{A-Z}{Z}M$ | 12. 8 |
| 13. Isotope | 14. False | 15. $3.01 \times 10^{20} \times 8$; 4.0×10^{-3} g | 16. 25% | 17. 7α , 6β | |
| 18. 3.6×10^{-16} g | | 19. 5.6223×10^5 atoms | 20. $0.6107 \mu\text{g}$ | | |
| 21. $\lambda_{\text{Th}} = 6.3 \times 10^{-4} \text{ year}^{-1}$; $\lambda_{\text{Fr}} = 3.087 \times 10^{-2} \text{ year}^{-1}$ | | 22. $^{14}_7\text{N} + ^4_2\text{He} \longrightarrow [^{18}_9\text{F}] \longrightarrow ^{17}_8\text{O} + ^1_1\text{H}$ | | | |
| 23. 8α , 6β ; 7.09×10^8 years. | | 24. $^{64}_{30}\text{Zn}$; $^{64}_{28}\text{Ni}$; $^{64}_{28}\text{Ni}$; 33.68 hr; 67.36 hr; 29.76 hr | | | |
| 25. $^{206}_{82}\text{Pb}$; 2^1_0n ; $^{86}_{36}\text{Kr}$ | | 26. (c) | 27. (c) | 28. (b) | 29. (a) |
| 30. (8) | 31. (3) | 32. (9) | | | |

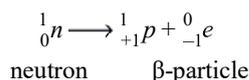
Explanations

1. (b) : ${}_{92}\text{U}^{238} \longrightarrow {}_{90}\text{U}^{234} + {}_2\text{He}^4$
2. (d) : α -rays consist of positively charged particles (He^{++}) and β -rays consist of negatively charged particles (${}_{-1}^0e$). Since they are oppositely charged so they get deflected in opposite directions. γ -rays are neutral (carry no charge) so they remain undeflected.

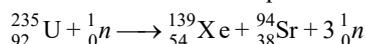
3. (d) : Number of half-lives ($t_{1/2}$) = $560/140 = 4$
 $N_t = N_0(1/2)^4 = N_0/16$.

\therefore 1 g of the element will reduce to $\frac{1}{16}$ g.

4. (b) : Since the number of neutrons is 16 in case of ${}_{13}^{29}\text{Al}$ whereas the number of neutrons is 14 in case of stable isotope ${}_{13}^{27}\text{Al}$, so ${}_{13}^{29}\text{Al}$ is likely to decompose by β -emission.

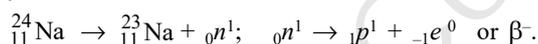


5. (d) : In any nuclear reaction the sum of mass numbers and of atomic numbers is equal on both sides of the equation.



6. (a) : n/p ratio of ${}_{11}^{24}\text{Na}$ nuclide is $13/11$, i.e. greater than unity and hence radioactive. To achieve stability, it would tend to adjust its n/p ratio to the value of unity.

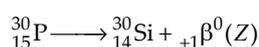
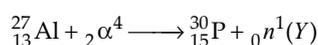
${}_{11}^{23}\text{Na}$, the more stable isotope can be obtained as follows :



7. (c) : ${}_{11}^{23}\text{Na} \rightarrow {}_{10}^{23}\text{X} + {}_{+1}^0\beta$

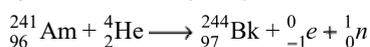
$$\therefore \frac{\text{Mass number}}{\text{Atomic number}} = \frac{23}{10}$$

8. (a) : ${}_{13}^{27}\text{Al} + {}_2\alpha^4 \longrightarrow {}_{14}^{30}\text{Si} + {}_1p^1(X)$

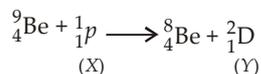


$X = \text{proton}$, $Y = \text{neutron}$, $Z = \text{positron}$

9. (a, d) : ${}_{13}^{27}\text{Al} + {}_2^4\text{He} \longrightarrow {}_{15}^{30}\text{P} + {}_0n^1$



10. (a,b) : ${}_{4}^9\text{Be} + {}_0^0\gamma \longrightarrow {}_{4}^8\text{Be} + {}_0^1n$



11. ${}_{Z}^{A-4}\text{M}$

12. $8; {}_6^{14}\text{C} \rightarrow {}_7^{14}\text{N} + {}_{-1}^0e$

Number of neutrons in C = $14 - 6 = 8$

13. Isotope; ${}_{Y}^X A \xrightarrow{-\alpha, -2\beta} {}_{Y}^{X-4} A$.

14. **False** : In β -emission the atomic number of daughter nuclei increases by 1.

15. (i) Number of C atoms in 14 g of ${}^{14}\text{C} = 6.02 \times 10^{23}$

$$\therefore \text{Number of C atoms in 1000 mg of } {}^{14}\text{C} = \frac{6.02 \times 10^{23}}{14}$$

Number of C atoms in 7 mg of ${}^{14}\text{C}$

$$= \frac{6.02 \times 10^{23} \times 7}{14 \times 1000} = 3.01 \times 10^{20}$$

Number of neutrons in 1 carbon atom = 8

\therefore Total number of neutrons in 7 mg of ${}^{14}\text{C}$

$$= 3.01 \times 10^{20} \times 8$$

- (ii) Assuming, weight of 1 neutron = weight of hydrogen

$$\text{Weight of 1 hydrogen atom} = \frac{1}{6.02 \times 10^{23}} \text{ g}$$

\therefore Weight of $3.01 \times 10^{20} \times 8$ hydrogen atoms.

$$= \frac{3.01 \times 10^{20} \times 8}{6.02 \times 10^{23}} \text{ g} = \frac{8}{2 \times 10^3} \text{ g} = 4.0 \times 10^{-3} \text{ g}$$

16. Half-life ($t_{1/2}$) = 5770 years

$$\text{Rate constant, } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} = 1.20 \times 10^{-4} \text{ years}^{-1}$$

Let the weight of original sample = 1 g

After 5770 years half of it will disintegrate and thus the

weight of sample left after 5770 years = $1 - 1/2 = 1/2$ g

After another 5770 years (i.e. a total time period of 11540 years) 50% of $1/2$ g will disintegrate and weight of sample

$$\text{left will be} = \frac{1}{2} - \left(\frac{1}{2} \times \frac{1}{2}\right) = \frac{1}{2} - \frac{1}{4} = \frac{1}{4} \text{ g}$$

i.e. 25% of original will be left.

17. ${}_{90}^{234}\text{Th} \longrightarrow {}_{82}^{206}\text{Pb}$

When one α -particle is emitted it results in a decrease of atomic mass by 4 units and atomic number by 2 units.

Here decrease in atomic mass = $234 - 206 = 28$

$$\therefore \text{number of } \alpha \text{-particles emitted} = \frac{28}{4} = 7$$

Decrease in atomic number due to emission of 7 α -particles = $7 \times 2 = 14$

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Hence atomic number decreases to $(90 - 14) = 76$

But atomic number of Pb is 82 which is more than 76 by 6 units.

By emission of one β -particle, there is no change in atomic mass but the atomic number increases by 1 unit. Thus for increase of atomic number by 6 units, number of β -particles emitted = 6.

18. Minimum number of β -particles required = 346 min^{-1}
 \therefore Number of β -particles required to carry out the experiment for 6.909×60 minutes = $346 \times 6.909 \times 60$
 = 143430

$$\text{Number of } \beta\text{-particles required} = \frac{143430}{6.023 \times 10^{23}} \text{ mol} \\ = 2.3814 \times 10^{-19} \text{ mol}$$

$$\text{Since } \lambda = \frac{0.693}{t_{1/2}}$$

$$\therefore \lambda = \frac{0.693}{66.6} = 0.0104 \text{ hr}^{-1}$$

For a first order reaction

$$\lambda = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$\text{or } \lambda = \frac{2.303}{6.909} \log \frac{a}{(a-x)} = \frac{2.303}{6.909} \log \frac{a}{(a-143430)}$$

$$\text{but, } \log \frac{a}{(a-x)} = \log \frac{a}{(a-143430)} = \frac{0.0104 \times 6.909}{2.303} \\ = 0.0312$$

$$\therefore \frac{a}{a-143430} = \text{Antilog } 0.0312 = 1.07$$

$$\text{or } a = 1.07 a - 1.07 \times 143430$$

$$\text{or } a = 1.07 a - 153470$$

$$\text{or } a = \frac{153470}{0.07} = 2192428$$

Since atomic mass of Mo = 99

\therefore mass of 6.023×10^{23} atoms of Mo = 99 g

and mass of 2192428 atoms of Mo

$$= \frac{99 \times 2192428}{6.023 \times 10^{23}} = 3.6 \times 10^{-16} \text{ g}$$

19. The ratio ${}^3_1\text{H} : {}^1_1\text{H} = 8 \times 10^{-18} : 1$

The number of H atoms in 18 g (one mole) of water = $2N$
 = $2 \times 6.023 \times 10^{23}$

\therefore Number of ${}^3_1\text{H}$ atoms in 18 g of water = $2N \times 8 \times 10^{-18}$
 = $2 \times 6.023 \times 10^{23} \times 8 \times 10^{-18}$

Hence number of ${}^3_1\text{H}$ atoms in 10 g of water

$$= \frac{2 \times 6.023 \times 10^{23} \times 8 \times 10^{-18} \times 10}{18} = 5.3532 \times 10^6 \text{ atoms}$$

To find the number of atoms left after 40 years, we can use the relation,

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N} \quad \text{or} \quad \lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$\text{or } \frac{0.693}{12.3} = \frac{2.303}{40} \log \frac{5.3532 \times 10^6}{N}$$

$$\text{or } \log \frac{5.3532 \times 10^6}{N} = \frac{0.693 \times 40}{12.3 \times 2.303}$$

$$\text{or } N = 5.6223 \times 10^5 \text{ atoms}$$

20. Initial amount of ${}_{90}\text{Sr}$ (N_0) = 1 μg

Amount of ${}_{90}\text{Sr}$ after 20 years (N) = ?

Time = 20 years

$t_{1/2}$ of ${}_{90}\text{Sr}$ = 28.1 year

$$\lambda = \frac{0.693}{28.1} \text{ year}^{-1}$$

Using the relation $\lambda = \frac{2.303}{20} \log \frac{N_0}{N}$, we get

$$\frac{0.693}{28.1} = \frac{2.303}{20} \log \frac{N_0}{N}$$

$$\text{or } \log \frac{N_0}{N} = \frac{0.693}{28.1} \times \frac{20}{2.303} = 0.2141$$

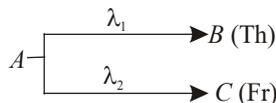
$$\text{or } \frac{N_0}{N} = 1.6375$$

$$\text{or } N = \frac{N_0}{1.6375} = \frac{1}{1.6375} \mu\text{g} = 0.6107 \mu\text{g}$$

21. $t_{1/2} = 21.8$ years

$$\text{So } \lambda = \frac{0.693}{21.8} \text{ year}^{-1}$$

The two parallel paths are



The λ is the sum of λ 's of both the parallel paths:

$$\lambda = \lambda(\text{Th}) + \lambda(\text{Fr}) = \frac{0.693}{21.8}$$

Under identical conditions, the yield is in the ratio of their decay constants:

$$\left(\frac{dx}{dt}\right)_{\text{Th}} = \lambda_{\text{Th}} [N_0] \quad \text{or} \quad \frac{\lambda_{\text{Th}}}{\lambda_{\text{Fr}}} = \frac{2}{98} = \frac{1}{49}$$

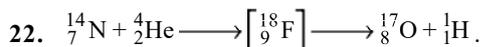
$$\text{or } \lambda_{\text{Fr}} = 49 \lambda_{\text{Th}}$$

$$\text{or } \frac{0.693}{21.8} = \lambda_{\text{Th}} + 49 \lambda_{\text{Th}} = 50 \lambda_{\text{Th}}$$

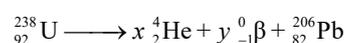
$$\text{or } \lambda_{\text{Th}} = \frac{0.693}{21.8 \times 50}$$

$$= 0.00063 \text{ year}^{-1} \text{ or } 6.3 \times 10^{-4} \text{ year}^{-1}$$

$$\lambda_{\text{Fr}} = 49 \lambda_{\text{Th}} = 0.03087 \text{ year}^{-1} \text{ or } 3.087 \times 10^{-2} \text{ year}^{-1}$$



23. Let x and y be the number of α - and β -particles emitted respectively



Comparing mass numbers,

$$238 = 4x + 0y + 206 = 4x + 206$$

$$\text{or } 4x = 32 \quad \text{or } x = 8$$

Comparing atomic numbers

$$92 = 2x - y + 82$$

$$\text{or } y = -92 + 2 \times 8 + 82 = 6$$

Thus the number of α -particles = 8

and the number of β -particles = 6

Given ore contains 0.1 g of Pb and 1 g of U

$$0.1 \text{ g of Pb is obtained from uranium} = \frac{238}{206} \times 0.1 = 0.1155 \text{ g}$$

$$\therefore \text{Initial amount of uranium, } N_0 = (1 + 0.1155) \text{ g}$$

$$N_0 = 1.1155 \text{ g; } N = 1 \text{ g}$$

Using the relation

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N}, \text{ we get}$$

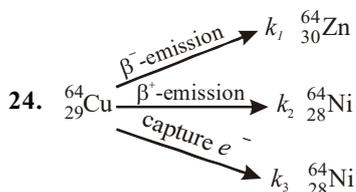
$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$\text{or } \frac{0.693}{4.5 \times 10^9} = \frac{2.303}{t} \log \frac{1.1155}{1}$$

$$\text{or } t = \frac{2.303 \times 4.5 \times 10^9}{0.693} \log 1.1155$$

$$= 7.09 \times 10^8 \text{ years}$$

$$\therefore \text{Age of ore} = 7.09 \times 10^8 \text{ years.}$$



Let the rate constants of the above emission process be k_1 , k_2 and k_3 respectively and the overall rate constant be k . Then

$$k = k_1 + k_2 + k_3 = \frac{0.693}{t_{1/2}} = \frac{0.693}{12.8} \text{ hr}^{-1}$$

$$\text{Also } k_1 = 0.38 k = 0.38 \times \frac{0.693}{12.8} \text{ hr}^{-1}$$

$$t_1 = \frac{0.693 \times 12.8}{0.38 \times 0.693} \text{ hr (} t_1 \text{ is the partial half - life for } \beta^- \text{ emission)}$$

$$= 33.68 \text{ hr}$$

Similarly t_2 and t_3 , partial half lives for β^+ -emission and e^- -capture are respectively

$$t_2 = \frac{0.693}{k_2} = \frac{0.693}{0.19 k} = \frac{0.693 \times 12.8}{0.19 \times 0.693} = 67.36 \text{ hr}$$

$$\text{and } t_3 = \frac{0.693}{k_3} = \frac{0.693}{0.43 k} = \frac{0.693}{0.43} \times \frac{12.8}{0.693} = 29.76 \text{ hr}$$

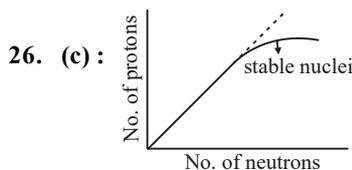
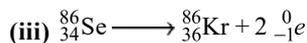
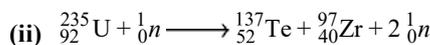
25. (i) The atomic number of final stable product

$$= 90 - 7 \times 2 + 1 \times 6 = 82$$

The mass number of final stable product

$$= 234 - 7 \times 4 + 0 = 206$$

Thus the unknown element should be ${}_{82}^{206}\text{Pb}$.



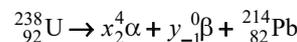
If the curve does not bend down towards the x -axis then the proton-proton repulsion would overcome the attractive forces of proton and neutron. Therefore, curve bends down to achieve stability of the nuclei. In heavier nuclides attractive forces between proton and neutron overcome proton-proton electrostatic repulsion.

27. (c) : In living material, the ratio of ${}^{14}\text{C}$ to ${}^{12}\text{C}$ remains relatively constant.

28. (b)

29. (a) : On applying the formula, $T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$.

30. (8) : Let x α - and y β -particles be emitted in the reaction,



Equating the mass numbers on both sides,

$$238 = 4x + y \times 0 + 214 \Rightarrow 4x = 24$$

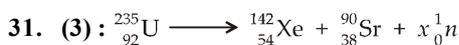
$$\therefore x = 6$$

Equating atomic numbers on both sides,

$$92 = 2x + (-y) + 82$$

$$92 = 2 \times 6 + (-y) + 82 \Rightarrow -y = -2 \quad \therefore y = 2$$

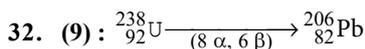
Hence in the nuclear reaction, ${}_{92}^{238}\text{U} \rightarrow {}_{82}^{214}\text{Pb}$, 6 α - and 2 β -particles or a total of 8 particles are emitted.



Sum of atomic numbers of reactants and products are equal.

From the sum of mass numbers,

$$235 = 142 + 90 + x \Rightarrow x = 3$$



To calculate pressure, only gaseous products need to be considered.

Initially, only 1 mol of air is present and finally, after complete decay, 8 moles of ${}^4_2\text{He}$ gas are produced and 1 mol of air will also remain in the mixture.

$$\text{Ratio of the final pressure to the initial pressure} = \frac{8+1}{1} = 9$$



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Surface Chemistry and Colloids

Multiple Choice Questions with ONE Correct Answer

- Rate of physisorption increases with
 - decrease in temperature
 - increase in temperature
 - decrease in pressure
 - decrease in surface area
 (2003)
- Adsorption of gases on solid surface is generally exothermic because
 - enthalpy is positive
 - entropy decreases
 - entropy increases
 - free energy increases
 (2004)
- Lyophilic sols are
 - Irreversible sols
 - They are prepared from inorganic compound
 - Coagulated by adding electrolytes
 - Self-stabilizing
 (2005)
- Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is
 - $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
 - $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$
 - $\text{CH}_3(\text{CH}_2)_6\text{COO}^-\text{Na}^+$
 - $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
 (2008)
- Among the electrolytes Na_2SO_4 , CaCl_2 , $\text{Al}_2(\text{SO}_4)_3$ and NH_4Cl , the most effective coagulating agent for Sb_2S_3 sol is

(a) Na_2SO_4	(b) CaCl_2
(c) $\text{Al}_2(\text{SO}_4)_3$	(d) NH_4Cl

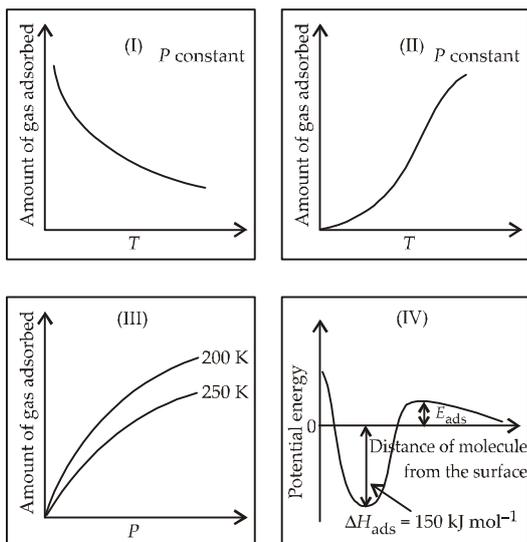
 (2009)
- Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C . For this process, the correct statement is
 - the adsorption requires activation at 25°C
 - the adsorption is accompanied by a decrease in enthalpy

- the adsorption increases with increase of temperature
- the adsorption is irreversible.

(2013)

Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

- The correct statement(s) pertaining to the adsorption of a gas on a solid surface is(are)
 - adsorption is always exothermic
 - physisorption may transform into chemisorption at high temperature
 - physisorption increases with increasing temperature but chemisorption decreases with increasing temperature.
 - chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation.
 (2010)
- Choose the correct reason(s) for the stability of the lyophobic colloidal particles.
 - Preferential adsorption of ions on their surface from the solution.
 - Preferential adsorption of solvent on their surface from the solution.
 - Attraction between different particles having opposite charges on their surface.
 - Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.
 (2012)
- The given graphs/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is(are) correct?



- (a) I is physisorption and II is chemisorption.
 (b) I is physisorption and III is chemisorption.
 (c) IV is chemisorption and II is chemisorption.
 (d) IV is chemisorption and III is chemisorption

(2012)

Subjective Problems

10. 1 g of charcoal adsorbs 100 ml 0.5 M CH_3COOH to form a monolayer, and thereby the molarity of CH_3COOH reduces to 0.49. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal = $3.0 \times 10^2 \text{ m}^2/\text{g}$.
 (2003)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

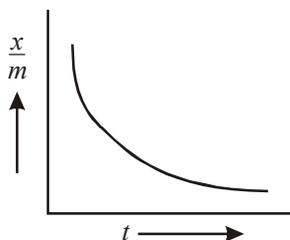
- (a) Statement-1 is true; statement - 2 is true; statement - 2 is a correct explanation for statement - 1.
 (b) Statement-1 is true; statement - 2 is true; statement - 2 is NOT a correct explanation for statement - 1.
 (c) Statement - 1 is true, statement - 2 is false.
 (d) Statement - 1 is false, statement - 2 is true.
11. **Statement-1** : Micelles are formed by surfactant molecules above the critical micellar concentration (CMC).
Statement-2 : The conductivity of a solution having surfactant molecules decreases sharply at the CMC.
 (2007)

ANSWER KEY

1. (a) 2. (b) 3. (d) 4. (a) 5. (c) 6. (b)
 7. (a, b, d) 8. (a, d) 9. (a, c) 10. $5 \times 10^{-19} \text{ m}^2$ 11. (b)

Explanations

1. (a) : With increase of temperature, there occurs a decrease in rate of physisorption.



Where x/m = mass of gas adsorbed per unit mass of adsorbent and t = temperature.

2. (b) : After the gas is adsorbed on surface, the freedom of movement of gaseous molecules is restricted. Due to this entropy of the gas decreases after adsorption. Hence ΔS becomes negative.
3. (d) : Lyophilic solutions are self-stabilizing because such sols are reversible and are highly hydrated in solution.
4. (a) : Options (a) and (b) both are capable of forming micelle
 (a) $\rightarrow \text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
 Cetyl trimethyl ammonium bromide
 (b) $\rightarrow \text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$
 Sodium lauryl sulphate
 But critical concentration for micelle formation decreases as the molecular weight of hydrocarbon chain of surfactant grows because in this true solubility diminishes and the tendency of surfactant molecule to undergo association increases. So option (a) is correct.
5. (c) : Sb_2S_3 is a negative sol and according to Hardy-Schulze rule:
 (i) Ions carrying charge opposite to that of sol particles are effective in causing coagulation.
 (ii) Coagulating power of an electrolyte is directly proportional to the valency of the active ions.

\therefore Out of the given options, the most effective coagulating agent is $\text{Al}_2(\text{SO}_4)_3$ or Al^{3+} ion.

6. (b) : The adsorption of methylene blue on activated charcoal is physical adsorption. It is accompanied by a decrease in enthalpy.
7. (a, b, d)
8. (a, d)
9. (a, c) : In physisorption as temperature increases, the extent of adsorption decreases thus, I and III are physisorptions. Chemical adsorption first increases with increase in temperature upto a certain extent and then decreases regularly thus II is chemisorption. In chemisorption, attractive forces between adsorbent and adsorbate molecules are strong bonds, thus enthalpy of adsorption is high and of the order 80 - 240 kJ/mol. As in IV $\Delta H_{\text{adsorption}} = 150$ kJ/mol, thus it also represents chemical adsorption.
10. Number of moles of acetic acid in 100 ml before adding charcoal = 0.05
 Number of moles of acetic acid in 100 ml after adding charcoal = 0.049
 Number of moles of acetic acid adsorbed on the surface of charcoal = $(0.05 - 0.049) = 0.001$
 \therefore Number of molecules of acetic acid adsorbed on the surface of charcoal = $0.001 \times 6.02 \times 10^{23}$
 $= 6.02 \times 10^{20}$
 Surface area of charcoal = $3.0 \times 10^2 \text{ m}^2 \text{ g}$
 Area occupied by one molecule of acetic acid on the surface of charcoal = $\frac{3.0 \times 10^2}{6.02 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$
11. (b) : A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid and the critical micelle concentration (CMC) is defined as the concentration of surfactants above which micelles are spontaneously formed.



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Classification of Elements and Periodicity in Properties

Multiple Choice Questions with ONE Correct Answer

- The correct order of second ionisation potential of carbon, nitrogen, oxygen and fluorine is
 (a) $C > N > O > F$ (b) $O > N > F > C$
 (c) $O > F > N > C$ (d) $F > O > N > C$
 (1981)
- The element with the highest first ionisation potential is
 (a) boron (b) carbon
 (c) nitrogen (d) oxygen (1982)
- The first ionisation potential in electron volts of nitrogen and oxygen atoms are respectively given by
 (a) 14.6, 13.6 (b) 13.6, 14.6
 (c) 13.6, 13.6 (d) 14.6, 14.6 (1987)
- Atomic radii of fluorine and neon in Angstrom units are respectively given by
 (a) 0.72, 1.60 (b) 1.60, 1.60
 (c) 0.72, 0.72 (d) None of these (1987)
- The electronegativity of the following elements increase in the order
 (a) C, N, Si, P (b) N, Si, C, P
 (c) Si, P, C, N (d) P, Si, N, C (198)
- The first ionisation potential of Na, Mg, Al and Si are in the order
 (a) $Na < Mg > Al < Si$ (b) $Na > Mg > Al > Si$
 (c) $Na < Mg < Al < Si$ (d) $Na > Mg > Al < Si$
 (1988)
- Which one of the following is the strongest base?
 (a) AsH_3 (b) NH_3 (c) PH_3 (d) SbH_3
 (1989)
- Which one of the following is the smallest in size?
 (a) N^{3-} (b) O^{2-} (c) F^- (d) Na^+
 (1989)
- Amongst the following elements (whose electronic configurations are given below), the one having the highest ionisation energy is
 (a) $[Ne] 3s^2 3p^1$ (b) $[Ne] 3s^2 3p^3$
 (c) $[Ne] 3s^2 3p^2$ (d) $[Ne] 3d^{10} 4s^2 4p^3$
 (1990)
- The statement that is not correct for the periodic classification of element is
 (a) the properties of elements are the periodic functions of their atomic numbers
 (b) non-metallic elements are lesser in number than metallic elements
 (c) the first ionisation energies of elements along a period do not vary in a regular manner with increase in atomic number
 (d) for transition elements the d -subshells are filled with electrons monotonically with increase in atomic number. (1992)
- Which has most stable +2 oxidation state?
 (a) Sn (b) Pb (c) Fe (d) Ag
 (1995)
- Which of the following has the maximum number of unpaired electrons?
 (a) Mg^{2+} (b) Ti^{3+} (c) V^{3+} (d) Fe^{2+}
 (1996)
- The incorrect statement among the following is
 (a) the first ionisation potential of Al is less than the first ionisation potential of Mg
 (b) the second ionisation potential of Mg is greater than the second ionisation potential of Na
 (c) the first ionisation potential of Na is less than the first ionisation potential of Mg
 (d) the third ionisation potential of Mg is greater than third ionisation potential of Al. (1997)

Classification of Elements and Periodicity in Properties

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14. Which of the following compounds is expected to be coloured?

- (a) Ag_2SO_4 (b) CuF_2 (c) MgF_2 (d) CuCl

(1997)

15. The correct order of radii is

- (a) $\text{N} < \text{Be} < \text{B}$ (b) $\text{F}^- < \text{O}^{2-} < \text{N}^{3-}$
(c) $\text{Na} < \text{Li} < \text{K}$ (d) $\text{Fe}^{3+} < \text{Fe}^{2+} < \text{Fe}^{4+}$

(2000)

16. The correct order of acidic strength is

- (a) $\text{Cl}_2\text{O}_7 > \text{SO}_2 > \text{P}_4\text{O}_{10}$ (b) $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$
(c) $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$ (d) $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$

(2000)

17. Amongst H_2O , H_2S , H_2Se and H_2Te , the one with the highest boiling point is

- (a) H_2O because of hydrogen bonding
(b) H_2Te because of higher molecular weight
(c) H_2S because of hydrogen bonding
(d) H_2Se because of lower molecular weight (2000)

18. Identify the correct order of acidic strengths of CO_2 , CuO , CaO , H_2O .

- (a) $\text{CaO} < \text{CuO} < \text{H}_2\text{O} < \text{CO}_2$
(b) $\text{H}_2\text{O} < \text{CuO} < \text{CaO} < \text{CO}_2$
(c) $\text{CaO} < \text{H}_2\text{O} < \text{CuO} < \text{CO}_2$
(d) $\text{H}_2\text{O} < \text{CO}_2 < \text{CaO} < \text{CuO}$ (2002)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

19. The statements that are true for the long form of the periodic table are

- (a) it reflects the sequence of filling the electrons in the order of sub-energy level *s*, *p*, *d* and *f*.
(b) it helps to predict the stable valence states of the elements
(c) it reflects trends in physical and chemical properties of the elements
(d) it helps to predict the relative ionicity of the bond between any two elements. (1988)

20. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because

- (a) the hydration energy of sodium sulphate is more than its lattice energy
(b) the lattice energy of barium sulphate is more than its hydration energy

- (c) the lattice energy has no role to play in solubility
(d) the hydration energy of sodium sulphate is less than its lattice energy. (1999)

Fill in the Blanks

21. The energy released when an electron is added to a neutral gaseous atom is called of the atom. (1982)
22. On Mulliken scale, the average of ionisation potential and electron affinity is known as (1982)

True / False

23. In Group IA, of alkali metals, the ionisation potential decrease down the group. Therefore, lithium is a poor reducing agent. (1987)
24. The decreasing order of electron affinity of F, Cl, Br is $\text{F} > \text{Cl} > \text{Br}$. (1993)
25. The basic nature of the hydroxides of Group 13 (III B) decreases progressively down the group. (1993)

Subjective Problems

26. Arrange the following in:
(i) Decreasing ionic size: Mg^{2+} , O^{2-} , Na^+ , F^- (1985)
(ii) Increasing acidic property: ZnO , Na_2O_2 , P_2O_5 , MgO (1985)
(iii) Increasing first ionisation potential: Mg, Al, Si, Na (1985)
(iv) Increasing size: Cl^- , S^{2-} , Ca^{2+} , Ar (1986)
(v) Increasing order of ionic size: N^{3-} , Na^+ , F^- , O^{2-} , Mg^{2+} (1991)
(vi) Increasing order of basic character: MgO , SrO , K_2O , NiO , Cs_2O (1991)
(vii) Arrange the following ions in order of their increasing radii: Li^+ , Mg^{2+} , K^+ , Al^{3+} . (1991)
27. The first ionisation energy of carbon atom is greater than that of boron atom whereas, the reverse is true for the second ionisation energy. Explain. (1989)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement - 2 is true; statement - 2 is a correct explanation for statement - 1.
 (b) Statement-1 is true; statement - 2 is true; statement - 2 is NOT a correct explanation for statement - 1.
 (c) Statement - 1 is true, statement - 2 is false.
 (d) Statement - 1 is false, statement - 2 is true.

28. Statement-1 : The first ionisation energy of Be is greater than that of B.

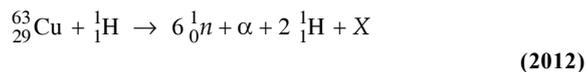
Statement-2 : $2p$ orbital is lower in energy than $2s$.
 (2000)

Integer Answer Type

29. Among the following, the number of elements showing only one non-zero oxidation state is

O, Cl, F, N, P, Sn, Tl, Na, Ti (2010)

30. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table?



ANSWER KEY

- | | | | | | |
|---------------|------------|-----------------------|--|---------|---------|
| 1. (c) | 2. (c) | 3. (a) | 4. (a) | 5. (c) | 6. (a) |
| 7. (b) | 8. (d) | 9. (b) | 10. (d) | 11. (b) | 12. (d) |
| 13. (b) | 14. (b) | 15. (b) | 16. (a) | 17. (a) | 18. (a) |
| 19. (b, c, d) | 20. (a, b) | 21. Electron affinity | 22. Electronegativity | | |
| 23. True | 24. False | 25. False | 26. (i) $\text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+}$; | | |
| | | | (ii) $\text{Na}_2\text{O}_2 < \text{MgO} < \text{ZnO} < \text{P}_2\text{O}_5$; | | |
| | | | (iii) $\text{Na} < \text{Al} < \text{Mg} < \text{Si}$; | | |
| | | | (iv) $\text{Ca}^{2+} < \text{Ar} < \text{Cl}^- < \text{S}^{2-}$; | | |
| | | | (v) $\text{Mg}^{2+} < \text{Na}^+ < \text{F}^- < \text{O}^{2-} < \text{N}^{3-}$; | | |
| | | | (vi) $\text{NiO} < \text{MgO} < \text{SrO} < \text{K}_2\text{O} < \text{Cs}_2\text{O}$; | | |
| | | | (vii) $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Li}^+ < \text{K}^+$. | | |
| 28. (c) | 29. (2) | 30. (8) | | | |

Explanations

- (c)** : As for IE_2 , in all the given cases *i.e.* $C^+(1s^2 2s^2 2p^1)$, $N^+(1s^2 2s^2 2p^2)$, $O^+(1s^2 2s^2 2p^3)$, $F^+(1s^2 2s^2 2p^4)$, we have to remove an electron from $2p$ -orbital so it must follow the order $C < N < O < F$, *i.e.*, according to decreasing size. However, for O^+ the p -orbitals are half filled and so it is more stable. Thus the correct order is $O > F > N > C$.
- (c)** : Since the nitrogen atom has half-filled $2p$ -orbitals it is more stable and has highest first ionisation energy amongst $B(1s^2 2s^2 2p^1)$, $C(1s^2 2s^2 2p^2)$, $N(1s^2 2s^2 2p^3)$ and $O(1s^2 2s^2 2p^4)$.
- (a)** : Because of half-filled $2p$ -orbitals in case of N, its ionisation potential is more than that of O.
- (a)** : In case of neon, the atomic radius is van der Waals radius which is larger than that of fluorine, which has a covalent radius.
- (c)** : Out of the given elements, Si and P are in third period where as C and N are in second period. The electronegativity value of elements in third period is lower as compared to those in second period. The electronegativity of N is higher than that of C (due to smaller size of N) and similarly electronegativity of Si is lower than that of P. Hence the correct order is $Si < P < C < N$.
- (a)** : First ionisation energy of Mg ($Z = 12$) is higher than that of Na ($Z = 11$) because of increased nuclear charge on Mg. The first ionisation energy of Mg is higher than that of Al because in case of $Mg(1s^2 2s^2 2p^6 3s^2)$ the electron has to be removed from $3s$ -orbital while in $Al(1s^2 2s^2 2p^6 3s^2 3p^1)$ it has to be removed from $3p$ -orbital. The IE of Si ($Z = 14$) is higher than those of Mg and Al because of increase in nuclear charge on Si. The correct order is $Na < Mg > Al < Si$.
- (b)** : Because of its smallest size nitrogen can give up its electron pair more easily and acts as a strongest base.
- (d)** : Since Na^+ has maximum nuclear charge so it is smallest in size amongst given ions which are isoelectronic.
- (b)** : Due to stable half-filled electronic configuration, (b) and (d) are more stable. As down the group, ionisation energy decreases, hence ionisation energy of (b) is highest.
- (d)** : In the transition elements, the last differentiating electron is accommodated on penultimate d -orbitals, *i.e.*, d -orbitals are successively filled. The general electronic configuration of transition elements is $(n - 1)d^{1-10} ns^{0, 1 \text{ or } 2}$.
- (b)** : $Pb^{2+}(5d^{10}6s^2)$ has most stable +2 oxidation state because in it we have completely filled $5d$ -orbitals. In case of $Fe^{2+}(3d^6)$ and $Ag^{2+}(4d)$ are less stable due to incompletely filled d -orbitals. $Sn^{2+}(4d^{10}5s^2)$ is stable due to completely filled d -orbitals. However Pb^{2+} is more stable than Sn^{2+} because of its larger size.
- (d)** : The number of unpaired electrons are 0, 1, 2 and 4 respectively in case of $Mg^{2+}(1s^2 2s^2 2p^6)$, $Ti^{3+}(1s^2 2s^2 2p^6 3s^2 3p^6 3d^1)$, $V^{3+}(1s^2 2s^2 2p^6 3s^2 3p^6 3d^2)$, $Fe^{2+}(1s^2 2s^2 2p^6 3s^2 3p^6 3d^6)$. So the maximum number of unpaired electrons are in Fe^{2+} ion.
- (b)** : Electronic configuration of Mg^+ is $1s^2 2s^2 2p^6 3s^1$. Electronic configuration of Na^+ is $1s^2 2s^2 2p^6$. Due to stable fully-filled electronic configuration of Na^+ , removal of another electron will be difficult. Hence IE_2 of Na is greater than IE_2 of Mg.
- (b)** : For various ions the electronic configurations are $Ag^+ - 4d^{10}$; $Cu^{2+} - 3d^9$; $Mg^{2+} - 2s^2 p^6$; $Cu^+ - 3d^{10}$. Thus we find that in case of Cu^{2+} there is one unpaired electron in $3d$ -orbital and so its salt can be expected to be coloured (due to $d-d$ transition).
- (b)** : There is a decrease in effective nuclear charge (*i.e.* Z/e ratio) from F^- to N^{3-} . The size decreases with increase in effective nuclear charge. Hence, the correct order of radii is $F^- < O^{2-} < N^{3-}$.
[Note: $\frac{Z}{e}$ for $F^- = \frac{9}{10}$ or 0.9; $O^{2-} = \frac{8}{10}$ or 0.8, $N^{3-} = \frac{7}{10}$ or 0.7]
- (a)** : Non-metallic oxides are acidic and their acidic character decreases with decreasing non-metallic character.
- (a)** : No hydrogen bond formation can occur in case of S, Se and Te because of their larger size and lower values of electronegativity.
- (a)** : Non-metallic oxides are acidic and metallic oxides are basic. An increase in metallic (*i.e.* electropositive) character increases the basic nature of the oxide and an increase in non-metallic (*i.e.* electronegative) character increases the acidic nature of the oxide. Hence, the correct order is $CaO < CuO < H_2O < CO_2$.
- (b, c, d)** : Electrons are not filled in order of sub-energy levels s, p, d and f in the same sequence.

20. (a, b) : BaSO_4 is sparingly soluble in water because its hydration energy is lesser than the lattice energy and thus ions are not separated from each other.

21. Electron affinity
22. Electronegativity

23. True

In group I, there occurs a decrease in *I.E.* as we move down the group from Li to Cs. The reducing properties increase as we move down the group. However the behaviour of lithium in solution is anomalous. Lithium, having high value of ionisation energy amongst alkali metals acts as a strongest reducing agent in solution due to its large heat of hydration.

24. False

Electron affinity values are high in case of halogens. The E.A. value decreases on moving down the group. However the value of fluorine is lower than that of chlorine. This is due to stronger interelectronic repulsion to the incoming electron in relatively compact $2p$ -subshell. The correct order is $\text{Cl} > \text{Br} > \text{F}$.

25. False

The basic nature of hydroxides of group 13 increases on moving down the group. It is due to increase in electropositive character on moving down the group. *i.e.* the metallic character increases as we move down the group.

26. (i) $\text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+}$. These are isoelectronic ions (each has 10 electrons). In such case the ionic radii decreases with increase in nuclear charge. The nuclear charge is 8 (for O^{2-}) 9 (for F^-), 11 (for Na^+) and 12 (for Mg^{2+}).

(ii) $\text{Na}_2\text{O}_2 < \text{MgO} < \text{ZnO} < \text{P}_2\text{O}_5$

In case of oxides, the acidic strength increases with increase in oxidation state of central atom.

(iii) In case of elements of 3rd period the first *I.E.* follows the order $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$. (Refer Q. No. 6) Therefore first ionisation energy : $\text{Na} < \text{Al} < \text{Mg} < \text{Si}$.

(iv) The correct order is $\text{Ca}^{2+} < \text{Ar} < \text{Cl}^- < \text{S}^{2-}$. These are isoelectronic with 18 electrons. Lower the nuclear charge, higher is the ionic radii.

(v) The correct order is $\text{Mg}^{2+} < \text{Na}^+ < \text{F}^- < \text{O}^{2-} < \text{N}^{3-}$. For isoelectronic ions, ionic radii decreases with increase in nuclear charge.

(vi) The increasing order of basic character is



In a group the basic character of oxide increases as we move from top to bottom. Thus we have $\text{K}_2\text{O} < \text{Cs}_2\text{O}$ (group 1) and $\text{MgO} < \text{SrO}$ (group 2)

Also as the group number increases the basic character decreases, so NiO is least basic, Ni is in group 10.

(vii) Out of the given species Al^{3+} and Mg^{2+} are isoelectronic (10 electrons) and size of Al^{3+} is smaller, so $\text{Al}^{3+} < \text{Mg}^{2+}$. Li^+ and K^+ belong to group I and Li^+ is higher up in the group so $\text{Li}^+ < \text{K}^+$.

The correct order is $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Li}^+ < \text{K}^+$.

27. Along the period from left to right, as atomic size increases, ionisation energy decreases. So, IE_1 of carbon is greater than IE_1 of boron.

The second *IE* in case of C^+ ($1s^2 2s^2 2p^1$) will be less than the second *IE* in case of B^+ ($1s^2 2s^2$). In C^+ the electron has to be removed from $2p$ -orbital whereas in B^+ it has to be removed from $2s$ -orbital.

28. (c) : $2s$ -orbital is lower in energy than $2p$ -orbital.

29. (2) : There are only two elements which show only one non-zero oxidation state :

Na exhibits only +1 and F exhibits only -1 oxidation state.

Rest of the elements show more than one non-zero oxidation state.

30. (8) : ${}_{29}^{63}\text{Cu} + {}_1^1\text{H} \rightarrow 6{}_0^1n + {}_2^4\text{He}(\alpha) + 2{}_1^1\text{H} + {}_{26}^{52}\text{X}$

Atomic number 26 represents Fe which belongs to group 8.

Alternative path : $Z = 26$

Electronic configuration = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Thus element X belongs to d -block and for d -block,

Group number = electrons in $(n - 1)$ subshell + number of electrons in valence shell

$$= 6 + 2 = 8$$



14

Metallurgy

Multiple Choice Questions with ONE Correct Answer

- In the aluminothermic process, aluminium acts as
(a) an oxidising agent (b) a flux
(c) a reducing agent (d) a solder (1981)
- Hydrogen gas will not reduce
(a) heated cupric oxide
(b) heated ferric oxide
(c) heated stannic oxide
(d) heated aluminium oxide (1985)
- Which of the following processes is used in the extractive metallurgy of magnesium?
(a) Fused salt electrolysis
(b) Self reduction
(c) Aqueous solution electrolysis
(d) Thermite reduction (2002)
- Which one contains both iron and copper?
(a) Cuprite (b) Chalcocite
(c) Chalcopyrite (d) Malachite (2005)
- Extraction of zinc from zinc blende is achieved by
(a) electrolytic reduction
(b) roasting followed by reduction with carbon
(c) roasting followed by reduction with another metal
(d) roasting followed by self-reduction. (2007)
- In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are
(a) O_2 and CO respectively
(b) O_2 and Zn dust respectively
(c) HNO_3 and Zn dust respectively
(d) HNO_3 and CO respectively (2012)
- Sulphide ores are common for the metals
(a) Ag, Cu and Pb (b) Ag, Cu and Sn
(c) Ag, Mg and Pb (d) Al, Cu and Pb (2013)

Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

- Of the following, the metals that cannot be obtained by electrolysis of the aqueous solution of their salts are
(a) Ag (b) Mg (c) Cu (d) Al (1990)
- Extraction of metal from the ore cassiterite involves
(a) carbon reduction of an oxide ore
(b) self-reduction of a sulphide ore
(c) removal of copper impurity
(d) removal of iron impurity. (2011)
- The carbon-based reduction method is NOT used for the extraction of
(a) tin from SnO_2 (b) iron from Fe_2O_3
(c) aluminium from Al_2O_3
(d) magnesium from $MgCO_3 \cdot CaCO_3$ (2013)
- Upon heating with Cu_2S , the reagent(s) that give copper metal is/are
(a) $CuFeS_2$ (b) CuO (c) Cu_2O (d) $CuSO_4$ (2014)
- Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is(are)
(a) impure Cu strip is used as cathode
(b) acidified aqueous $CuSO_4$ is used as electrolyte
(c) pure Cu deposits at cathode
(d) impurities settle as anode-mud. (2015)

Fill in the Blanks

- In the basic Bessemer process for the manufacture of steel the lining of the converter is made of The slag formed consists of (1980)
- In the thermite process is used as a reducing agent. (1980)
- Cassiterite is an ore of (1980)
- In extractive metallurgy of zinc, partial fusion of ZnO with coke is called and reaction of the ore to the molten metal is called (smelting, calcining, roasting, sintering) (1988)

Subjective Problems

17. Write the chemical equations involved in the extraction of lead from galena by self-reduction process. (1979)
18. Give reasons for the following:
- Metals can be recovered from their ores by chemical methods. (1984)
 - High purity metals can be obtained by zone refining method. (1984)
 - Why is sodium chloride added during electrolysis of fused anhydrous magnesium chloride? (1987)
 - Why is chalcocite roasted and not calcinated during recovery of copper? (1987)
19. Give the equations for the recovery of lead from galena by air reduction. (1987)

Matrix Match Type

20. Match the following extraction processes with the appropriate metals listed below :

Column I	Column II
(A) Silver	(P) Fused salt electrolysis
(B) Calcium	(Q) Carbon reduction
(C) Zinc	(R) Carbon monoxide reduction
(D) Iron	(S) Amalgamation
(E) Copper	(T) Self reduction

(1979)

21. Match the extraction process listed in column I with metals listed in column II.

Column I	Column II
A. Self reduction	P. Lead
B. Carbon reduction	Q. Silver
C. Complex formation and displacement by metal	R. Copper
D. Electrolytic reduction	S. Sodium

(2006)

22. Match the conversions in Column I with the type(s) of reaction(s) given in Column II. Indicate your answer by darkening the appropriate box.

Column I	Column II
A. $\text{PbS} \rightarrow \text{PbO}$	P. roasting
B. $\text{CaCO}_3 \rightarrow \text{CaO}$	Q. Calcination
C. $\text{ZnS} \rightarrow \text{Zn}$	R. carbon reduction
D. $\text{Cu}_2\text{S} \rightarrow \text{Cu}$	S. self reduction

(2008)

23. Match the anionic species given in Column I that are present in the ore(s) given in Column II.

Column I	Column II
(A) Carbonate	(P) Siderite
(B) Sulphide	(Q) Malachite
(C) Hydroxide	(R) Bauxite
(D) Oxide	(S) Calamine
	(T) Argentite

(2015)

ANSWER KEY

1. (c) 2. (d) 3. (a) 4. (c) 5. (b) 6. (b)
7. (a) 8. (b, d) 9. (a, c, d) 10. (c, d) 11. (b, c, d) 12. (b, c, d)
13. Magnesia and lime; Calcium phosphate
15. Tin
20. (A) \rightarrow S; (B) \rightarrow P; (C) \rightarrow Q; (D) \rightarrow Q, R; (E) \rightarrow T.
22. (A) \rightarrow P; (B) \rightarrow Q; (C) \rightarrow P, R; (D) \rightarrow P, S
21. (A) \rightarrow P, R; (B) \rightarrow P; (C) \rightarrow Q; (D) \rightarrow S
23. (A) \rightarrow P, Q; and S; (B) \rightarrow T; (C) \rightarrow Q and R; (D) \rightarrow R

Explanations

- (c)**: Aluminium (Al) reduces Fe_2O_3 or Cr_2O_3 and so Al acts as a reducing agent.

$$\text{Fe}_2\text{O}_3 + 2\text{Al} \longrightarrow 2\text{Fe} + \text{Al}_2\text{O}_3$$
- (d)**: Aluminium (Al) is more electropositive than hydrogen. Thus aluminium oxide will not be reduced by hydrogen.
- (a)**: $\text{MgCl}_2 \longrightarrow \text{Mg}^{2+} + 2\text{Cl}^-$
 (Fused, anhydrous)

$$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg} \text{ (cathode)}$$

$$2\text{Cl}^- \longrightarrow \text{Cl}_2 \uparrow + 2e^- \text{ (anode)}$$
- (c)**: Chalcopyrite is CuFeS_2 i.e. it contains both Cu and Fe. Cuprite is Cu_2O ; it contains only Cu. Chalcocite is Cu_2S ; it contains only Cu. Malachite is $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$; it contains only Cu.
- (b)**: Extraction of Zn from ZnS is achieved by roasting followed by reduction with carbon (smelting). This method is different from self reduction.

$$2\text{ZnS} + 3\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2$$

$$\text{ZnS} + 2\text{O}_2 \longrightarrow \text{ZnSO}_4$$

$$2\text{ZnSO}_4 \longrightarrow 2\text{ZnO} + 2\text{SO}_2 + \text{O}_2$$

$$\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$$
- (b)**: Silver ore is oxidised by using oxygen from air as follows:

$$4\text{Ag} + 8\text{NaCN} + 2\text{H}_2\text{O} + \text{O}_2(\text{air}) \longrightarrow 4\text{NaAg}(\text{CN})_2 + 4\text{NaOH}$$

$$\text{Ag}(0) \xrightarrow{\text{oxidation}} \text{Ag}(+1)$$
 Silver is precipitated from the solution by addition of Zn powder in a finely divided condition.

$$2\text{NaAg}(\text{CN})_2 + \text{Zn} \longrightarrow \text{Na}_2\text{Zn}(\text{CN})_4 + 2\text{Ag}$$
 Sodium zincocyanide

$$\text{Ag}(+1) \xrightarrow{\text{reduction}} \text{Ag}(0)$$
- (a)**: Sulphide ore of Ag \rightarrow Silver glance (Ag_2S); Cu \rightarrow Copper pyrites (CuFeS_2) and Pb \rightarrow Galena (PbS).
- (b, d)**: The reduction potentials of both Mg and Al are less than that of water. Thus the ions of both Mg and Al in aqueous solution cannot be reduced and in such a case water will be reduced.

$$2\text{H}_2\text{O} + 2e^- \longrightarrow \text{H}_2 + 2\text{OH}^-$$
- (a, c, d)**: Tin is extracted from cassiterite ore. It is reduced by carbon

$$\text{SnO}_2 + 2\text{C} \longrightarrow \text{Sn} + 2\text{CO}$$
 Crude metal contains impurities Fe, Tungsten and Cu.
- (c, d)**: Al_2O_3 and $\text{MgCO}_3 \cdot \text{CaCO}_3$ are reduced by electrolytic reduction method.
- (b, c, d)**: (a) $\text{CuFeS}_2 + \text{Cu}_2\text{S} \xrightarrow{\Delta}$ No reaction
 (b) $2\text{CuO} \xrightarrow{\Delta} \text{Cu}_2\text{O} + 1/2 \text{O}_2$
 (c) $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \xrightarrow{\Delta} 6\text{Cu} + \text{SO}_2$
 (d) $\text{CuSO}_4 \xrightarrow{\Delta} \text{CuO} + \text{SO}_2 + 1/2 \text{O}_2$
 Both CuO and CuSO_4 upon heating produce Cu_2O and CuO respectively and further Cu_2O and CuO on heating with Cu_2S give Cu.
- (b, c, d)**: (a) Impure copper is made the anode and a thin sheet of pure copper is made the cathode, while copper sulphate solution acidified with sulphuric acid is taken as the electrolyte. Pure copper deposits at cathode and impurities settle as anode-mud.
 At anode : $\text{Cu}_{(s)} \longrightarrow \text{Cu}_{(aq)}^{2+} + 2e^-$
 At cathode : $\text{Cu}_{(aq)}^{2+} + 2e^- \longrightarrow \text{Cu}_{(s)}$
- Magnesia and lime; calcium phosphate
- Aluminium
- Tin; SnO_2
- Sintering; smelting.
- During roasting, in excess supply of air, in a reverberatory furnace the following reactions occur.

$$2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$$

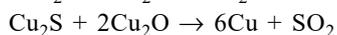
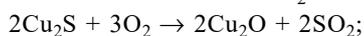
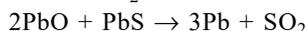
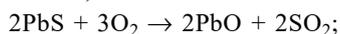
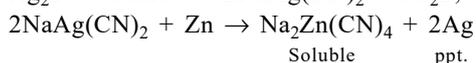
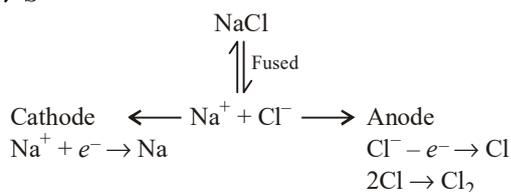
$$\text{PbS} + 2\text{O}_2 \longrightarrow \text{PbSO}_4$$

$$\text{PbSO}_4 + \text{PbS} \longrightarrow 2\text{Pb} + 2\text{SO}_2$$

$$\text{PbS} + 2\text{PbO} \longrightarrow 3\text{Pb} + \text{SO}_2$$
- (i) Metals generally occur as oxides, carbonates, sulphides which can be calcinated or roasted.
 (ii) Zone refining method is based on the difference in solubility of impurities in molten and solid states of the metal. This method can be used for those metals which can be readily melted and can be easily crystallized out from the melt e.g. Ge, Si, etc.
 (iii) Sodium chloride is added to prevent hydrolysis of magnesium chloride and also to provide conductivity to the electrolyte. It also lowers the fusion temperature of anhydrous MgCl_2 .
 (iv) Chalcocite (Cu_2S) being a sulphide ore, has to be roasted (heated in excess of air) and not calcinated, so as to convert it to its oxide (Cu_2O).
- Following reactions occur during recovery of lead (Pb) from galena (PbS).

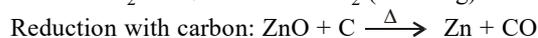
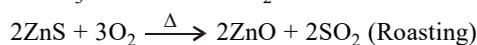
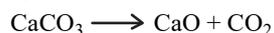
$$2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2 \uparrow$$

$$\text{PbS} + 2\text{PbO} \longrightarrow 3\text{Pb} + \text{SO}_2 \uparrow$$
- (A) \rightarrow (S); (B) \rightarrow (P); (C) \rightarrow (Q); (D) \rightarrow (Q, R); (E) \rightarrow (T)

21. A → P, R**B → P****C → Q****D → S****22. (A) → P; (B) → Q; (C) → P, R; (D) → P, S**

Sulphides of Cu, Pb, when roasted in air are converted partially in to oxides. On further roasting in the absence of air, self reduction takes place.

Calcination is used when concentrated ore is in the form of hydroxide or carbonate, volatile matter is burnt away.

**23. (A) → (P, Q and S)**

Carbonate ores are

(P) Siderite : FeCO_3

(Q) Malachite : $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$

(S) Calamine : ZnCO_3

(B) → (T)

Sulphide ore is (T) Argentite : Ag_2S .

(C) → (Q and R)

Hydroxide ion is present in

(Q) Malachite : $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$

(R) Bauxite : $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ or $\text{AlO}_x(\text{OH})_{3-2x}$
where $0 < x < 1$

(D) → (R)

Oxide ore is bauxite (R) only.



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The s-Block Elements

Multiple Choice Questions with ONE Correct Answer

- The temporary hardness of water due to calcium bicarbonate can be removed by adding
 - CaCO_3
 - $\text{Ca}(\text{OH})_2$
 - CaCl_2
 - HCl
 (1979)
- Calcium is obtained by
 - electrolysis of molten CaCl_2
 - electrolysis of a solution of CaCl_2 in water
 - reduction of CaCl_2 with carbon
 - roasting of limestone.
 (1980)
- A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of
 - sodium atoms
 - sodium hydride
 - sodium amide
 - solvated electrons
 (1981)
- Heavy water is
 - H_2^{18}O
 - water obtained by repeated distillation
 - D_2O
 - water at 4°C
 (1985)
- The hydration energy of Mg^{2+} is larger than that of
 - Al^{3+}
 - Na^+
 - Be^{2+}
 - Mg^{3+}
 (1984)
- The oxide that gives hydrogen peroxide on treatment with a dilute acid is
 - PbO_2
 - Na_2O_2
 - MnO_2
 - TiO_2
 (1985)
- Molecular formula of Glauber's salt is
 - $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
 - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 - $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
 - $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
 (1985)
- The pair of compounds which cannot exist together in solution is
 - NaHCO_3 and NaOH
 - Na_2CO_3 and NaHCO_3
 - Na_2CO_3 and NaOH
 - NaHCO_3 and NaCl
 (1986)
- The metallic lustre exhibited by sodium is explained by
 - diffusion of sodium ions
 - oscillations of loose electrons
 - excitation of free proton
 - existence of body centered cubic lattice
 (1987)
- The volume strength of 1.5 N H_2O_2 solution is
 - 4.8
 - 8.4
 - 3.0
 - 8.0
 (1991)
- The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order.

K_2CO_3 (I), MgCO_3 (II), CaCO_3 (III), BeCO_3 (IV)

 - $\text{I} < \text{II} < \text{III} < \text{IV}$
 - $\text{IV} < \text{II} < \text{III} < \text{I}$
 - $\text{IV} < \text{II} < \text{I} < \text{III}$
 - $\text{II} < \text{IV} < \text{III} < \text{I}$
 (1996)
- Property of all the alkaline earth metals that increases with their atomic number is
 - ionisation energy
 - solubility of their hydroxides
 - solubility of their sulphate
 - electronegativity
 (1997)
- Among the following statements, the incorrect one is
 - calamine and siderite are carbonates
 - argentite and cuprite are oxides
 - zinc blende and pyrites are sulphides
 - malachite and azurite are ores of copper
 (1997)
- The chemical composition of 'slag' formed during the smelting process in the extraction of copper is
 - $\text{Cu}_2\text{O} + \text{FeS}$
 - FeSiO_3
 - CuFeS_2
 - $\text{Cu}_2\text{S} + \text{FeO}$
 (2001)
- The set representing the correct order of first ionisation potential is
 - $\text{K} > \text{Na} > \text{Li}$
 - $\text{Be} > \text{Mg} > \text{Ca}$
 - $\text{B} > \text{C} > \text{N}$
 - $\text{Ge} > \text{Si} > \text{C}$
 (2001)

16. A sodium salt on treatment with MgCl_2 gives white precipitate only on heating. The anion of the sodium salt is

- (a) HCO_3^- (b) CO_3^{2-} (c) NO_3^- (d) SO_4^{2-}
(2004)

17. MgSO_4 on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate. What is its formula?

- (a) $\text{Mg}(\text{NH}_4)\text{PO}_4$ (b) $\text{Mg}_3(\text{PO}_4)_2$
(c) $\text{MgCl}_2 \cdot \text{MgSO}_4$ (d) MgSO_4 . (2006)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

18. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water the sodium ions are exchanged with

- (a) H^+ ions (b) Ca^{++} ions
(c) SO_4^{--} ions (d) Mg^{++} ions
(1990)

19. The species that do not contain peroxide ions are

- (a) PbO_2 (b) H_2O_2 (c) $\text{Sr}(\text{O}_2)_2$ (d) BaO_2
(1998)

20. Highly pure dilute solution of sodium in liquid ammonia

- (a) shows blue colour
(b) exhibits electrical conductivity
(c) produces sodium amide
(d) produces hydrogen gas. (1998)

21. The compound(s) formed upon combustion of sodium metal in excess air is(are)

- (a) Na_2O_2 (b) Na_2O (c) NaO_2 (d) NaOH .
(2009)

22. The reagent(s) used for softening the temporary hardness of water is(are)

- (a) $\text{Ca}_3(\text{PO}_4)_2$ (b) $\text{Ca}(\text{OH})_2$
(c) Na_2CO_3 (d) NaOCl (2010)

Fill in the Blanks

23. Anhydrous MgCl_2 is obtained by heating the hydrated salt with (1980)

24. The absorption of hydrogen by palladium is commonly known as (1983)

25. Sodium dissolved in liquid ammonia conducts electricity because of (1985)

26. The electrolysis of molten sodium hydride liberates gas at the (1989)

27. Ca^{2+} has smaller ionic radius than K^+ because it has (1993)

28. A solution of sodium in liquid ammonia at -33°C conducts electricity. On cooling, the conductivity of this solution (1997)

True / False

29. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ on heating gives anhydrous MgCl_2 . (1982)

30. The softness of group I-A metals increases down the group with increasing atomic number. (1986)

31. Sodium when burnt in excess of oxygen gives sodium oxide. (1987)

Subjective Problems

32. Water is a liquid, while H_2S is a gas at ordinary temperature Explain. (1978)

33. CO_2 does not burn in air and does not support combustion, but a burning Mg wire continues to burn in it. Explain. (1980)

34. (a) One litre of a sample of hard water contains 1 mg of CaCl_2 and 1 mg of MgCl_2 . Find the total hardness in terms of parts of CaCO_3 per 10^6 parts of water by weight.

(b) A sample of hard water contains 20 mg of Ca^{++} ions per litre. How many milliequivalent of Na_2CO_3 would be required to soften 1 litre of the sample?

(c) 1 g of Mg is burnt in a closed vessel which contains 0.5 g of O_2 .

(i) Which reactant is left in excess?

(ii) Find the weight of the excess reactant.

(iii) How many millilitres of 0.5 N H_2SO_4 will dissolve the residue in the vessel. (1980)

35. Give reasons for the following :

(i) Sodium carbonate is made by Solvay process but the same process is not extended to the manufacture of potassium carbonate. (1981)

(ii) Hydrogen peroxide acts as an oxidising as well as a reducing agent. (1986)

(iii) Magnesium oxide is used for the lines of steel making furnace. (1987)

(iv) The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts. Why? (1997)

(v) BeCl_2 can be easily hydrolysed. (1999)

36. How will you prepare bleaching powder from slaked lime? (1982)

The s-Block Elements

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37. Write down the balanced equations for the reactions when:
- Calcium phosphate is heated with a mixture of sand and carbon. (1985)
 - Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia. (1988)
 - Potassium ferricyanide reacts with hydrogen peroxide in basic solution. (1989)
 - Carbon dioxide is passed through a suspension of limestone in water. (1991)
38. Give briefly the isolation of magnesium from sea water by the Dow process. Give equations for the steps involved. (1993)
39. Complete and balance the following reaction:
- $$\text{Ca}_5(\text{PO}_4)_3\text{F} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \xrightarrow{\text{Heat}}$$
- + 5CaSO₄·2H₂O + (1994)
40. A 5.0 cm³ solution of H₂O₂ liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H₂O₂ solution in terms of volume strength at STP. (1995)
41. Explain the difference in the nature of bonding in LiF and LiI. (1996)
42. Write the reaction involved in manufacture of triple super phosphate from fluorapatite. (1997)
43. To a 25 ml H₂O₂ solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 ml of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H₂O₂ solution. (1997)
44. Give reactions for the oxidation of hydrogen peroxide with potassium permanganate in acidic medium. (1997)
45. Element *A* burns in nitrogen to give an ionic compound *B*. Compound *B* reacts with water to give *C* and *D*. A solution of *C* becomes 'milky' on bubbling carbon dioxide. Identify *A*, *B*, *C* and *D*. (1997)
46. Arrange the following sulphates of alkaline earth metals in order of decreasing thermal stability:
BeSO₄, MgSO₄, CaSO₄, SrSO₄ (1997)
47. Work out the following using chemical equations:
Chlorination of calcium hydroxide produces bleaching powder. (1998)
48. Hydrogen peroxide acts both as an oxidising and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of H₂O₂ using chemical equations. (1998)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.
49. **Statement-1** : The alkali metals can form ionic hydrides which contain the hydride ion H⁻.
Statement-2 : The alkali metals have low electronegativity; their hydrides conduct electricity when fused and liberate hydrogen at the anode. (1994)
50. **Statement-1** : Alkali metals dissolve in liquid ammonia to give blue solutions.
Statement-2 : Alkali metals in liquid ammonia give solvated species of the type [M(NH₃)_{*n*}]⁺ (*M* = alkali metals). (2007)

ANSWER KEY

- | | | | | | |
|---------------------------|---|---------------------|------------|---------------------------------|------------|
| 1. (b) | 2. (a) | 3. (d) | 4. (c) | 5. (b) | 6. (b) |
| 7. (d) | 8. (a) | 9. (b) | 10. (b) | 11. (b) | 12. (b) |
| 13. (b) | 14. (b) | 15. (b) | 16. (a) | 17. (a) | 18. (b, d) |
| 19. (a, c) | 20. (a, b) | 21. (a, b) | 22. (b, c) | 23. Anhydrous hydrogen chloride | |
| 24. Occlusion | 25. Ammoniated electrons | 26. Hydrogen, anode | | | |
| 27. Higher nuclear charge | 28. Decreases | 29. False | 30. True | | |
| 31. False | 34. 2 parts; 1 milli equivalent; Mg; 0.25 g; 62.5 ml. | | | | |
| 49. (b) | 50. (b) | | | | |

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The *p*-Block Elements

Multiple Choice Questions with ONE Correct Answer

- Which are the incorrect statements?
 - NO is heavier than O₂.
 - The formula of heavy water is D₂O.
 - Nitrogen diffuses faster than oxygen through an orifice.
 - NH₃ can be used as refrigerant. (1978)
- Ammonia gas can be dried by
 - conc. H₂SO₄
 - PCl₅
 - CaCl₂
 - quick lime (1978)
- Select the correct answer in each case given below. If none of the given answers is correct, write NONE (1 mark would be DEDUCTED for each wrong answer). Answer the various parts in the serial order (i), (ii), (iii), etc.

Example : The colour of hydrogen is
black, yellow, orange, red

Answer : NONE

 - Ammonia can be dried by
 - concentrated H₂SO₄
 - P₂O₅
 - Anhydrous CuSO₄
 - Anhydrous CaCl₂
 - Lead pencil contains
 - Pb
 - FeS
 - Graphite
 - PbS
 - Which of the following is coloured?
 - NO
 - N₂O
 - SO₃
 - CO
 - A solution of KBr is treated with each of the following. Which one would liberate bromine?
 - Cl₂
 - HI
 - I₂
 - SO₂
 - Which of the following is the most stable to heat?
 - HCl
 - HOCl
 - HBr
 - HI (1980)
- HBr and HI reduce sulphuric acid, HCl can reduce KMnO₄ and HF can reduce
 - H₂SO₄
 - KMnO₄
 - K₂Cr₂O₇
 - none of these (1981)
- Which of the following statements about anhydrous aluminium chloride is correct?
 - It exists as AlCl₃ molecules.
 - It is not easily hydrolysed.
 - It sublimes at 100°C under vacuum.
 - It is a strong Lewis base. (1981)
- Moderate electrical conductivity is shown by
 - silica
 - graphite
 - diamond
 - carborundum (1982)
- Chlorine acts as a bleaching agent only in presence of
 - dry air
 - moisture
 - sunlight
 - pure oxygen (1983)
- Nitrogen dioxide cannot be obtained by heating
 - KNO₃
 - Pb(NO₃)₂
 - Cu(NO₃)₂
 - AgNO₃ (1985)
- A gas that cannot be collected over water is
 - N₂
 - O₂
 - SO₂
 - PH₃ (1985)
- The compound which gives off oxygen on moderate heating is
 - cupric oxide
 - mercuric oxide
 - zinc oxide
 - aluminium oxide (1986)
- The bonds present in N₂O₅ are
 - only ionic
 - covalent and coordinate
 - only covalent
 - covalent and ionic (1986)
- Which of the following oxides of nitrogen is a coloured gas?
 - N₂O
 - NO
 - N₂O₅
 - NO₂ (1987)
- Amongst the trihalides of nitrogen which one is least basic?
 - NF₃
 - NCl₃
 - NBr₃
 - NI₃ (1987)
- Bromine can be liberated from potassium bromide solution by action of

- (a) iodine solution (b) chlorine water
(c) sodium chloride (d) potassium iodide
(1987)
15. There is no S – S bond in
(a) $S_2O_4^{2-}$ (b) $S_2O_5^{2-}$ (c) $S_2O_3^{2-}$ (d) $S_2O_7^{2-}$
(1991)
16. In P_4O_{10} each P atom is linked with O atoms.
(a) 2 (b) 3 (c) 4 (d) 5 (1995)
17. H_2SO_4 cannot be used to prepare HBr from NaBr as it
(a) reacts slowly with NaBr
(b) oxidises HBr
(c) reduces HBr
(d) disproportionates HBr (1995)
18. Hydrolysis of one mole of peroxodisulphuric acid produces
(a) two moles of sulphuric acid
(b) two moles of peroxomonosulphuric acid
(c) one mole of sulphuric acid and one mole of peroxomonosulphuric acid
(d) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide. (1996)
19. Which of the following statements is correct for $CsBr_3$?
(a) It is a covalent compound.
(b) It contains Cs^{3+} and Br^- ions.
(c) It contains Cs^+ and Br_3^- ions.
(d) It contains Cs^+ , Br^- and lattice Br_2 molecule (1996)
20. KF combines with HF to form KHF_2 . The compound contains the species
(a) K^+ , F^- and H^+ (b) K^+ , F^- and HF
(c) K^+ and $[HF_2]^-$ (d) $[KHF]^-$ and F^- (1996)
21. Sodium thiosulphate is prepared by
(a) reducing Na_2SO_4 solution with H_2S
(b) boiling Na_2SO_3 solution with S in alkaline medium
(c) neutralising $H_2S_2O_3$ solution with NaOH
(d) boiling Na_2SO_3 solution with S in acidic medium (1996)
22. Which of the following halides is least stable and has doubtful existence?
(a) Cl_4 (b) GeI_4 (c) SnI_4 (d) PbI_4
(1996)
23. Which one of the following oxides is neutral?
(a) CO (b) SnO_2 (c) ZnO (d) SiO_2
(1996)
24. Which one of the following species is not a pseudohalide?
(a) CNO^- (b) $RCOO^-$ (c) OCN^- (d) NNN^-
(1997)
25. One mole of calcium phosphide on reaction with excess water gives
(a) one mole of phosphine
(b) two moles of phosphoric acid
(c) two moles of phosphine
(d) one mole of phosphorus pentoxide (1999)
26. On heating ammonium dichromate, the gas evolved is
(a) oxygen (b) ammonia
(c) nitrous oxide (d) nitrogen (1999)
27. In the commercial electrochemical process for aluminium extraction the electrolyte used is
(a) $Al(OH)_3$ in NaOH solution
(b) an aqueous solution of $Al_2(SO_4)_3$
(c) a molten mixture of Al_2O_3 and Na_3AlF_6
(d) a molten mixture of Al_2O_3 and $Al(OH)_3$ (1999)
28. In compounds of type ECl_3 , where $E = B, P, As$ or Bi , the angles $Cl-E-Cl$ for different E are in the order
(a) $B > P = As = Bi$ (b) $B > P > As > Bi$
(c) $B < P = As = Bi$ (d) $B < P < As < Bi$
(1999)
29. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out
(a) in the presence of NaCl
(b) in the presence of fluorine
(c) in the presence of cryolite which forms a melt with lower melting temperature
(d) in the presence of cryolite which forms a melt with higher melting temperature (2000)
30. The number of P – O – P bonds in cyclic metaphosphoric acid is
(a) zero (b) two (c) three (d) four
(2000)
31. Ammonia can be dried by
(a) conc. H_2SO_4 (b) P_4O_{10}
(c) CaO (d) anhydrous $CaCl_2$
(2000)
32. The number of S – S bonds in sulphur trioxide trimer (S_3O_9) is
(a) three (b) two (c) one (d) zero
(2001)
33. Polyphosphates are used as water softening agents because they
(a) form soluble complexes with anionic species
(b) precipitate anionic species
(c) form soluble complexes with cationic species
(d) precipitate cationic species (2002)

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34. For H_3PO_3 and H_3PO_4 the correct choice is
 (a) H_3PO_3 is dibasic and reducing
 (b) H_3PO_3 is dibasic and non-reducing
 (c) H_3PO_4 is tribasic and reducing
 (d) H_3PO_3 is tribasic and non-reducing (2002)
35. H_3BO_3 is
 (a) monobasic and weak Lewis acid
 (b) monobasic and weak Bronsted acid
 (c) monobasic and strong Lewis acid
 (d) tribasic and weak Bronsted acid (2003)
36. $(\text{Me})_2\text{SiCl}_2$ on hydrolysis will produce
 (a) $(\text{Me})_2\text{Si}(\text{OH})_2$ (b) $(\text{Me})_2\text{Si}=\text{O}$
 (c) $-\text{[O}-(\text{Me})_2\text{Si-O}]_n-$ (d) $\text{Me}_2\text{SiCl}(\text{OH})$ (2003)
37. Total number of lone pair of electrons in XeOF_4 is
 (a) 0 (b) 1 (c) 2 (d) 3 (2004)
38. The acid having O — O bond is
 (a) $\text{H}_2\text{S}_2\text{O}_3$ (b) $\text{H}_2\text{S}_2\text{O}_6$
 (c) $\text{H}_2\text{S}_2\text{O}_8$ (d) $\text{H}_2\text{S}_4\text{O}_6$ (2004)
39. Pb and Sn are extracted from their chief ore by
 (a) carbon reduction and self reduction respectively
 (b) self reduction and carbon reduction respectively
 (c) electrolysis and self reduction respectively
 (d) self reduction and electrolysis respectively (2004)
40. Name of the structure of silicates in which three oxygen atoms of $[\text{SiO}_4]^{4-}$ are shared is
 (a) pyrosilicate (b) sheet silicate
 (c) linear chain silicate
 (d) three dimensional silicate (2005)
41. Which is the most thermodynamically stable allotropic form of phosphorus?
 (a) Red (b) White (c) Black (d) Yellow (2005)
42. Which of the following is not oxidised by O_3 ?
 (a) KI (b) FeSO_4
 (c) KMnO_4 (d) K_2MnO_4 (2005)
43. Which blue liquid is obtained on reacting equimolar amounts of two gases at -30°C ?
 (a) N_2O (b) N_2O_3 (c) N_2O_4 (d) N_2O_5 (2005)
44. When PbO_2 reacts with concentrated HNO_3 the gas evolved is
 (a) NO_2 (b) O_2 (c) N_2 (d) N_2O (2005)
45. $\text{B}(\text{OH})_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na}[\text{B}(\text{OH})_4] + \text{H}_2\text{O}$
 How can this reaction is made to proceed in forward direction?
 (a) Addition of *cis*-1,2-diol
 (b) Addition of borax
 (c) Addition of *trans*-1,2-diol
 (d) Addition of Na_2HPO_4 . (2006)
46. The percentage of *p*-character in the orbitals forming P — P bonds in P_4 is
 (a) 25 (b) 33 (c) 50 (d) 75. (2007)
47. Aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ on reaction with Cl_2 gives
 (a) $\text{Na}_2\text{S}_4\text{O}_6$ (b) NaHSO_4
 (c) NaCl (d) NaOH (2008)
48. The reaction of P_4 with *X* leads selectively to P_4O_6 . The *X* is
 (a) dry O_2
 (b) a mixture of O_2 and N_2
 (c) moist O_2
 (d) O_2 in the presence of aqueous NaOH . (2009)
49. Extra pure N_2 can be obtained by heating
 (a) NH_3 with CuO (b) NH_4NO_3
 (c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (d) $\text{Ba}(\text{N}_3)_2$ (2011)
50. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of
 (a) NO (b) NO_2
 (c) N_2O (d) N_2O_4 (2013)
51. The product formed in the reaction of SOCl_2 with white phosphorous is
 (a) PCl_3 (b) SO_2Cl_2 (c) SCl_2 (d) POCl_3 (2014)
52. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is

$$\text{XeF}_6 \xrightarrow{\text{Complete hydrolysis}} \text{P} + \text{other product}$$

$$\downarrow \text{OH}^-/\text{H}_2\text{O}$$

$$\text{Q}$$

$$\downarrow \text{slow disproportionation in OH}^-/\text{H}_2\text{O}$$
 products
 (a) 0 (b) 1 (c) 2 (d) 3 (2014)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

53. In the electrolysis of alumina, cryolite is added to
 (a) lower the melting point of alumina
 (b) increase the electrical conductivity
 (c) minimise the anode effect
 (d) remove impurities from alumina (1986)

54. Nitrogen(I) oxide is produced by
 (a) thermal decomposition of ammonium nitrate
 (b) disproportionation of N_2O_4
 (c) thermal decomposition of ammonium nitrite
 (d) interaction of hydroxylamine hydrochloride and nitrous acid. (1989)
55. The compounds used as refrigerant are
 (a) NH_3 (b) CCl_4 (c) CF_4 (d) CF_2Cl_2 (1990)
56. The major role of fluorspar (CaF_2), which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6), is
 (a) as a catalyst
 (b) to make the fused mixture very conducting
 (c) to lower the temperature of the melt
 (d) to decrease the rate of oxidation of carbon at the anode. (1993)
57. The material used in the solar cells contains
 (a) Cs (b) Si (c) Sn (d) Ti (1993)
58. Sodium nitrate decomposes above $800^\circ C$ to give
 (a) N_2 (b) O_2 (c) NO_2 (d) Na_2O (1998)
59. White phosphorus (P_4) has
 (a) six P — P single bonds
 (b) four P — P single bonds
 (c) four lone pairs of electrons
 (d) PPP angle of $60^\circ C$ (1998)
60. Ammonia, on reaction with hypochlorite anion, can form
 (a) NO (b) NH_4Cl (c) N_2H_4 (d) HNO_2 (1999)
61. The species present in solution when CO_2 is dissolved in water are
 (a) CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-}
 (b) H_2CO_3 , CO_3^{2-} (c) CO_3^{2-} , HCO_3^-
 (d) CO_2 , H_2CO_3 . (2006)
62. The nitrogen oxide(s) that contain(s) N — N bond(s) is(are)
 (a) N_2O (b) N_2O_3 (c) N_2O_4 (d) N_2O_5 . (2009)
63. In the reaction : $2X + B_2H_6 \rightarrow [BH_2(X)_2]^+ [BH_4]^-$, the amine(s) X is(are)
 (a) NH_3 (b) CH_3NH_2
 (c) $(CH_3)_2NH$ (d) $(CH_3)_3N$. (2009)
64. Which of the following hydrogen halides react(s) with $AgNO_3$ (aq.) to give a precipitate that dissolves in $Na_2S_2O_3$ (aq.)?
 (a) HCl (b) HF (c) HBr (d) HI (2012)
65. With respect to graphite and diamond, which of the statement(s) given is(are) correct?
 (a) Graphite is harder than diamond.
 (b) Graphite has higher electrical conductivity than diamond.
 (c) Graphite has higher thermal conductivity than diamond.
 (d) Graphite has higher C — C bond order than diamond. (2012)
66. The correct statement(s) about O_3 is(are)
 (a) O — O bond lengths are equal
 (b) thermal decomposition of O_3 is endothermic
 (c) O_3 is diamagnetic in nature
 (d) O_3 has a bent structure. (2013)
67. The correct statement(s) for orthoboric acid is/are
 (a) it behaves as a weak acid in water due to self ionization
 (b) acidity of its aqueous solution increases upon addition of ethylene glycol
 (c) it has a three dimensional structure due to hydrogen bonding
 (d) it is a weak electrolyte in water. (2014)
68. The correct statement(s) regarding, (i) $HClO$, (ii) $HClO_2$, (iii) $HClO_3$ and (iv) $HClO_4$, is(are)
 (a) The number of $Cl=O$ bonds in (ii) and (iii) together is two
 (b) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three
 (c) The hybridization of Cl in (iv) is sp^3
 (d) Amongst (i) to (iv), the strongest acid is (i). (2015)
69. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are
 (a) CH_3SiCl_3 and $Si(CH_3)_4$
 (b) $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$
 (c) $(CH_3)_2SiCl_2$ and CH_3SiCl_3
 (d) $SiCl_4$ and $(CH_3)_3SiCl$ (2015)

Fill in the Blanks

70. Iodine reacts with hot NaOH solution. The products are NaI and (1980)
71. The lowest possible oxidation state of nitrogen is (1980)
72. is a weak acid. (HF, HCl, HI) (1981)
73. The increase in the solubility of iodine in an aqueous solution of potassium iodide is due to the formation of (1982)

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74. Hydrogen gas is liberated by the action of aluminium with concentrated solution of (1987)
75. phosphorus is reactive because of its highly strained tetrahedral structure. (1987)
76. acid gives hypo ion. (hydrobromic, hypobromous, perbromic, bromide, bromite, perbromate). (1988)
77. Sulphur acts as agent in vulcanization of rubber. (1989)
78. The basicity of phosphorous acid (H_3PO_3) is (1990)
79. The hydrolysis of alkyl substituted chlorosilanes gives (1991)
80. In P_4O_{10} , the number of oxygen atoms bonded to each phosphorus atom is (1992)
81. The lead chamber process involves oxidation of SO_2 by atomic oxygen under the influence of as catalyst. (1992)
82. The hydrolysis of trialkylchlorosilane $R_3\text{SiCl}$, yields (1994)
83. One recently discovered allotrope of carbon (*e.g.*, C_{60}) is commonly known as (1994)
84. Solubility of iodine in water is greatly increased by the addition of iodide ions because of the formation of (1994)
85. The angle P-P-P in P_4 molecule is degree. (1997)
86. When an aqueous solution of sodium fluoride is electrolysed, the gas liberated at the anode is (1997)
87. A liquid which is permanently supercooled is frequently called a (1997)
88. Compounds that formally contain Pb^{4+} are easily reduced to Pb^{2+} . The stability of the lower oxidation state is due to (1997)

True / False

89. Red phosphorus is less volatile than white phosphorus because the former has tetrahedral structure. (1982)
90. When PbO_2 reacts with a dilute acid, it gives hydrogen peroxide. (1982)
91. Dilute HCl oxidises metallic Fe to Fe^{2+} . (1983)

92. In aqueous solution chlorine is a stronger oxidising agent than fluorine. (1984)
93. The H — N — H bond angle in NH_3 is greater than H — As — H bond angle in AsH_3 . (1984)
94. Carbon tetrachloride is inflammable. (1985)
95. All the Al — Cl bonds in Al_2Cl_6 are equivalent. (1989)
96. Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state. (1991)
97. Diamond is harder than graphite. (1993)
98. The tendency for catenation is much higher for C than for Si. (1993)
99. HBr is a stronger acid than HI because of hydrogen bonding. (1993)

Subjective Problems

100. (a) State, with balanced equations, what happens when:
 (i) Tin is treated with moderately concentrated nitric acid.
 (ii) Silver is treated with hot concentrated sulphuric acid.
 (iii) Aluminium is reacted with hot concentrated caustic soda solution.
 (iv) Ammonium dichromate is heated.
 (v) Hydrogen sulphide is passed through a solution of potassium permanganate acidified with dilute sulphuric acid.
 (b) Write balanced equations involved in the preparation of :
 (i) Anhydrous aluminium chloride from alumina.
 (ii) Bleaching powder from slaked lime.
 (iii) Tin metal from cassiterite.
 (iv) Chlorine from sodium chloride.
 (v) Nitric oxide from nitric acid. (1979)
101. Account for the following. Limit your answer to two sentences.
 (i) Hydrogen bromide cannot be prepared by the action of concentrated sulphuric acid on sodium bromide.
 (ii) When a blue litmus paper is dipped into a solution of hypochlorous acid, it first turns red and then later gets decolourised. (1979)
102. Suggest a simple qualitative test to distinguish between each of the following pairs.
 (i) PbCO_3 and PbSO_4
 (ii) CaCl_2 and MgCl_2
 (iii) Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_3$ (1979)

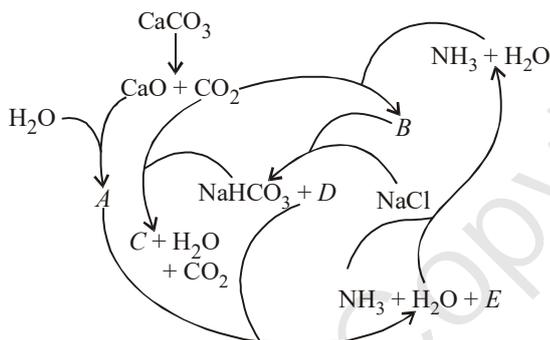
- 103.** Explain the following in not more than two sentences.
 (i) Conc. HNO_3 turns yellow in sunlight.
 (ii) Bleaching powder loses its bleaching property when it is kept in an open bottle for a long time. (1980)
- 104.** 19 g of molten SnCl_2 is electrolysed for some time. Inert electrodes are used. 0.119 g of Sn is deposited at the cathode. No substance is lost during the electrolysis. Find the ratio of the weights of SnCl_2 : SnCl_4 after electrolysis. (1980)
- 105.** Give structural formula for the following:
 (i) Phosphorous acid, H_3PO_3 (1981)
 (ii) Pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$ (1981)
- 106.** Complete the following equations (no balancing is needed)
 (i) $\text{HCO}_3^- + \text{Al}^{3+} \longrightarrow \text{Al}(\text{OH})_3 + \dots$ (1981)
 (ii) $\text{AlBr}_3 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_3\text{PO}_4 \longrightarrow$
 $\text{K}_3\text{PO}_4 + \text{AlPO}_4 + \text{H}_2\text{O} + \dots + \dots$ (1981)
- 107.** Give reasons for the following:
 (i) Carbon acts as an abrasive and also as a lubricant. (1981)
 (ii) Sulphur melts to a clear mobile liquid at 119°C , but on further heating above 160°C , it becomes viscous. (1981)
 (iii) In the preparation of hydrogen iodide from alkali metal iodides, phosphoric acid is preferred to sulphuric acid. (1982)
 (iv) Orthophosphoric acid, H_3PO_4 , is tribasic, but phosphorous acid, H_3PO_3 , is dibasic. (1982)
 (v) A bottle of liquor ammonia should be cooled before opening the stopper. (1983)
 (vi) Solid carbon dioxide is known as dry ice. (1983)
 (vii) Anhydrous HCl is a bad conductor of electricity but aqueous HCl is a good conductor of electricity. (1985)
 (viii) Graphite is used as a solid lubricant. (1985)
 (ix) Fluorine cannot be prepared from fluorides by chemical oxidation. (1985)
 (x) The mixture of hydrazine and hydrogen peroxide with a copper(II) catalyst is used as a rocket propellant. (1987)
 (xi) Orthophosphorous acid is not tribasic acid. (1987, 1989)
 (xii) The molecule of magnesium chloride is linear whereas that of stannous chloride is angular. (1987)
- (xiii) Valency of oxygen is generally two whereas sulphur shows valency of two, four and six. (1988)
 (xiv) Phosphine has lower boiling point than ammonia. (1989)
 (xv) Ammonium chloride is acidic in liquid ammonia solvent. (1991)
 (xvi) The hydroxides of aluminium and iron are insoluble in water. However, NaOH is used to separate one from the other. (1991)
 (xvii) Bond dissociation energy of F_2 is less than that of Cl_2 . (1992)
 (xviii) Sulphur dioxide is a more powerful reducing agent in an alkaline medium than in acidic medium. (1992)
 (xix) The experimentally determined N—F bond length in NF_3 is greater than the sum of the single bond covalent radii of N and F. (1995)
 (xx) Mg_3N_2 when reacted with water gives off NH_3 but HCl is not obtained from MgCl_2 on reaction with water at room temperature. (1995)
 (xxi) $(\text{SiH}_3)_3\text{N}$ is a weaker base than $(\text{CH}_3)_3\text{N}$. (1995)
- 108.** Write balanced equations for the following reactions :
 (i) White phosphorus (P_4) is boiled with a strong solution of sodium hydroxide in an inert atmosphere. (1982/87)
 (ii) Sodium iodate is treated with sodium bisulphite solution. (1982, 1990)
 (iii) A mixture of potassium chlorate, oxalic acid and sulphuric acid is heated. (1985)
 (iv) Ammonium sulphate is heated with a mixture of nitric oxide and nitrogen dioxide. (1985)
 (v) Hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide. (1985)
 (vi) Tin is treated with concentrated nitric acid. (1985)
 (vii) Pb_3O_4 is treated with nitric acid. (1985)
 (viii) Dilute nitric acid is slowly reacted with metallic tin. (1987)
 (ix) Potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid. (1987)
 (x) Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide. (1988)
 (xi) Hypophosphorous acid is heated. (1989)

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- (xii) Sodium bromate reacts with fluorine in presence of alkali. (1989)
- (xiii) Sodium chlorate reacts with sulphur dioxide in dilute sulphuric acid medium. (1989)
- (xiv) Preparation of crystalline silicon from SiCl_4 . (1990)
- (xv) Preparation of phosphine from CaO and white phosphorus. (1990)
- (xvi) Preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide. (1990)
- (xvii) Aqueous solution of sodium nitrate is heated with zinc dust and caustic soda solution. (1990)
- (xviii) Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda. (1991)
- (xix) Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate. (1991)
- (xx) Elemental phosphorus reacts with concentrated HNO_3 to give phosphoric acid. (1991)
- (xxi) Sulphur is precipitated in the reaction of hydrogen sulphide with sodium bisulphite solution. (1991)
- (xxii) Phosphorus is treated with concentrated nitric acid.
OR
Manufacture of phosphoric acid from phosphorus. (1997)
- (xxiii) Reaction of aluminium with aqueous sodium hydroxide. (1997)
- (xxiv) Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. (1997)
- (xxv) $\text{P}_4\text{O}_{10} + \text{PCl}_5 \rightarrow$ (1998)
- (xxvi) $\text{SnCl}_4 + \text{C}_2\text{H}_5\text{Cl} + \text{Na} \rightarrow$ (1998)
- 109.** Show with equations how the following compound is prepared (equations need not be balanced) :
Sodium thiosulphate from sodium sulphite. (1982)
- 110.** Give balanced equations for the extraction of aluminium from bauxite by electrolysis. (1982)
- 111.** State the conditions under which the following preparation is carried out. Give the necessary equations which need not be balanced : alumina from aluminium. (1983)
- 112.** Write down the resonance structures of nitrous oxide.
OR
Write the two resonance structures of N_2O that satisfy the octet rule. (1990)
- 113.** Arrange the following in:
(i) $\text{HCl}, \text{HBr}, \text{HF}, \text{HI} \Rightarrow$ increasing bond strength (1986)
(ii) $\text{HOCl}, \text{HOClO}_2, \text{HOClO}_3, \text{HOClO} \Rightarrow$ increasing order of thermal stability. (1988)
(iii) $\text{CO}_2, \text{N}_2\text{O}_5, \text{SiO}_2, \text{SO}_3 \Rightarrow$ increasing order of acidic character (1988)
(iv) $\text{CCl}_4, \text{MgCl}_2, \text{AlCl}_3, \text{PCl}_5, \text{SiCl}_4 \Rightarrow$ increasing order of extent of hydrolysis. (1991)
- 114.** Mention the products formed in the following:
(i) Chlorine gas is bubbled through a solution of ferrous bromide. (1986)
(ii) Iodine is added to solution of stannous chloride. (1986)
(iii) Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride. (1986)
- 115.** Write the two resonance structures of ozone which satisfy the octet rule. (1991)
- 116.** $\text{PbS} \xrightarrow[\text{air}]{\text{heat in}} A + \text{PbS} \xrightarrow{B} \text{Pb} + \text{SO}_2$;
Identify A and B . (1991)
- 117.** Complete and balance the following chemical reactions:
(i) Red phosphorus is reacted with iodine in presence of water.
 $\text{P} + \text{I}_2 + \text{H}_2\text{O} \rightarrow \dots + \dots$ (1992)
(ii) Anhydrous potassium nitrate is heated with excess of metallic potassium.
 $\text{KNO}_3(s) + \text{K}(s) \rightarrow \dots + \dots$ (1992)
(iii) $\text{NH}_3 + \text{NaOCl} \rightarrow \dots + \dots$ (1993)
(iv) $\text{Sn} + 2\text{KOH} + 4\text{H}_2\text{O} \rightarrow \dots + \dots$ (1994)
- 118.** Draw the structure of P_4O_{10} and identify the number of single and double P – O bonds. (1996)
- 119.** Gradual addition of KI solution to $\text{Bi}(\text{NO}_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions. (1996)
- 120.** Complete the following chemical equations:
(a) $\text{KI} + \text{Cl}_2 \rightarrow$ (b) $\text{KClO}_3 + \text{I}_2 \rightarrow$ (1996)
- 121.** A soluble compound of a poisonous element M , when heated with $\text{Zn}/\text{H}_2\text{SO}_4$ gives a colourless and extremely poisonous gaseous compound N , which on passing through a heated tube gives a silvery mirror of element M . Identify M and N . (1997)

122. Draw the structure of a cyclic silicate, $(\text{Si}_3\text{O}_9)^{6-}$ with proper labelling. (1998)
123. Thionyl chloride can be synthesized by chlorinating SO_2 using PCl_5 . Thionyl chloride is used to prepare anhydrous ferric chloride starting from its hexahydrated salt. Alternatively, the anhydrous ferric chloride can also be prepared from its hexahydrated salt by treating with 2, 2-dimethoxypropane. Discuss all this using balanced chemical equations. (1998)
124. Reaction of phosphoric acid with $\text{Ca}_5(\text{PO}_4)_3\text{F}$ yields a fertilizer "triple superphosphate". Represent the same through balanced chemical equation. (1998)
125. In the following equation, $A + 2B + \text{H}_2\text{O} \rightarrow C + 2D$ ($A = \text{HNO}_2$, $B = \text{H}_2\text{SO}_3$, $C = \text{NH}_2\text{OH}$). Identify D . Draw the structures of A , B , C and D . (1999)
126. In the contact process for industrial manufacture of sulphuric acid some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of SO_2 ? (1999)
127. The Haber process can be represented by the following scheme :

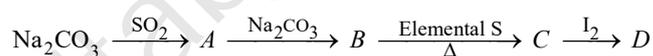


Identify A , B , C , D and E . (1999)

128. Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction. (2000)
129. Draw the molecular structures of XeF_2 , XeF_4 and XeO_2F_2 indicating the location of lone pair(s) of electrons. (2000)
130. Give reason(s) why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus as a tetraatomic molecule. (2000)
131. Compound (X) on reduction with LiAlH_4 gives a hydride (Y) containing 21.72% hydrogen along with other products. The compound (Y) reacts with air explosively resulting in boron trioxide. Identify (X) and (Y). Give balanced reactions involved in the formation of (Y) and its reaction with air. Draw the structure of (Y). (2001)

132. Starting from SiCl_4 , prepare the following in steps not exceeding the number given in parentheses (give reactions only) :
- Silicon (1)
 - Linear silicone containing methyl groups only (4)
 - Na_2SiO_3 (3) (2001)
133. Write balanced equations for the reactions of the following compounds with water :
- Al_4C_3
 - CaNCN
 - BF_3
 - NCl_3
 - XeF_4 (2002)
134. How is boron obtained from borax? Give chemical equations with reaction conditions. Write the structure of B_2H_6 and its reaction with HCl . (2002)
135. Write down reactions involved in the extraction of Pb . What is the oxidation number of lead in litharge? (2003)

136. Identify the following :



Also mention the oxidation state of S in all the compounds. (2003)

137. AlF_3 is insoluble in anhydrous HF but it becomes soluble in presence of little amount of KF . Addition of boron trifluoride to the resulting solution causes reprecipitation of AlF_3 . Explain with balanced chemical equations. (2004)

138. How many grams of CaO are required to neutralize 852 g of P_4O_{10} ? Draw structure of P_4O_{10} molecule. (2005)

139. Intermediate $\xleftarrow[\text{HNO}_3]{\text{conc.}} (A) \xrightarrow{\text{NaBr, MnO}_2} (B)$ brown coloured gas of pungent odour
- (C) Explosive substance
- (D) Identify (A), (B), (C) and (D). Give the reaction for $(A) \rightarrow (B)$ and $(A) \rightarrow (C)$. (2005)

Matrix Match Type

140. Write the matching pairs :

Bleaching agent	Aluminium
Smelling salt	Carbon
Cryolite	Tin
Bell metal	Ammonium carbonate
Fluorspar	Ammonium phosphate
Fertilizer	Calcium
Anthracite	Chlorine

(1980)

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141. Arrange :

List A	List B	
I. Explosive	A. NaN_3	
II. Artificial gem	B. Fe_3O_4	
III. Self reduction	C. Cu	
IV. Magnetic material	D. Al_2O_3	
	E. $\text{Pb}(\text{N}_3)_2$	
	F. Fe_2O_3	
	G. Sn	
	H. SiC	(1995)

142. Match the following :

Column I	Column II	
A. $\text{Bi}^{3+} \rightarrow (\text{BiO})^+$	P. Heat	
B. $[\text{AlO}_2]^- \rightarrow \text{Al}(\text{OH})_3$	Q. Hydrolysis	
C. $\text{SiO}_4^{4-} \rightarrow \text{Si}_2\text{O}_7^{6-}$	R. Acidification	
D. $(\text{B}_4\text{O}_7^{2-}) \rightarrow [\text{B}(\text{OH})_3]$	S. Dilution by water	(2006)

143. Match each of the reactions given in column I with the corresponding product(s) given in column II.

Column I	Column II	
(A) $\text{Cu} + \text{dil. HNO}_3$	(p) NO	
(B) $\text{Cu} + \text{conc. HNO}_3$	(q) NO_2	
(C) $\text{Zn} + \text{dil. HNO}_3$	(r) N_2O	
(D) $\text{Zn} + \text{conc. HNO}_3$	(s) $\text{Cu}(\text{NO}_3)_2$	
	(t) $\text{Zn}(\text{NO}_3)_2$	(2009)

144. All the compounds listed in Column I react with water. Match the result of the respective reactions with the appropriate options listed in Column II.

Column I	Column II	
A. $(\text{CH}_3)_2\text{SiCl}_2$	p. Hydrogen halide formation	
B. XeF_4	q. Redox reaction	
C. Cl_2	r. Reacts with glass	
D. VCl_5	s. Polymerization	
	t. O_2 formation	(2010)

145. The unbalanced chemical reactions given in List I show missing reagent or condition (?) which are provided in List II. Match List I with List II and select the correct answer using the code given below the lists :

List I	List II
P. $\text{PbO}_2 + \text{H}_2\text{SO}_4 \xrightarrow{?} \text{PbSO}_4 + \text{O}_2 + \text{other product}$	1. NO
Q. $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \xrightarrow{?} \text{NaHSO}_4 + \text{other product}$	2. I_2
R. $\text{N}_2\text{H}_4 \xrightarrow{?} \text{N}_2 + \text{other product}$	3. Warm
S. $\text{XeF}_2 \xrightarrow{?} \text{Xe} + \text{other product}$	4. Cl_2

	P	Q	R	S
(a)	4	2	3	1
(b)	3	2	1	4
(c)	1	4	2	3
(d)	3	4	2	1

(2013)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

146. **Statement-1** : Although PF_5 , PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.
Statement-2 : Phosphorus has lower electronegativity than nitrogen. (1994)

147. **Statement-1** : F atom has less negative electron affinity than Cl atom.
Statement-2 : Additional electrons are repelled more effectively by $3p$ electrons in Cl atom than by $2p$ electrons in F atom. (1998)

148. **Statement-1** : $\text{Al}(\text{OH})_3$ is amphoteric in nature.
Statement-2 : Al—O and O—H bonds can be broken with equal ease in $\text{Al}(\text{OH})_3$. (1998)

149. **Statement-1** : Between SiCl_4 and CCl_4 only SiCl_4 reacts with water.
Statement-2 : SiCl_4 is ionic and CCl_4 is covalent. (2001)

150. **Statement-1** : Boron always forms covalent bond.
Statement-2 : The small size of B^{3+} favours formation of covalent bond. (2007)

151. **Statement-1** : In water, orthoboric acid behaves as a weak monobasic acid.
Statement-2 : In water, orthoboric acid acts as a proton donor. (2007)

152. **Statement-1**: Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds.
Statement - 2: The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to inert pair effect. (2008)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension-1

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6. XeF_4 reacts violently with water to give XeO_3 . The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

- 153.** Argon is used in arc welding because of its
- low reactivity with metal
 - ability to lower the melting point of metal
 - flammability
 - high calorific value.
- 154.** The structure of XeO_3 is
- linear
 - planar
 - pyramidal
 - T-shaped.
- 155.** XeF_4 and XeF_6 are expected to be
- oxidising
 - reducing
 - unreactive
 - strongly basic. (2007)

Comprehension-2

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH_3 and PH_3 . Phosphine is a flammable gas and is prepared from white phosphorus.

- 156.** Among the following, the correct statement is
- Phosphates have no biological significance in humans
 - Between nitrates and phosphates, phosphates are less abundant in earth's crust.
 - Between nitrates and phosphates, nitrates are less abundant in earth's crust
 - Oxidation of nitrates is possible in soil.
- 157.** Among the following, the correct statement is
- Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.
 - Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional.

- Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional.
- Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.

- 158.** White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a
- dimerization reaction
 - disproportionation reaction
 - condensation reaction
 - precipitation reaction (2008)

Comprehension-3

Bleaching powder and bleach solution are produced on a large scale and used in several house-hold products. The effectiveness of bleach solution is often measured by iodometry.

- 159.** Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is
- Cl_2O
 - Cl_2O_7
 - ClO_2
 - Cl_2O_6
- 160.** 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $\text{Na}_2\text{S}_2\text{O}_3$ was used to reach the end point. The molarity of the household bleach solution is
- 0.48 M
 - 0.96 M
 - 0.24 M
 - 0.024 M (2012)

Comprehension-4

The reactions of Cl_2 gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two (different) oxoacids of chlorine, *P* and *Q*, respectively. The Cl_2 gas reacts with SO_2 gas, in presence of charcoal, to give a product *R*. *R* reacts with white phosphorus to give a compound *S*. On hydrolysis, *S* gives an oxoacid of phosphorus, *T*.

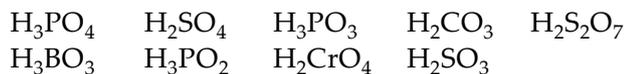
- 161.** *R*, *S* and *T*, respectively, are
- SO_2Cl_2 , PCl_5 and H_3PO_4
 - SO_2Cl_2 , PCl_3 and H_3PO_3
 - SOCl_2 , PCl_3 and H_3PO_2
 - SOCl_2 , PCl_5 and H_3PO_4
- 162.** *P* and *Q*, respectively, are the sodium salts of
- hypochlorous and chloric acids
 - hypochlorous and chlorous acids
 - chloric and perchloric acids
 - chloric and hypochlorous acids. (2013)

Integer Answer Type

163. The value of n in the molecular formula $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$ is

(2010)

164. The total number of diprotic acids among the following is



(2010)

165. Among the following, the number of compounds that can react with PCl_5 to give POCl_3 is O_2 , CO_2 , SO_2 , H_2O , H_2SO_4 , P_4O_{10}

(2011)

166. Consider the following list of reagents :

Acidified $\text{K}_2\text{Cr}_2\text{O}_7$, alkaline KMnO_4 , CuSO_4 , H_2O_2 , Cl_2 , O_3 , FeCl_3 , HNO_3 and $\text{Na}_2\text{S}_2\text{O}_3$. The total number of reagents that can oxidise aqueous iodide to iodine is

(2014)

167. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is

(2015)

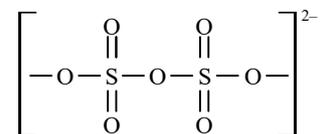
ANSWER KEY

- | | | | |
|---|---|--|----------------------------|
| 1. (a) | 2. (d) | 3. (i) None, (ii) Graphite, (iii) None, (iv) Cl_2 , (v) HCl | 4. (d) |
| 5. (c) | 6. (b) | 7. (b) | 8. (a) |
| 11. (b) | 12. (d) | 13. (a) | 14. (b) |
| 17. (b) | 18. (c) | 19. (c) | 20. (c) |
| 23. (a) | 24. (b) | 25. (c) | 26. (d) |
| 29. (c) | 30. (c) | 31. (c) | 32. (d) |
| 35. (a) | 36. (c) | 37. (b) | 38. (c) |
| 41. (c) | 42. (c) | 43. (b) | 44. (b) |
| 47. (b) | 48. (b) | 49. (d) | 50. (b) |
| 53. (a, b) | 54. (a, d) | 55. (a, d) | 56. (b, c) |
| 59. (a, c, d) | 60. (c) | 61. (a) | 62. (a, b, c) |
| 65. (b, d) | 66. (a, c, d) | 67. (b, d) | 68. (b, c) |
| 71. -3 | 72. HF | 73. KI_3 | 74. Sodium hydroxide; |
| 76. Hypobromous, bromite | 77. Cross-linking | 78. Two | 79. Silicones |
| 81. Oxides of nitrogen | 82. $\text{R}_3\text{Si}(\text{OH})$ | 83. Fullerene | 84. I_3^- complex |
| 86. O_2 | 87. Glass | 88. Inert pair effect | 89. False |
| 91. True | 92. False | 93. True | 94. False |
| 97. True | 98. True | 99. False | 100. True |
| 142. (A) \rightarrow Q, S; (B) \rightarrow Q; (C) \rightarrow R; (D) \rightarrow Q, R | 143. (A) \rightarrow p, s; (B) \rightarrow q, s; (C) \rightarrow r, t; (D) \rightarrow q, t | 144. (A) \rightarrow p, s; (B) \rightarrow p, q, r, t; (C) \rightarrow p, q; (D) \rightarrow p | 145. (d) |
| 148. (a) | 149. (c) | 150. (a) | 151. (c) |
| 154. (c) | 155. (a) | 156. (c) | 157. (c) |
| 160. (c) | 161. (a) | 162. (a) | 163. (3) |
| 166. (7) | 167. (6) | 164. (6) | 165. (5) |

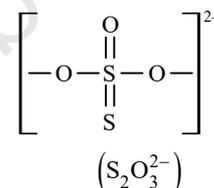
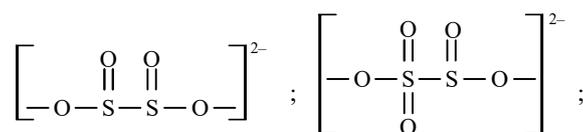
Explanations

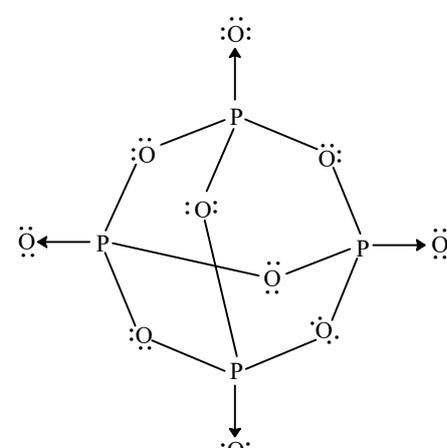
- (a): $\text{NO} = 14 + 16 = 30$ and $\text{O}_2 = 16 + 16 = 32$
From molecular mass, it is clear that NO is lighter than O_2 .
- (d): For drying, quick lime is used as it does not react with ammonia but reacts readily with moisture.
- (i) None
(ii) Graphite
(iii) None
(iv) Cl_2
(v) HCl
- (d): Due to the small size of F, HF is a poor reducing agent and cannot reduce KMnO_4 , H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$.
- (c): AlCl_3 exists as Al_2Cl_6 (i.e., a dimer). Due to the presence of incomplete octet, Al has a tendency to gain electrons. Hence, AlCl_3 acts as a Lewis base. AlCl_3 undergoes hydrolysis easily and forms $\text{Al}(\text{OH})_3$.
 $\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{HCl}$.
- (b): Graphite is a conductor. It shows conductivity due to the presence of free fourth electron on each C atom.
- (b): Cl_2 shows bleaching action only in presence of moisture.
 $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO}$
 $\text{HClO} \rightarrow \text{HCl} + [\text{O}]$
(unstable) (nascent)
Nascent oxygen thus formed is responsible for bleaching action of Cl_2 .
- (a): Nitrates of heavy metals and lithium when heated decompose to produce NO_2 . KNO_3 on heating does not give NO_2 .
- (c): SO_2 is soluble in water ($\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$) and so it cannot be collected over water.
- (b): $2\text{HgO} \xrightarrow{\text{heat}} 2\text{Hg} + \text{O}_2$
- (b): $\text{O}=\text{N}-\text{O}-\text{N}=\text{O}$
- (d): The colour of NO_2 is reddish brown. All others are colourless.
- (a): NF_3 is least basic due to highest value of electronegativity of fluorine.
- (b): Since Cl_2 is a stronger oxidising agent than Br_2 , so Cl_2 water will liberate bromine from KBr solution.
 $2\text{KBr} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{Br}_2 \uparrow$

15. (d): In $\text{S}_2\text{O}_7^{2-}$, there is no S — S bond.



In it there is S — O — S bond. In all other given ionic compounds we find S — S bond.



16. (c): Four : 

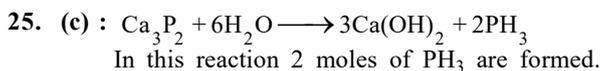
(Structure of P_4O_{10}).

17. (b): HBr is not prepared by heating NaBr with concentrated H_2SO_4 because HBr is a strong reducing agent and it reduces H_2SO_4 to SO_2 and is itself oxidised to Br_2 .
 $\text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HBr}$
 $\text{H}_2\text{SO}_4 + \text{HBr} \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
18. (c): $\text{H}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_5 + \text{H}_2\text{SO}_4$
peroxodi- peroxomono- sulphuric acid
sulphuric acid sulphuric acid
19. (c): We can represent CsBr_3 as Cs^+Br_3^-
20. (c): $\text{KF} + \text{HF} \rightarrow \text{KHF}_2 \rightleftharpoons \text{K}^+ + \text{HF}_2^-$
21. (b): $\text{Na}_2\text{SO}_3 + \text{S} \rightarrow \text{Na}_2\text{S}_2\text{O}_3$

The p-Block Elements

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22. (d) : It is because of inert pair effect.
 23. (a) : CO is a neutral oxide.
 24. (b) : Pseudohalides are monovalent ions made by an electronegative atom and have properties similar to those of halide ions. The corresponding dimers of pseudohalides are known as pseudohalogens. RCOO^- is not a pseudohalide.



27. (c) : For commercial extraction of aluminium we use a molten mixture of Al_2O_3 and Na_3AlF_6 (cryolite).
 Al_2O_3 is electrolyte and Na_3AlF_6 is added to decrease the melting point of Al_2O_3 and increase the conductivity.

28. (b) : In BCl_3 , the state of hybridisation,

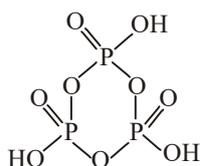
$$H = \frac{1}{2} (3 + 3 + 0 - 0) = 3 \text{ i.e. } sp^2.$$

So the bond angle is 120° .

The state of hybridisation in case of P, As and Bi is sp^3 hybridisation and due to the presence of a lone pair on the central atom the bond angle is less than normal tetrahedral angle of $109^\circ 28'$, i.e., bond angle $< 109^\circ 28'$. Since the central atom (P, As, Bi) belong to the same group, the bond angle of ECl_3 decreases as we go down the group, i.e., from P to As to Bi, thus the correct order of bond angle is $\text{BCl}_3 > \text{PCl}_3 > \text{AsCl}_3 > \text{BiCl}_3$.

29. (c) : In the presence of cryolite which forms a melt with lower melting point.

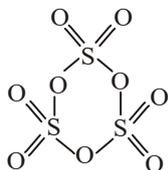
30. (c) : Its structure is



In this structure we find three P — O — P bonds.

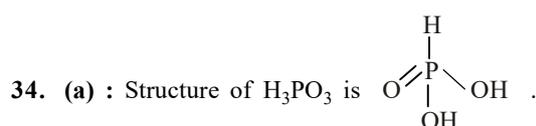
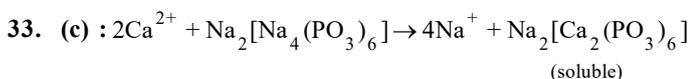
31. (c) : NH_3 does not react with CaO .

32. (d) :



Structure of S_3O_9 is also called $\gamma\text{-SO}_3$

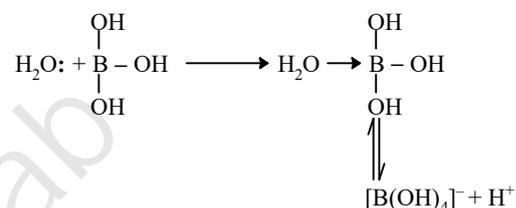
In it there is no S — S bond. The sulphur atoms are linked to each other *via* oxygen.



Since it has only two $-\text{OH}$ groups so it is dibasic.

In it, the oxidation state of P is +3 whereas P can also have an oxidation state of +5, so H_3PO_3 can be oxidised (from +3 to +5 state). Since it can be oxidised so it is a reducing agent.

35. (a) : In boric acid (H_3BO_3), the boron atom has only six electrons and so it is electron deficient, i.e., it is a Lewis acid with one p -orbital vacant in its valence shell which has no d -orbitals. Thus it can accommodate only one electron pair in its outermost shell.

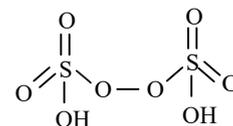


36. (c) : Due to very large size of Si atom than that of oxygen atom, it fails to form a π -bond and so the product of hydrolysis of Me_2SiCl_2 is polymeric i.e.



37. (b) : In XeOF_4 , Xe is sp^3d^2 hybridised and has a lone pair of electrons.

38. (c) : From amongst the given oxyacids of S only $\text{H}_2\text{S}_2\text{O}_8$ has O — O linkage. $\text{H}_2\text{S}_2\text{O}_8$ is known as Marshall's acid.



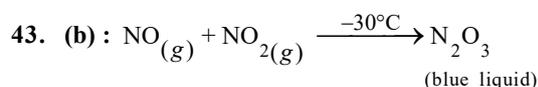
The other oxy acid of S having O — O linkage is H_2SO_5 known as Caro's acid.

39. (b) : Tin can be extracted by carbon reduction method only whereas lead can be extracted either by self reduction method or by carbon reduction method.

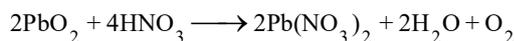
40. (b) : When three oxygen atoms of each $[\text{SiO}_4]^{4-}$ are shared it results in a two dimensional sheet structure.

41. (c) : Because the ignition temperature of black phosphorus is highest among various allotropes of phosphorus, so black phosphorus is most stable.

42. (c) : In KMnO_4 , the oxidation state of Mn is +7 which is the highest possible oxidation state of Mn and thus no further oxidation is possible.

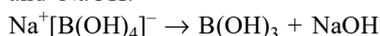


44. (b) : PbO_2 is a strong oxidising agent. It liberates O_2 on treatment with acids.

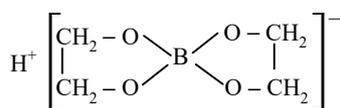
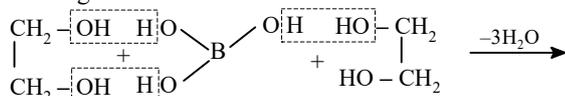


45. (a) : $\text{B}(\text{OH})_3 + \text{NaOH} \rightarrow \text{Na}^+[\text{B}(\text{OH})_4]^-$

Above given reaction is not possible, because sodium metaborate, $\text{Na}^+[\text{B}(\text{OH})_4]^-$ formed by the reaction between $\text{B}(\text{OH})_3$ and NaOH gets hydrolysed to regenerate $\text{B}(\text{OH})_3$ and NaOH .



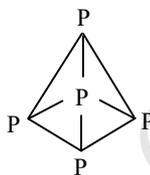
However, if some quantity of polyhydroxy compound like catechol, *cis*-1,2-diol, glycerol, etc. is added to the reaction mixture, the polyhydroxy compound combines with H_3BO_3 or $\text{B}(\text{OH})_3$ and forms chelated complex compound. This complex gives H^+ ions, which makes H_3BO_3 to behave as a strong acid.



chelated complex compound

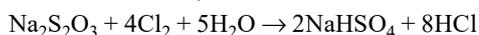
Trans-1,2-diol cannot be used in this reaction since it will not result in chelate formation.

46. (d) : In P_4 , the P-P linkage is formed by $sp^3 - sp^3$ hybridised orbital overlapping. So the percentage of *p*-character will be 75%.



Tetrahedral

47. (b) : Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) shows reducing action as it is oxidised by chlorine.



48. (b) : $\text{P}_4 + 3\text{O}_2 \longrightarrow \text{P}_4\text{O}_6$

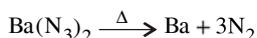
Nitrogen prevents further oxidation of P_4O_6 to P_4O_{10} .

P_4 when treated with dry O_2 gives P_4O_6 and finally P_4O_{10} .

With moist oxygen, P_4 gives H_3PO_3 .



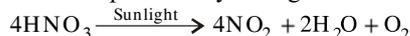
49. (d) : 99% pure nitrogen is obtained by reaction of NH_3 with CuO but extra (highly) pure nitrogen is obtained by NaN_3 or $\text{Ba}(\text{N}_3)_2$.



Ammonium nitrate NH_4NO_3 on heating gives N_2O which on heating gives $\text{N}_2 + \text{O}_2$. Therefore pure N_2 can not be prepared by ammonium nitrate.

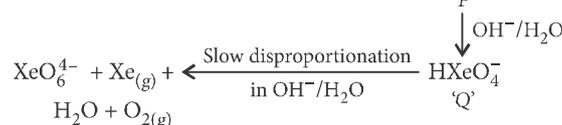
Ammonium dichromate on heating gives $\text{N}_2 + \text{Cr}_2\text{O}_3$ (gas). Therefore pure N_2 can not be prepared by $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. Therefore option (d) is correct.

50. (b) : Nitric acid usually acquires yellow-brown colour due to its decomposition by sunlight into NO_2 .



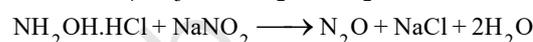
51. (a) : $\text{P}_4 + 8\text{SOCl}_2 \longrightarrow 4\text{PCl}_3 + 4\text{SO}_2 + 2\text{S}_2\text{Cl}_2$
(White)

52. (c) : $\text{XeF}_6 + 3\text{H}_2\text{O} \xrightarrow{\text{Complete hydrolysis}} \text{XeO}_3 + 6\text{HF}$



53. (a,b) : Cryolite is added to lower the melting point of electrolyte (melt) and to increase the electrical conductivity.

54. (a,d) : $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$

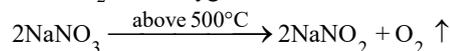


55. (a,d) : NH_3 and CF_2Cl_2 (Freon-12) are used as refrigerants.

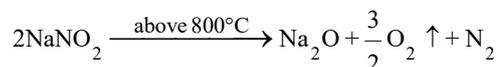
56. (b,c) : Fluorspar (CaF_2) is added to make fused mixture (alumina dissolved in fused cryolite) very conducting and to lower the temperature of the melt.

57. (a, b)

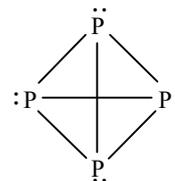
58. (a,b,d) : When heated above 500°C , NaNO_3 decomposes to give NaNO_2 and oxygen.



On further heating to above 800°C , NaNO_2 further decomposes to give Na_2O , N_2 and O_2 .



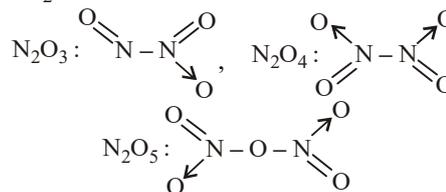
59. (a,c,d) : In P_4 (white phosphorus), the four atoms are situated at the corners of a tetrahedron. There are six P-P single bonds with P-P-P bond angle of 60° . Each P has a lone pair of electrons.



60. (c) : $2\text{NH}_3 + \text{OCl}^- \longrightarrow \text{NH}_2 - \text{NH}_2 + \text{H}_2\text{O} + \text{Cl}^-$

61. (a) : $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$

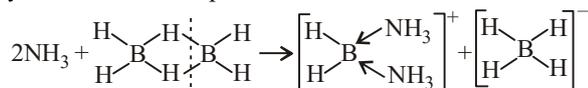
62. (a,b,c) : $\text{N}_2\text{O} : \text{N}=\text{N}=\text{O} \longleftrightarrow \text{N}\equiv\text{N}-\text{O}$



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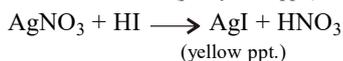
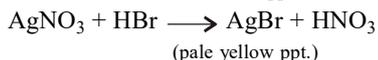
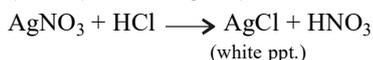
63. (a,b,c) : The reaction of B_2H_6 with NH_3 , 1° and 2° amines yield an ionic compound.



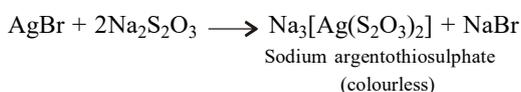
However with 3° amine, B_2H_6 forms an adduct.



64. (a, c, d) : With $AgNO_3$, HCl, HBr and HI give precipitate.

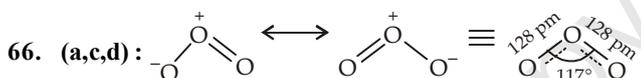


But HF does not give any precipitate, AgF is formed which is soluble in water.



Similar reactions are observed with AgCl and AgI.

65. (b, d) : Diamond is the hardest substance known and C - C bond length is 1.54 Å in diamond. It is non-conductor of electricity. While in graphite, after sp^2 hybridisation one electron is free and it overlaps with another electron to form π -bond, thus bond length in graphite is shorter (1.42 Å) and bond order is higher than diamond. The π -electron is free to move thus graphite is good conductor of electricity but graphite is bad conductor of heat than diamond.

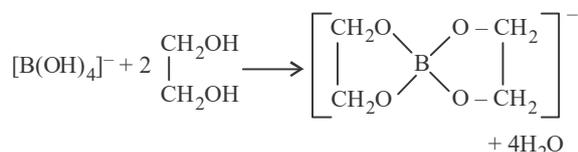


Oxygen-oxygen bond lengths are equal (128 pm). All electrons are paired so it is diamagnetic in nature. It has a bent structure.

67. (b,d) : (b) H_3BO_3 behaves as a weak monobasic acid *i.e.*, Lewis acid. It accepts a pair of electrons from OH^- ion.

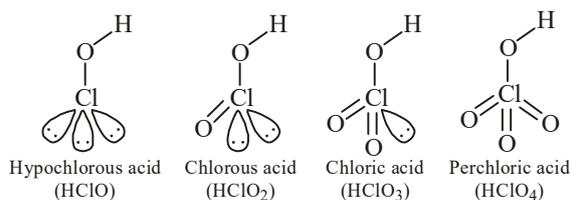


(d) On adding ethylene glycol, its acidity increases.



H_3BO_3 does not undergo self-ionization and planar BO_3^{3-} units are joined by unsymmetrical hydrogen bonds to give a layered structure.

68. (b,c) :

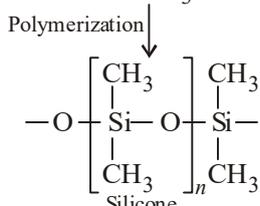
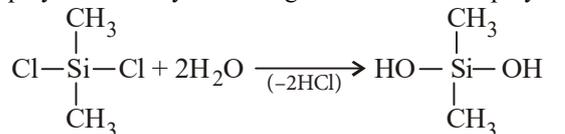


In all these oxoacids, Cl is sp^3 -hybridized.

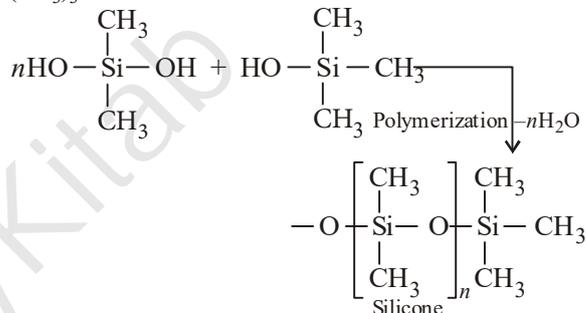
Acid strength of oxoacids of the same halogen increases with increase in oxidation number of the halogen, *e.g.*;

$$H^+{}^7ClO_4 > H^+{}^5ClO_3 > H^+{}^3ClO_2 > H^+{}^1ClO$$

69. (b) : Hydrolysis of dichlorodimethylsilane followed by polymerization yields straight chain or linear polymers.



The chain length of polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends as shown below :



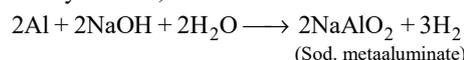
70. $NaIO_3$

71. -3

72. HF; HF is the weakest of the three. $HX \rightleftharpoons H^+ + X^-$. ΔD is minimum in case of HF because of strong H-F bond, large heat of hydration (due to H-bonding in HF) and low value of electron affinity for F-atom.

73. KI_3 ; $KI + I_2 \rightarrow KI_3$.

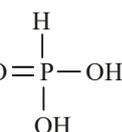
74. Sodium hydroxide;



75. White : In white phosphorus, each phosphorus atom is linked to the other three atoms by covalent bonds. PPP bond angle is 60° , due to which the molecule remains under strain and hence is active in nature.

76. Hypobromous, bromite; $HBrO \rightleftharpoons H^+ + BrO^-$.

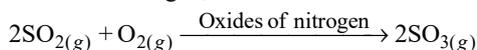
77. Cross-linking.

78. Two; Structure of H_3PO_3 is 

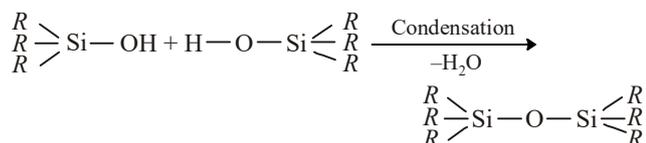
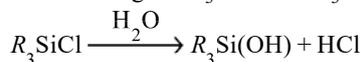
79. Silicones, $\begin{array}{c} R \\ | \\ R-Si-Cl \\ | \\ R \end{array} \xrightarrow[(-2HCl)]{+2H_2O} \begin{array}{c} R \\ | \\ R-Si-OH \\ | \\ R \end{array}$
- $$HO-Si-OH + HO-Si-OH \xrightarrow{-H_2O} HO-Si-O-Si-OH$$
- (Silicone)

80. Four ; (Please refer answer 16)

81. Oxides of nitrogen;

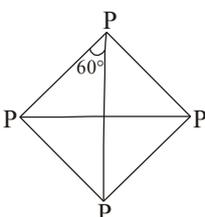


82. $\text{R}_3\text{Si}(\text{OH})$; On hydrolysis R_3SiCl yields $\text{R}_3\text{Si}(\text{OH})$ which may be condensed to give $\text{R}_3\text{SiO} - \text{SiR}_3$.



83. Fullerene; C_{60} is also known as buckminsterfullerene and is made from interlocking hexagonal and pentagonal rings of carbon atom.

84. I_3^- complex; $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$



85. 60° ; P (Structure of P_4)

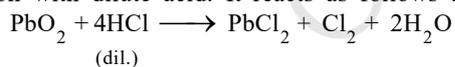
86. O_2 ; Electrolysis of aqueous NaF yields O_2 at anode.

87. Glass; Glass is a supercooled liquid.

88. Inert pair effect ; When ns^2 electrons of outermost shell do not participate in bonding it is called inert pair and the effect is called inert pair effect.

89. **False** : Red phosphorus is polymeric and it exists as chains of P_4 tetrahedra linked together. Thus red phosphorus is less volatile than white phosphorus.

90. **False** : PbO_2 is a dioxide. It does not give H_2O_2 on reaction with dilute acid. It reacts as follows :



91. **True** : $\text{Fe} + 2\text{HCl} \xrightarrow{(\text{dil.})} \text{FeCl}_2 + \text{H}_2$

92. **False**: Because of their high electron affinity values halogens can easily pick up electrons from other substances and so they are good oxidising agents. The oxidising power of halogens decreases as we move down the group and so F_2 is the strongest oxidising agent. Fluorine can oxidise any of the other halide ion (X^-) in solutions. Cl_2 can displace Br^- and I^- ions from their solutions. Br_2 can displace I^- from their solutions.

93. **True**

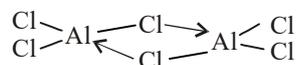
In metal hydrides of group 15 elements, the metal is in sp^3 hybrid state. However the bond angle ($\text{H}-\text{M}-\text{H}$) is less than $109^\circ 28'$. It is because of greater repulsion between lone pair-bond pair as compared to between bond pair-bond pair. In case of NH_3 the $\text{H}-\text{N}-\text{H}$ bond angle is $106^\circ 45'$ and in AsH_3 the bond angle is 91.5° .

94. **False**

CCl_4 is quite stable because of its high thermal stability as compared to other tetrachlorides of the group.

95. **False**

The structure of Al_2Cl_6 is



The Al-Cl bonds of terminal chlorine atoms are different than those of bridge chlorine atoms.

96. **True**

Total number of valence electrons in a molecule of NO is 11 (5 of N + 6 of O). It is impossible for all of them to be paired. Hence the molecule of NO contains unpaired electrons and due to this, gaseous nitric oxide is paramagnetic.



In liquid and solid states, nitric oxide is polymerised and exists as dimer (N_2O_4) which is diamagnetic (due to absence of unpaired electrons).

97. **True**

In diamond each C atom is sp^3 hybridised and is linked to four other C atoms. The C atoms are arranged in tetrahedral geometry. Because of covalent bonds by which C atoms are held together diamond is the hardest substance known. Graphite has a two dimensional sheet structure and in it the the C-atoms are in sp^2 hybridised state and the different layers are held by van der Waals forces. Because of wide separation and weak interlayer bonds, the two adjacent layers in graphite can easily slide over each other and so graphite is soft.

98. **True**

In carbon the number of valence electrons is equal to the number of valence orbitals and due to this carbon shows the property of catenation. In tetravalent state carbon is fully saturated and due to this C-C bond is quite stable. C-C bond energy > Si-Si bond energy and due to this carbon has a greater tendency for catenation.

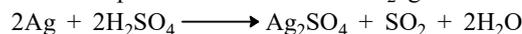
99. **False**

Neither HBr nor HI has hydrogen bonding. HI is stronger acid than HBr because H-I bond is weaker than H-Br bond (atomic size of I is larger than Br) and so H-I bond can be broken easily to give H^+ .

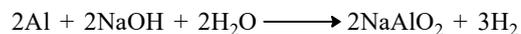
100. (a) (i) NO_2 gas is evolved.



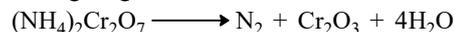
(ii) Silver sulphate is formed and SO_2 gas is evolved.



(iii) Hydrogen is evolved and sodium metaaluminate is formed.

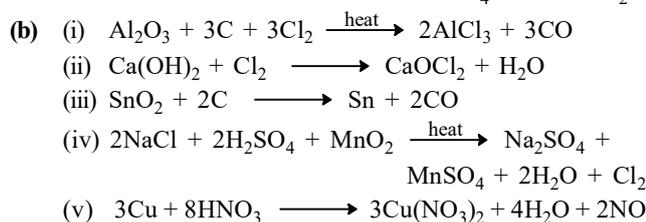
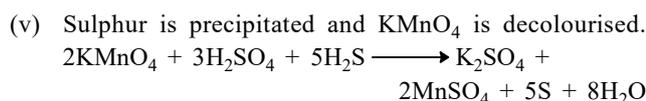


(iv) Nitrogen gas is evolved.



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101. (i) HBr is a reducing agent. Therefore, it reduces H_2SO_4 to SO_2 .

(ii) Blue litmus turns red because of the acidic nature of HClO, later on, colour is decolourised as it is also an oxidising agent.

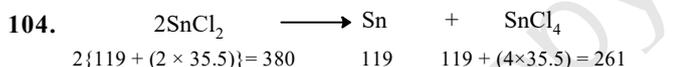
102. (i) PbCO_3 gives out CO_2 on adding dilute HCl, while PbSO_4 remains unaffected.

(ii) CaCl_2 imparts a dull red colour to flame while MgCl_2 does not impart any colour to the flame.

(iii) $\text{Na}_2\text{S}_2\text{O}_3$ shows a display of colour with AgNO_3 solution while Na_2SO_3 does not show such display.

103. (i) Concentrated nitric acid partially decomposes to give NO_2 which gets dissolved in nitric acid. As NO_2 has a brownish red colour, it imparts colour to the nitric acid.

(ii) In contact with moisture in air, bleaching powder releases chlorine. Therefore, on keeping it in an open bottle for a long time it loses its capacity to bleach.



119 g Sn is deposited on decomposition of 380 g SnCl_2
 $\therefore 0.119$ g of Sn is formed due to the decomposition of SnCl_2

$$= \frac{380}{119} \times 0.119 \text{ g} = 0.380 \text{ g}$$

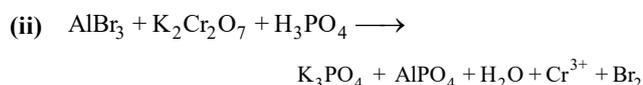
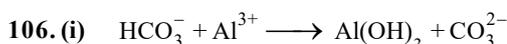
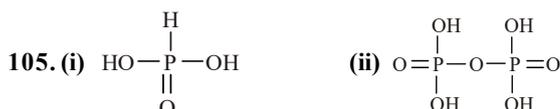
380 g of SnCl_2 decomposes to give $\text{SnCl}_4 = 261$ g

$\therefore 0.380$ g SnCl_2 decompose to give $\text{SnCl}_4 = \frac{261}{380} \times 0.380$ g
 $= 0.261$ g

Weight of SnCl_2 left after decomposition
 $= 19.000 - 0.380 \text{ g} = 18.620 \text{ g}$

Weight of SnCl_4 formed = 0.261 g

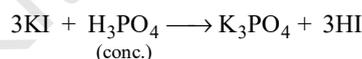
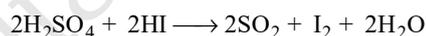
Ratio of $\text{SnCl}_2 : \text{SnCl}_4$ is 18.620 : 0.261 or 71.34 : 1



107. (i) Carbon exists in various allotropic forms such as diamond, graphite, coal, etc. In diamond there is sp^3 hybridisation of each carbon atom and it has a three dimensional structure. In it C—C bonds are covalent and due to this diamond is hard and is used as an abrasive. The graphite has a two dimensional sheet structure and in it the carbon atoms are sp^2 hybridised. These layers of carbon atoms are held together by weak van der Waals forces and so they can easily slip over one another and this imparts lubricating properties to graphite.

(ii) In S_8 we have van der Waals forces to hold the rings. Due to this sulphur has a melting point of 119°C . When sulphur melts, the van der Waals forces are overcome and the S_8 rings slip and roll over one another. It gives rise to a clear mobile liquid. Above 160°C , the S_8 ring starts to open up and form long chains which get tangled with each other, and it gradually increases the viscosity of sulphur.

(iii) It is not possible to prepare HI by heating alkali metal iodide (e.g. KI) with concentrated H_2SO_4 because HI is a strong reducing agent and sulphuric acid oxidises it to form I_2 . Phosphoric acid does not oxidise HI.



(iv) H_3PO_4 is tribasic and H_3PO_3 is dibasic.



(v) Liquor ammonia possesses high vapour pressure at room temperature so before opening a bottle of liquor ammonia, it should be cooled to lower down the vapour pressure of ammonia inside the bottle, otherwise the NH_3 will bump out of the bottle.

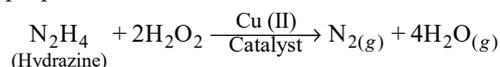
(vi) Solid CO_2 is called dry ice because solid CO_2 sublimates and leaves no stains on surface.

(vii) Anhydrous HCl is a non-polar compound so it is a bad conductor. In aqueous solution HCl ionises to give H^+ and Cl^- ions and then it becomes a good conductor.

(viii) Graphite has a two dimensional sheet structure and in it the carbon atoms are sp^2 hybridised. These layers of carbon atom are held together by weak van der Waals forces and so they can easily slip over one another and this imparts lubricating properties to graphite.

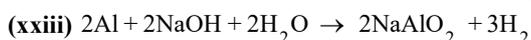
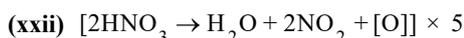
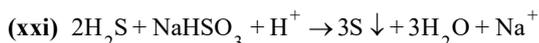
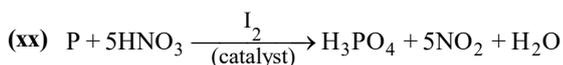
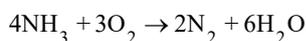
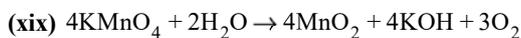
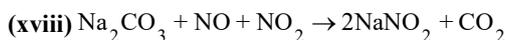
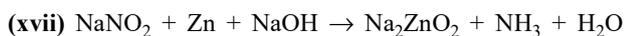
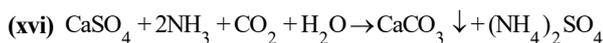
(ix) The value of E_{red}° is maximum for fluorine. It is placed at the top of the electrochemical series. Thus it cannot be oxidised by any reagent. It is the strongest oxidising agent.

(x) We use the mixture, of N_2H_4 and H_2O_2 (in presence of Cu(II) catalyst), as a rocket propellant. The reaction is highly exothermic and a large volume of gases is evolved, which can propel a rocket.

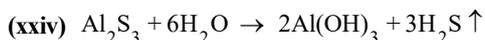


The p-Block Elements

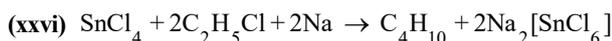
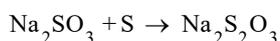
181



sod. metaaluminate

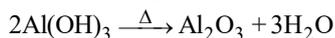
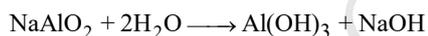


(ppt) (smell of rotten eggs)

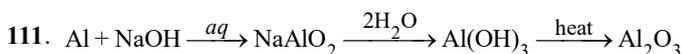
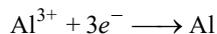
109. By boiling Na_2SO_3 solution with powder of sulphur in absence of air.

The excess of sulphur is removed by filtration and the filtrate is evaporated to get crystals of sodium thiosulphate.

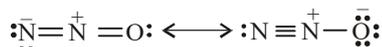
110. Various equations are:



Electrolysis in presence of cryolite yields aluminium at cathode.



112. The two resonating structures are:

113. (i) $\text{HI} < \text{HBr} < \text{HCl} < \text{HF}$

The strength of H—X bond decreases as we move down the group. On moving down the group the atomic size increases so H—X bond length increases. The larger the H—X bond length, lower is the bond energy and so lesser is the bond strength.

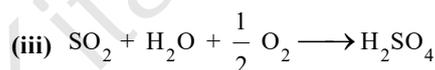
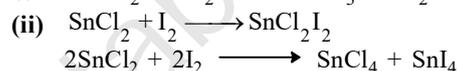
(ii) $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$

As the oxidation state of Cl increases (or the number of oxygen atoms increases), the -ve charge dispersal becomes

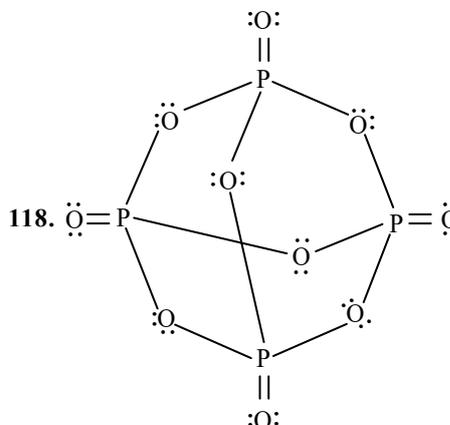
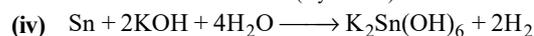
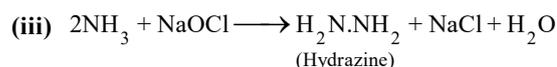
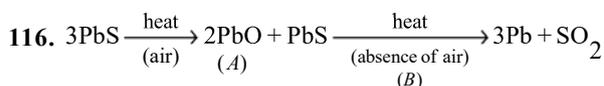
more and more from Cl atom due to higher electronegativity value of oxygen. Lesser the charge on Cl atom more is the stability.

(iii) $\text{SiO}_2 < \text{CO}_2 < \text{N}_2\text{O}_5 < \text{SO}_3$ In case of oxides of non-metals, the acid strength increases with increase in oxidation state. The oxidation states of various elements are Si = +4, C = +4, N = +5, S = +6 in the given oxides. Due to the small size of C-atom, CO_2 is more acidic than SiO_2 .(iv) Since vacant *d*-orbitals are not available in case of C so carbon cannot extend its coordination number beyond four. Its halides are therefore not hydrolysed by water. In case of silicon, vacant *d*-orbitals are available in the valence shell and so silicon can extend its coordination number beyond four and because of this its halides are hydrolysed by water.

Hence the increasing order of extent hydrolysis is



115. The two resonating structures are :



Number of P—O bonds (single bonds) = 12

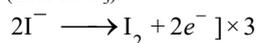
Number of P=O bonds (double bonds) = 4

119. The dark brown ppt. that initially appears on addition of KI solution to $\text{Bi}(\text{NO}_3)_3$ solution is due to free iodine liberated as follows :

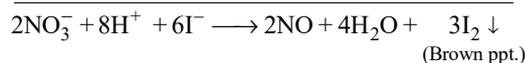
$\text{Bi}(\text{NO}_3)_3$ is hydrolysed to form HNO_3 . The HNO_3 formed, being an oxidising agent, liberates I_2 from KI.



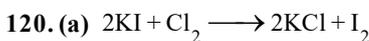
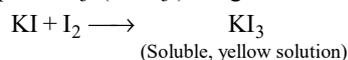
(from HNO_3)



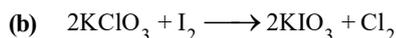
(from KI)



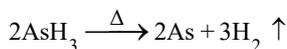
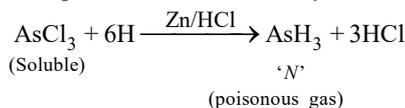
In excess of KI, I_2 gets dissolved due to formation of complex KI_3 (i.e. I_3^-) to give a clear yellow solution.



Cl_2 lies above I_2 in electrochemical series so Cl_2 is more powerful oxidising agent than I_2 . Thus Cl_2 can displace I^- to form I_2 .



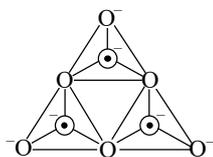
121. The poisonous element may be As. Thus we have



‘M’
(silvery mirror)

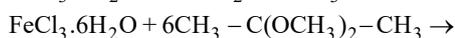
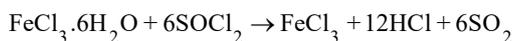
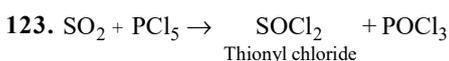
Hence $M = \text{As}$ and $N = \text{AsH}_3$.

122. In cyclic silicates, three tetrahedra of $(\text{SiO}_3^{2-})_n$ are joined to form $\text{Si}_3\text{O}_9^{6-}$. In such a structure two oxygen atoms per tetrahedra are shared.



Structure of $\text{Si}_3\text{O}_9^{6-}$

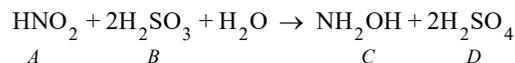
In this structure O represents oxygen and • represents silicon.



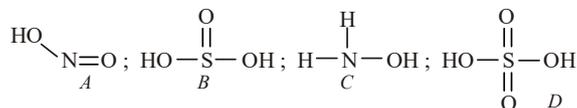
Triple super phosphate

(Fertilizer)

125. The reaction is



The structure of A, B, C and D are as follows:

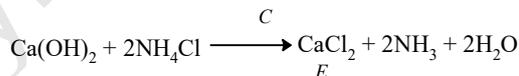
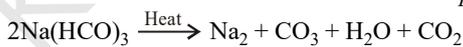
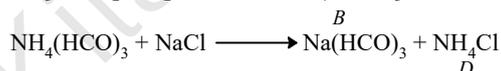
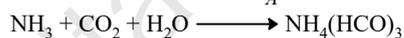


126. In contact process the SO_3 produced is dissolved in concentrated H_2SO_4 to produce oleum. SO_3 produced is not dissolved in water because it forms dense fog of sulphuric acid particles.

In contact process the catalyst used is V_2O_5 .

127. In this case

$A = \text{Ca}(\text{OH})_2$, $B = \text{NH}_4(\text{HCO}_3)$, $C = \text{Na}_2\text{CO}_3$, $D = \text{NH}_4\text{Cl}$, and $E = \text{CaCl}_2$.



128. We know that more electronegative halogen can displace lesser electronegative halogen from its halide. Thus



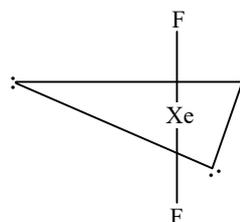
129. The hybridisation (H) in case of XeF_2 , XeF_4 and XeO_2F_2

$$\text{In XeF}_2: H = \frac{8+2-0+0}{2} = 5, \text{ i.e., } dsp^3 \text{ or } sp^3d$$

$$\text{In XeF}_4: H = \frac{8+4-0+0}{2} = 6, \text{ i.e., } d^2sp^3 \text{ or } sp^3d^2$$

$$\text{In XeO}_2\text{F}_2: H = \frac{8+2-0+0}{2} = 5, \text{ i.e., } sp^3d$$

Thus in XeF_2 , the hybrid state of Xe is sp^3d but its shape is linear due to VSEPR theory. In it we find three lone pairs and due to their presence the geometry of XeF_2 is distorted from trigonal bipyramidal (expected for sp^3d) to linear.

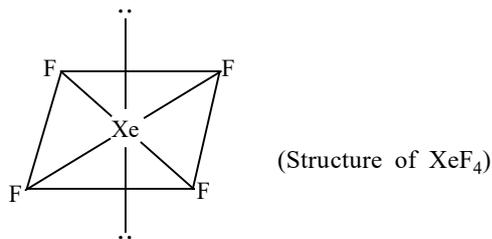


(Structure of XeF_2)

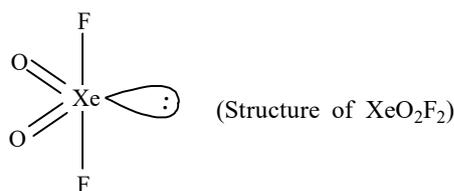
In XeF_4 , the hybrid state of Xe is sp^3d^2 but its shape is square planar due to the presence of two lone pairs because of which the geometry of XeF_4 is distorted from octahedral (expected for sp^3d^2) to square planar.

The p-Block Elements

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In case of XeO₂F₂, the hybrid state of Xe is sp^3d but its geometry is planar due to VSEPR theory. Because of presence of a lone pair of electrons its geometry is distorted from trigonal bipyramidal (expected for sp^3d) to planar.



130. In its elemental form nitrogen exists as a diatomic molecule (N₂). This is due to the fact that nitrogen can form $p\pi-p\pi$ multiple bonds (N \equiv N). However formation of multiple bonds is not possible in case of phosphorus because of repulsion between non-bonded electrons of the core. In case of small nitrogen atom there is no such repulsion as they have only $1s^2$ electrons in their inner core.

131. $Y + \text{air} \longrightarrow \text{B}_2\text{O}_3$

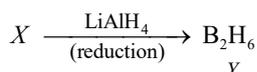
From this we can guess that Y must be B₂H₆.



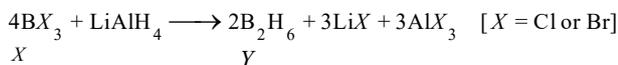
$$\% \text{ of hydrogen in B}_2\text{H}_6 = \frac{6}{27.62} \times 100 = 21.72$$

$$[\text{Mol. wt. of B}_2\text{H}_6 = 21.62 + 6 = 27.62]$$

Thus percentage of hydrogen is 21.72 in B₂H₆.

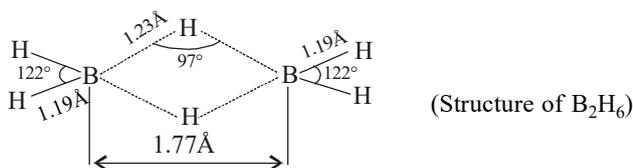


From this we can guess that X is boron trihalide.



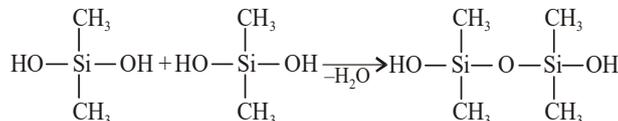
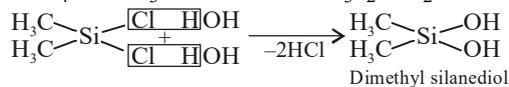
Structure of Y , i.e., B₂H₆

In it two electrons of a B — H bond are involved in the formation of three centre bond (Banana bond). These bonds are shown by dotted line in the following diagram in which one of these bonds lies above and the other lies below the main plane.



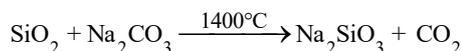
132. (i) $\text{SiCl}_4 + 2\text{Mg (or Zn)} \longrightarrow \text{Si} + 2\text{MgCl}_2 \text{ (or ZnCl}_2)$

(ii) $\text{SiCl}_4 + 2\text{CH}_3\text{MgCl} \longrightarrow (\text{CH}_3)_2\text{SiCl}_2 + 2\text{MgCl}_2$



This type of polymerisation continues at both ends to form linear silicone.

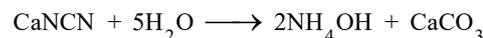
(iii) $\text{SiCl}_4 + 4\text{H}_2\text{O} \xrightarrow{-4\text{HCl}} \underset{\text{(unstable)}}{\text{Si(OH)}_4}$



133. (i) $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \longrightarrow 4\text{Al(OH)}_3 + 3\text{CH}_4 \uparrow$

(ii) $\text{CaNCN} + 3\text{H}_2\text{O} \longrightarrow \text{CaCO}_3 + 2\text{NH}_3$
ppt.

Ammonia (NH₃) formed when dissolved in water yields NH₄OH.

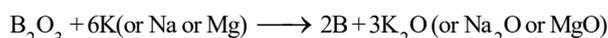
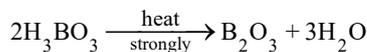
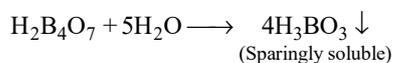


(iii) $4\text{BF}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{BO}_3 + 3\text{HBF}_4$
(Boric acid) (Fluoroboric acid)

(iv) $\text{NCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{NH}_3 + 3\text{HClO}$
(Hypochlorous acid)

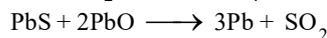
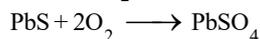
(v) $2\text{XeF}_4 + 3\text{H}_2\text{O} \longrightarrow \text{Xe} + \text{XeO}_3 + \text{F}_2 + 6\text{HF}$
Xenon trioxide

134. When we add hot concentrated HCl to borax (Na₂B₄O₇·10H₂O), the sparingly soluble H₃BO₃ (boric acid) is formed which on further heating gives B₂O₃ (boric oxide). B₂O₃ when reduced with Mg, Na or K yields B (Boron).

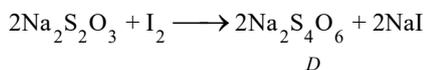
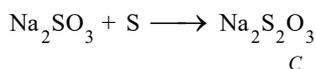
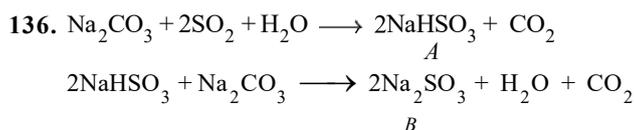


For structure of B₂H₆ refer answer no. 121.

135. $2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$



In litharge (PbO), the oxidation number of Pb is +2.



oxidation states of S :

In *A* it is $+4(1 + 1 + x - 6 = 0 \text{ or } x = +4)$

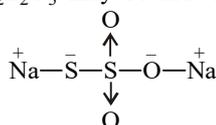
In *B* it is $+4(2 \times 1 + x - 6 = 0 \text{ or } x = +4)$

In *C* it is $+2(2 \times 1 + 2x - 6 = 0 \text{ or } x = +2)$

In *D* it is $+2.5(2 \times 1 + 4x - 12 = 0 \text{ or } x = +2.5)$

Note: The values of oxidation states of S in *C* and *D* given are average values.

Structure of $\text{Na}_2\text{S}_2\text{O}_3$ may be drawn as



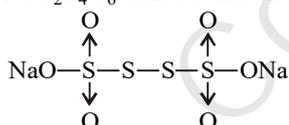
Here, the two sulphur atoms have different oxidation states.

(i) Oxidation number of donor sulphur atom is +5. It gives up four electrons in co-ordination and one electron in covalent bond formation with oxygen.

(ii) Sulphur, bonded with Na, lies in -1 state since one electron of Na lies towards the sulphur. Electrons of S—S bond are equally shared between two sulphur atoms.

Thus +5 and -1 are two oxidation states of the two sulphur atoms.

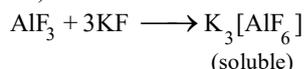
The structure of $\text{Na}_2\text{S}_4\text{O}_6$ can be drawn as



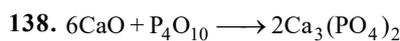
From the structure, it is clear that the sulphur atoms acting as donor atoms have +5 oxidation number (each). On the other hand, the sulphur atom involved in pure covalent bond formation has zero oxidation number.

Thus oxidation numbers shown by S in this compound are +5 and 0.

137. HF is weakly dissociated (due to hydrogen bonding in it). Where as KF is highly dissociated giving a high concentration of F^- which leads to the formation of AlF_6^{3-} (soluble)



Since BF_3 is more acidic than AlF_3 (atomic size of B is smaller than that of Al), it pulls out F^- from AlF_6^{3-} and thus AlF_3 gets precipitated



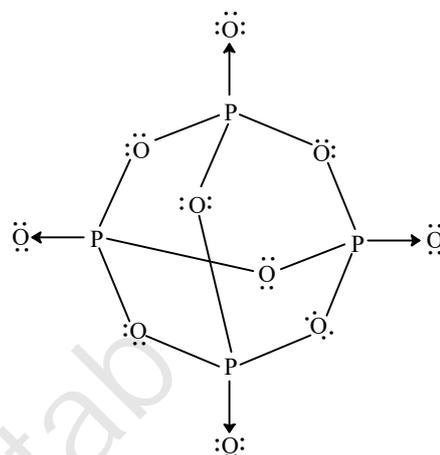
Number of moles of P_4O_{10}

$$= \frac{852}{284} = 3 \quad [\text{Mol. wt. of } \text{P}_4\text{O}_{10} = 284]$$

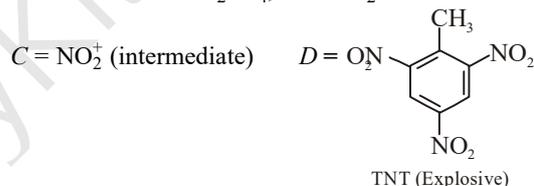
Number of moles of CaO for 3 moles of $\text{P}_4\text{O}_{10} = 3 \times 6 = 18$

$$\text{Weight of CaO} = 18 \times 56 \text{ g} \quad [\text{Mol. wt. of CaO} = 56]$$

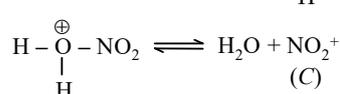
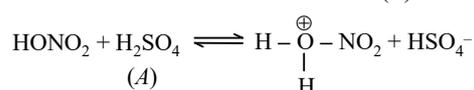
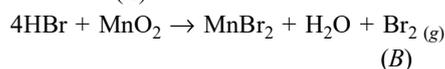
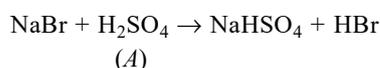
$$= 1008 \text{ g}$$



139. *A* = concentrated H_2SO_4 , *B* = Br_2



Reactions involved are :



140. Bleaching agent	Chlorine
Smelling salt	Ammonium carbonate
Cryolite	Aluminium
Bell metal	Tin
Fluorspar	Calcium
Fertilizer	Ammonium phosphate
Anthracite	Carbon

141. (I) - (E) : $\text{Pb}(\text{N}_3)_2$ is used as an explosive.

(II) - (H) : SiC is called artificial gem.

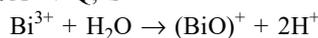
(III) - (C) : Cu is reduced from its sulphide (Cu_2S) by self-reduction.

(IV) - (F) : $\text{Fe}_2\text{O}_3(\text{Fe}^{3+})$ is paramagnetic because of presence of unpaired electrons in it.

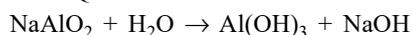
The p-Block Elements

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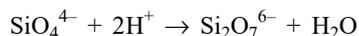
142. A → Q, S



B → Q

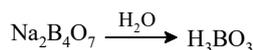
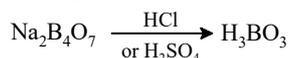


C → R

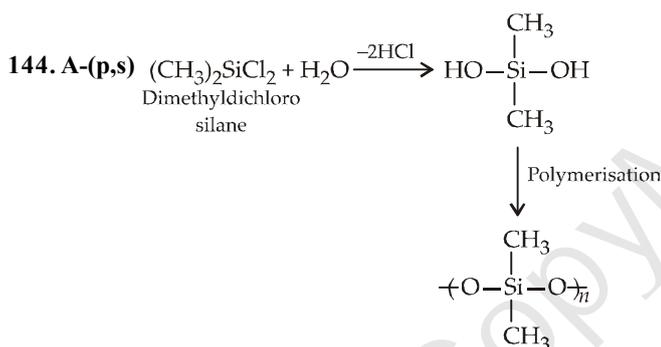
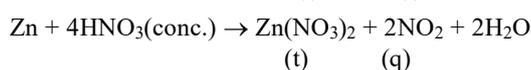
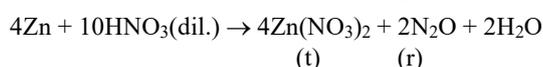
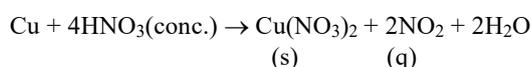
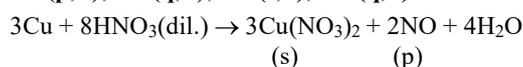


Pyrosilicate is formed by treating orthosilicate with acid.

D → Q, R



143. A - (p, s); B - (q, s); C - (r, t); D - (q, t):



B-(p, q, r, t)



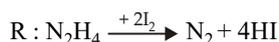
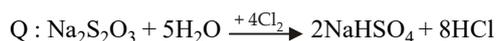
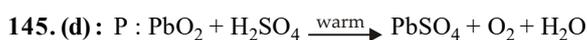
HF reacts with glass and the process is known as etching of glass.

C-(p, q)

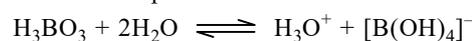
In presence of moisture, chlorine acts as an oxidising and a bleaching agent.



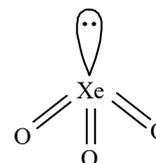
D-(p)

146. (b) : Nitrogen cannot expand its octet because of absence of *d*-orbitals in valence shell.

147. (c) : Due to the small size of fluorine atom, electron density is high which hinders the addition of an extra electron.

148. (a) : The basic nature of the hydroxides of group III elements increases down the group. This can be explained as follows. Small size of boron atom is responsible for high positive charge density on atom. This pulls off electrons from water molecules resulting in the weakening of O–H bond and, therefore facilitates the release of proton giving acidic solution. As the size of the ion increases, the tendency to rupture the O–H bond decreases and hence acidic nature decreases, *i.e.*, basic nature increases. Hence $\text{Al}(\text{OH})_3$ and $\text{Ga}(\text{OH})_3$ are amphoteric in nature.149. (c) : SiCl_4 undergoes hydrolysis because of the presence of vacant *d*-orbitals in the valence shell of Si. In case of carbon there are no vacant *d*-orbitals to accommodate electron pairs donated by water molecules during hydrolysis. Both SiCl_4 and CCl_4 are covalent. Thus assertion is correct but reason is not correct.150. (a) : B^{3+} has very small size and due to its very high charge, it has high polarising power. So as per Fajan's rule, boron forms covalent compound. Moreover, due to its small size, the ionisation potential value of B is too high to form B^{3+} ion.151. (c) : Orthoboric acid H_3BO_3 is soluble in water and behaves as a weak monobasic acid. It does not donate protons. Hence it is not a protic acid but it is a Lewis acid.152. (c) : The oxidizing action shows the following order $\text{Pb}^{4+} > \text{Sn}^{4+} > \text{Ge}^{4+}$

The lower oxidation states for the group 14 element is more stable for heavier elements in the group due to inert pair effect.

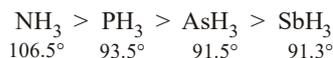
153. (a) : Argon being inert, creates inert atmosphere to prevent the oxidation of metal by O_2 of air.154. (c) : In XeO_3 there are total of 4 electron pairs around central atom. Out of which 3 are bonding electron pairs and one is non-bonding electron pair. Therefore, the hybridisation of central atom is sp^3 and geometry is trigonal pyramidal.

155. (a) : Xenon fluorides are strongly oxidising, since xenon is more stable in its atomic state.

156. (c) : Among phosphates and nitrates, nitrates are more soluble in water hence less abundant in earth crust.

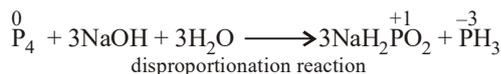
Further oxidation of nitrates (NO_3^-) is not possible because its oxidation state is +5 which is its highest oxidation state.

157. (c) : The actual bond angle is in order of



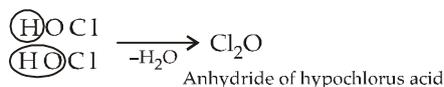
The bond angle in ammonia is less than $109^\circ 28'$ due to repulsion between lone pair present on nitrogen atom and bonded pairs of electrons. The decreased bond angle in other hydrides can be explained by the fact that the sp^3 hybridization becomes less and less distinct with increasing size of the central atom.

158. (b) : In disproportionation reaction, the same element of compound is oxidized and reduced.

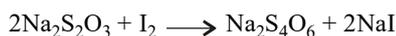


159. (a): Bleaching powder is $\text{Ca}(\text{OCl})\text{Cl}$.

It contains OCl^- ion *i.e.*, HOCl acid.



160. (c) : $2\text{CH}_3\text{COOH} + \text{CaOCl}_2 \longrightarrow (\text{CH}_3\text{COO})_2\text{Ca} + \text{H}_2\text{O} + \text{Cl}_2$



1 millimole of $\text{CaOCl}_2 = 1$ millimole of I_2

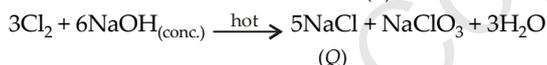
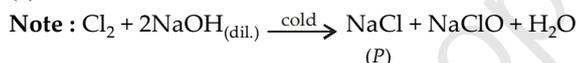
$$= \frac{1}{2} \text{ millimole of } \text{Na}_2\text{S}_2\text{O}_3$$

$$\text{Millimoles of } \text{CaOCl}_2 = \frac{1}{2} \times 0.25 \times 48 = 6$$

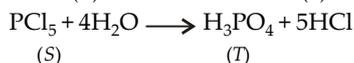
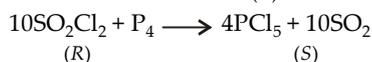
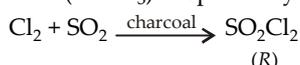
Molarity \times volume = 6 millimoles

Molarity \times 25 = 6 millimoles = 0.24 M

161. (a)



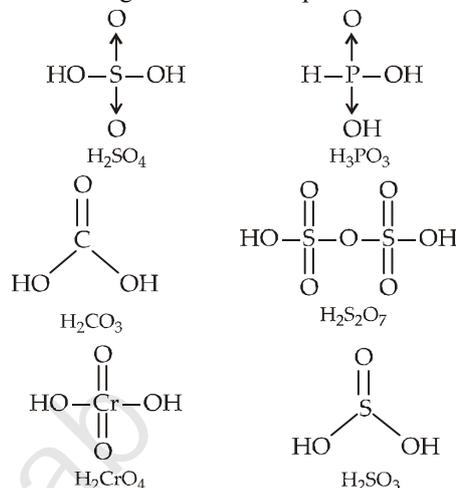
(P) and (Q) are salts of hypochlorous acid (HOCl) and chloric acid (HClO_3) respectively.



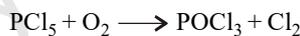
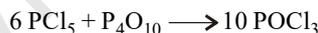
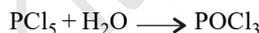
162. (a)

163. (3) : $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$: It is Beryl, with formula $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, where, $n = 3$. It is a blue coloured gemstone. It is an aluminosilicate, with Be as impurity.

164. (6) : Six out of the given acids are diprotic.

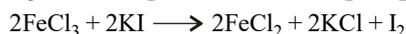
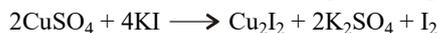


165. (5) : $\text{PCl}_5 + \text{SO}_2 \longrightarrow \text{POCl}_3 + \text{SOCl}_2$



(Note : $\text{PCl}_5 \text{ PCl}_3 + \text{O}_2\text{POCl}_3$)

166. (7) : $6\text{KI} + \text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{SO}_4 \longrightarrow$



167. (6) : $[\text{B}_2\text{H}_6 + 6\text{CH}_3\text{OH} \longrightarrow 2\text{B}(\text{OCH}_3)_3 + 6\text{H}_2] \times 3$



Thus, no. of moles of boron containing product formed by reacting 3 moles of B_2H_6 completely with methanol is 6.



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The Transition Elements

Multiple Choice Questions with ONE Correct Answer

- Which of the following dissolve in hot concentrated NaOH solution?
(a) Fe (b) Zn (c) Cu (d) Ag (1980)
- One of the constituent of German silver is
(a) Ag (b) Cu (c) Mg (d) Al (1980)
- Which of the following is the weakest base?
(a) NaOH (b) Ca(OH)₂
(c) KOH (d) Zn(OH)₂ (1980)
- How many unpaired electrons are present in Ni²⁺?
(a) 0 (b) 2 (c) 4 (d) 8 (1981)
- Sodium thiosulphate is used in photography because of its
(a) reducing behaviour (b) oxidising behaviour
(c) complex forming behaviour
(d) reaction with light (1981)
- Iron is rendered passive by treatment with
(a) H₂SO₄ (b) H₃PO₄
(c) HCl (d) conc. HNO₃ (1982)
- In the metallurgy of iron, when limestone is added to the blast furnace, the calcium ion ends up in
(a) slag (b) gangue
(c) metallic calcium (d) calcium carbonate (1982)
- Zinc-copper couple that can be used as a reducing agent is obtained by
(a) mixing zinc dust and copper gauze
(b) zinc coated with copper
(c) copper coated with zinc
(d) zinc and copper wires welded together (1984)
- Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by
(a) MnSO₄·4H₂O (b) CuSO₄·5H₂O
(c) FeSO₄·6H₂O (d) NiSO₄·6H₂O (1988)
- Among the following ion which one has the highest paramagnetism?
(a) [Cr(H₂O)₆]³⁺ (b) [Fe(H₂O)₆]²⁺
(c) [Cu(H₂O)₆]²⁺ (d) [Zn(H₂O)₆]²⁺ (1993)
- Which one is solder?
(a) Cu and Pb (b) Zn and Cu
(c) Pb and Sn (d) Fe and Zn (1995)
- Which pair gives Cl₂ at room temperature ?
(a) conc. HCl + KMnO₄ (b) NaCl + conc. H₂SO₄
(c) NaCl + MnO₂ (d) NaCl + conc. HNO₃ (1995)
- Which compound does not dissolve in hot, dilute HNO₃?
(a) HgS (b) PbS (c) CuS (d) CdS (1996)
- An aqueous solution of FeSO₄, Al₂(SO₄)₃ and chrome alum is heated with excess of Na₂O₂ and filtered. The materials obtained are
(a) a colourless filtrate and a green residue
(b) a yellow filtrate and a green residue
(c) a yellow filtrate and a brown residue
(d) a green filtrate and a brown residue (1996)
- Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is
(a) CrO₃ (b) Cr₂O₃ (c) Cr (d) CrO(O₂) (1997)
- The number of moles of KMnO₄ that will be needed to react with one mole of sulphite ion in acidic solution is
(a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) 1 (1997)
- In the dichromate dianion,
(a) 4 Cr — O bonds are equivalent
(b) 6 Cr — O bonds are equivalent
(c) all Cr — O bonds are equivalent
(d) all Cr — O bonds are nonequivalent (1999)

18. The chemical processes in the production of steel from haematite ore involve
 (a) reduction (b) oxidation
 (c) reduction followed by oxidation
 (d) oxidation followed by reduction (2000)
19. Anhydrous ferric chloride is prepared by
 (a) heating hydrated ferric chloride at a high temperature in a stream of air
 (b) heating metallic iron in a stream of dry chlorine gas
 (c) reaction of metallic iron with hydrochloric acid
 (d) reaction of metallic iron with nitric acid (2002)
20. When MnO_2 is fused with KOH , a coloured compound is formed, the product and its colour is
 (a) K_2MnO_4 , purple green (b) KMnO_4 , purple
 (c) Mn_2O_3 , brown (d) Mn_3O_4 , black (2003)
21. In the process of extraction of gold,
 Roasted gold ore + $\text{CN}^- + \text{H}_2\text{O} \xrightarrow{\text{O}_2} [\text{X}] + \text{OH}^-$
 $[\text{X}] + \text{Zn} \rightarrow [\text{Y}] + \text{Au}$
 Identify the complexes $[\text{X}]$ and $[\text{Y}]$
 (a) $\text{X} = [\text{Au}(\text{CN})_2]^-$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
 (b) $\text{X} = [\text{Au}(\text{CN})_4]^{3-}$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
 (c) $\text{X} = [\text{Au}(\text{CN})_2]^-$, $\text{Y} = [\text{Zn}(\text{CN})_6]^{4-}$
 (d) $\text{X} = [\text{Au}(\text{CN})_4]^-$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$ (2003)
22. The spin magnetic moment of cobalt in the compound $\text{Hg}[\text{Co}(\text{SCN})_4]$ is
 (a) $\sqrt{3}$ (b) $\sqrt{8}$ (c) $\sqrt{15}$ (d) $\sqrt{24}$ (2004)
23. The product of oxidation of I^- with MnO_4^- in alkaline medium is
 (a) IO_3^- (b) I_2 (c) IO^- (d) IO_4^- (2004)
24. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ on heating liberates a gas. The same gas will be obtained by
 (a) heating NH_4NO_2
 (b) heating NH_4NO_3
 (c) treating H_2O_2 with NaNO_2
 (d) treating Mg_3N_2 with H_2O (2004)
25. Which pair of compounds is expected to show similar colour in aqueous medium?
 (a) FeCl_2 and CuCl_2 (b) VOCl_2 and CuCl_2
 (c) VOCl_2 and FeCl_2 (d) FeCl_2 and MnCl_2 (2005)
26. A solution when diluted with H_2O and boiled, it gives a white precipitate. On addition of excess $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$?
 (a) $\text{Zn}(\text{OH})_2$ (b) $\text{Al}(\text{OH})_3$
 (c) $\text{Mg}(\text{OH})_2$ (d) $\text{Ca}(\text{OH})_2$. (2006)
27. CuSO_4 decolourises on addition of KCN , the product is
 (a) $[\text{Cu}(\text{CN})_4]^{2-}$
 (b) Cu^{2+} gets reduced to form $[\text{Cu}(\text{CN})_4]^{3-}$
 (c) $\text{Cu}(\text{CN})_2$
 (d) CuCN . (2006)
28. Among the following metal carbonyls, the C – O bond order is lowest in
 (a) $[\text{Mn}(\text{CO})_6]^+$ (b) $[\text{Fe}(\text{CO})_5]$
 (c) $[\text{Cr}(\text{CO})_6]$ (d) $[\text{V}(\text{CO})_6]^-$. (2007)
29. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of
 (a) nitrogen (b) oxygen
 (c) carbon dioxide (d) argon (2008)
30. The spin only magnetic moment value (in Bohr magneton units) of $\text{Cr}(\text{CO})_6$ is
 (a) 0 (b) 2.84 (c) 4.90 (d) 5.92. (2009)
31. The colour of light absorbed by an aqueous solution of CuSO_4 is
 (a) orange-red (b) blue-green
 (c) yellow (d) violet (2012)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

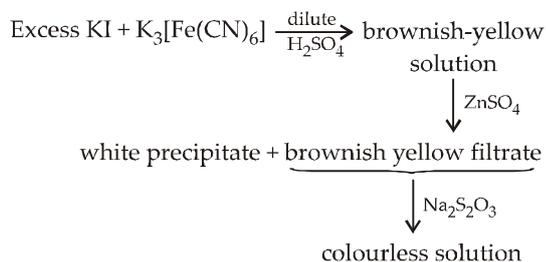
32. Potassium manganate (K_2MnO_4) is formed when
 (a) chlorine is passed into aqueous KMnO_4 solution
 (b) manganese dioxide is fused with potassium hydroxide in air
 (c) formaldehyde reacts with potassium permanganate in presence of a strong alkali
 (d) potassium permanganate reacts with concentrated sulphuric acid (1988)
33. The aqueous solutions of the following salts will be coloured in the case of
 (a) $\text{Zn}(\text{NO}_3)_2$ (b) LiNO_3
 (c) $\text{Co}(\text{NO}_3)_2$ (d) CrCl_3 (1990)
34. Which of the following alloys contains(s) Cu and Zn?
 (a) Bronze (b) Brass
 (c) Gun metal (d) Type metal (1993)
35. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese

The Transition Elements

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- (a) gives hardness to steel
 (b) helps the formation of oxides of iron
 (c) can remove oxygen and sulphur
 (d) can show highest oxidation state of +7. (1998)
36. Reduction of the metal centre in aqueous permanganate ion involves
 (a) 3 electrons in neutral medium
 (b) 5 electrons in neutral medium
 (c) 3 electrons in alkaline medium
 (d) 5 electrons in acidic medium (2011)

37. For the given aqueous reactions, which of the statement(s) is(are) true?



- (a) The first reaction is a redox reaction.
 (b) White precipitate is $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$.
 (c) Addition of filtrate to starch solution gives blue colour.
 (d) White precipitate is soluble in NaOH solution. (2012)
38. The correct statement(s) about Cr^{2+} and Mn^{3+} is(are) [Atomic numbers of Cr = 24 and Mn = 25]
 (a) Cr^{2+} is a reducing agent
 (b) Mn^{3+} is an oxidizing agent
 (c) both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration
 (d) when Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration. (2015)

Fill in the Blanks

39. Mn^{2+} can be oxidised to MnO_4^- by
 (SnO_2 , PbO_2 , BaO_2) (1981)
40. Galvanization of iron denotes coating with (1983)
41. Silver chloride is sparingly soluble in water because its lattice energy is greater than (1987)
42. The salts and are isostructural.
 ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) (1988)
43. The type of magnetism exhibited by $[\text{Mn}(\text{H}_2\text{O}_6)]^{2+}$ ion is (1994)
44. Silver jewellery items tarnish slowly in air due to their reaction with (1997)

True / False

45. Copper metal reduces Fe^{2+} in an acidic medium. (1982)
46. Silver fluoride is fairly soluble in water. (1982)
47. Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water. (1984)
48. Dipositive zinc exhibits paramagnetism due to loss of two electrons from 3rd-orbital of neutral atom. (1987)
49. Cu^+ disproportionates to Cu^{2+} and elemental copper in solution. (1991)

Subjective Problems

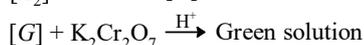
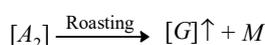
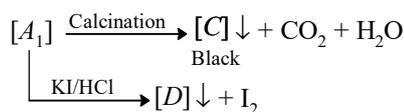
50. A white amorphous powder (A) on heating yields a colourless, non-combustible gas (B) and a solid (C). The latter compound assumes a yellow colour on heating and changes to white on cooling. (C) dissolves in dilute acid and the resulting solution gives a white precipitate on adding $\text{K}_4\text{Fe}(\text{CN})_6$ solution.
 (A) dissolves in dilute HCl with the evolution of gas, which is identical in all respects with (B). The gas (B) turns lime water milky, but the milkyness disappears with the continuous passage of gas. The solution of (A), as obtained above, gives a white precipitate (D) on the addition of excess of NH_4OH and passing H_2S . Another portion of the solution gives initially a white precipitate (E) on the addition of sodium hydroxide solution, which dissolves on further addition of the base. Identify the compounds (A), (B), (C), (D) and (E). (1979)
51. Compound A is a light green crystalline solid. It gives the following tests :
 (i) It dissolves in dilute sulphuric acid. No gas is produced.
 (ii) A drop of KMnO_4 is added to the above solution. The pink colour disappears.
 (iii) Compound A is heated strongly. Gases B and C, with pungent smell, come out. A brown residue D is left behind.
 (iv) The gas mixture (B and C) is passed into a dichromate solution. The solution turns green.
 (v) The green solution from step (iv) gives a white precipitate E with a solution of barium nitrate.
 (vi) Residue D from step (iii) is heated on charcoal in a reducing flame. It gives a magnetic substance E.
 Name the compounds A, B, C, D and E. (1980)

52. (i) A sample of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ is strongly heated in air. The residue is Mn_3O_4 .
 (ii) The residue is dissolved in 100 ml of 0.1 N FeSO_4 containing dilute H_2SO_4 .
 (iii) The solution reacts completely with 50 ml of KMnO_4 solution.
 (iv) 25 ml of the KMnO_4 solution used in step (iii) requires 30 ml of 0.1 N FeSO_4 solution for complete reaction. Find the amount of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ present in the sample. (1980)
53. Complete the following equation (no balancing is needed):
 $\text{SO}_2 + \text{MnO}_4^- + \dots \longrightarrow \text{SO}_4^{2-} + \text{Mn}^{2+} + \dots$ (1981)
54. An unknown solid mixture contains one or two of the following: CaCO_3 , BaCl_2 , AgNO_3 , Na_2SO_4 , ZnSO_4 and NaOH . The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When dilute hydrochloric acid is gradually added to the above solution, a precipitate is produced which dissolves with further addition of the acid. What is/are present in the solid? Give equations to explain the appearance of the precipitate and its dissolution. (1981)
55. State with balanced equations what happens when :
 (i) Sulphur dioxide gas is bubbled through an aqueous solution of copper sulphate in presence of potassium thiocyanate. (1982)
 (ii) Aqueous solution of ferric sulphate and potassium iodide are mixed. (1984)
 (iii) Aqueous solution of potassium manganate and acid are mixed. (1984)
 (iv) Aqueous solution of potassium chromate and acid are mixed. (1984)
 (v) Potassium permanganate interacts with manganese dioxide in presence of potassium hydroxide; (1985)
 (vi) Potassium ferrocyanide is heated with concentrated sulphuric acid. (1985)
 (vii) Gold is dissolved in *aqua regia*. (1987)
 (viii) Silver chloride is treated with aqueous sodium cyanide and the products thus formed is allowed to react with zinc in alkaline medium. (1989)
 (ix) Cobalt (II) solution reacts with KNO_2 in acetic acid medium. (1989)
 (x) A mixture of potassium dichromate and sodium chloride is heated with concentrated H_2SO_4 . (1990)
 (xi) Iron reacts with cold dilute nitric acid. (1990)
 (xii) Potassium permanganate is added to a hot solution of manganous sulphate. (1990)
- (xiii) Copper reacts with HNO_3 to give NO and NO_2 in molar ratio of 2 : 1.
 $\text{Cu} + \text{HNO}_3 \rightarrow \dots + \text{NO} + \text{NO}_2 + \dots$ (1992)
- (xiv) Na_2CO_3 is added to a solution of copper sulphate.
 $\text{CuSO}_4 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \dots \text{Na}_2\text{SO}_4 + \dots$ (1992)
- (xv) Potassium dichromate and concentrated hydrochloric acid are heated together.
 $\text{K}_2\text{Cr}_2\text{O}_7 + \text{HCl} \rightarrow \text{KCl} + \dots + \dots \text{H}_2\text{O}$ (1992)
- (xvi) $\text{AgBr} + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \dots + \dots$ (1993)
- (xvii) $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} + \text{MnSO}_4 \rightarrow \dots + \dots + \dots$ (1993)
- (xviii) $[\text{MnO}_4]^{2-} + \text{H}^+ \rightarrow \dots + [\text{MnO}_4]^- + \text{H}_2\text{O}$ (1994)
- (xix) $\text{SO}_{2(aq)} + \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ \rightarrow \dots + \dots + \dots$ (1994)
- (xx) Write a balanced equation for the reaction of argentite with KCN and name the products in solution. (1996)
- (xxi) Write balanced equations for the oxidation of cuprous oxide to cupric hydroxide by alkaline KMnO_4 . (1997)
- (xxii) Write balanced equations for the reaction of alkaline perbromate with zinc giving tetrahydroxozincate anion. (1997)
- (xxiii) Write balanced equations for the reaction of zinc with dilute nitric acid. (1997)
56. (a) Write balanced equations for the extraction of silver from silver glance by cyanide process. (1988)
 (b) Write balanced equations for the extraction of copper from copper pyrites by self-reduction. (1990)
57. Give reasons for the following :
 (i) Silver bromide is used in photography. (1983)
 (ii) Most transition metal compounds are coloured. (1986)
 (iii) Zinc and not copper is used for the recovery of metallic silver from complex $[\text{Ag}(\text{CN})_2]^-$. Explain. (1987)
 (iv) The colour of mercurous chloride, Hg_2Cl_2 , changes from white to black when treated with ammonia. (1988)
 (v) The species $[\text{CuCl}_4]^{2-}$ exists while $[\text{CuI}_4]^{2-}$ does not. (1992)
 (vi) CrO_3 is an acid anhydride. (1999)
58. State the conditions under which the following preparation is carried out. Give the necessary equations which need not be balanced.
 Potassium permanganate from manganese dioxide. (1983)

The Transition Elements

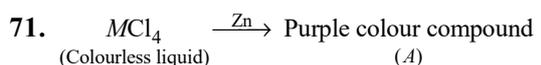
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59. What happens when :
- aqueous ammonia is added dropwise to a solution of copper sulphate till it is in excess. (1985)
 - CrCl_3 solution is treated with sodium hydroxide and then with hydrogen peroxide. (1985)
60. Mention the products formed when zinc oxide is treated with excess of sodium hydroxide solution. (1986)
61. What is the actual reducing agent of haematite in blast furnace? (1987)
62. The acidic, aqueous solution of ferrous ion forms a brown complex in the presence of NO_3^- , by the following two steps. Complete and balance the equations :
- $$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{NO}_3^- + \text{H}^+ \rightarrow \dots + [\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O}$$
- $$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \dots \rightarrow \dots + \text{H}_2\text{O} \quad (1993)$$
63. Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation. (1996)
64. Write equations for the reaction of :
- silver bromide with hypo in photographic process.
 - cobaltous chloride with excess of KNO_2 in aqueous acidic solution. (1997)
65. When the ore haematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel but also a silicate slag that is useful in making building materials such as cement. Discuss the same and show through balanced chemical equations. (1998)
66. Work out the following using chemical equations
In moist air copper corrodes to produce a green layer on the surface. (1998)
67. Write the chemical reaction associated with the 'brown ring test'. (2000)
68. (i) Write the chemical reactions involved in the extraction of metallic silver from argentite.
(ii) Write the balanced chemical equation for developing photographic films. (2000)
69. Some reactions of two ores, A_1 and A_2 of the metal M are given below :

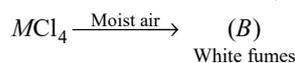


Identify A_1 , A_2 , M , C , D and G and explain using the required chemical reactions. (2004)

70. Write the chemical reaction involved in developing of a black and white photographic film. An aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution is acidified to give a milky white turbidity. Identify the product and write the balanced half chemical reaction for it. (2005)



$M = \text{Transition metal (Colourless liquid)}$



Identify (A), (B) and MCl_4 . Also explain colour difference between MCl_4 and (A). (2005)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
(c) Statement-1 is true, statement-2 is false.
(d) Statement-1 is false, statement-2 is true.

72. **Statement-1** : To a solution of potassium chromate if a strong acid is added it changes its colour from yellow to orange.

Statement-2 : The colour change is due to the oxidation of potassium chromate. (1988)

73. **Statement-1** : Zn^{2+} is diamagnetic.

Statement-2 : The electrons are lost from 4s orbital to form Zn^{2+} . (1998)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension-1

p-Amino-*N,N*-dimethylaniline is added to a strongly acidic solution of X . The resulting solution is treated with a few drops of aqueous solution of Y to yield a blue colouration due to the formation of methylene blue. Treatment of the aqueous solution of Y with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of Y with the solution of potassium hexacyanoferrate(III) leads to a brown colouration due to the formation of Z .

74. The compound X is
 (a) NaNO_3 (b) NaCl
 (c) Na_2SO_4 (d) Na_2S
75. The compound Y is
 (a) MgCl_2 (b) FeCl_2
 (c) FeCl_3 (d) ZnCl_2
76. The compound Z is
 (a) $\text{Mg}_2[\text{Fe}(\text{CN})_6]$ (b) $\text{Fe}[\text{Fe}(\text{CN})_6]$
 (c) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (d) $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ (2009)

Comprehension-2

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$). However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS_2). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction.

77. Partial roasting of chalcopyrite produces
 (a) Cu_2S and FeO (b) Cu_2O and FeO
 (c) CuS and Fe_2O_3 (d) Cu_2O and Fe_2O_3
78. Iron is removed from chalcopyrite as
 (a) FeO (b) FeS (c) Fe_2O_3 (d) FeSiO_3
79. In self-reduction, the reducing species is
 (a) S (b) O^{2-} (c) S^{2-} (d) SO_2 (2010)

Comprehension-3

When a metal rod M is dipped into an aqueous colourless concentrated solution of compound N , the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate O . Addition of aqueous NH_3 dissolves O and gives an intense blue solution.

80. The metal rod M is
 (a) Fe (b) Cu
 (c) Ni (d) Co
81. The compound N is
 (a) AgNO_3 (b) $\text{Zn}(\text{NO}_3)_2$
 (c) $\text{Al}(\text{NO}_3)_3$ (d) $\text{Pb}(\text{NO}_3)_2$
82. The final solution contains
 (a) $[\text{Pb}(\text{NH}_3)_4]^{2+}$ and $[\text{CoCl}_4]^{2-}$
 (b) $[\text{Al}(\text{NH}_3)_4]^{3+}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (c) $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (d) $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$ (2011)

Integer Answer Type

83. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is (2009)
84. In dilute aqueous H_2SO_4 , the complex diaquodioxalatoferate (II) is oxidized by MnO_4^- . For this reaction, the ratio of the rate of change of $[\text{H}^+]$ to the rate of change of $[\text{MnO}_4^-]$ is (2015)

ANSWER KEY

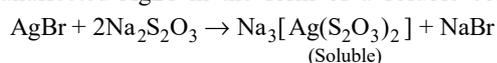
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|---|-------------------|--------------------|--------------------------|----------------------|---------------|
| 1. (b) | 2. (b) | 3. (d) | 4. (b) | 5. (c) | 6. (d) |
| 7. (a) | 8. (b) | 9. (b) | 10. (b) | 11. (c) | 12. (a) |
| 13. (a) | 14. (c) | 15. (b) | 16. (a) | 17. (b) | 18. (d) |
| 19. (b) | 20. (a) | 21. (a) | 22. (c) | 23. (a) | 24. (a) |
| 25. (b) | 26. (a) | 27. (b) | 28. (d) | 29. (b) | 30. (a) |
| 31. (a) | 32. (b, c) | 33. (c, d) | 34. (b, c) | 35. (a, c) | 36. (a, c, d) |
| 37. (a, c, d) | 38. (a, b, c) | 39. PbO_2 | 40. Zinc | 41. Hydration energy | |
| 42. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ | 43. Paramagnetism | | 44. H_2S | 45. False | |
| 46. True | 47. True | 48. False | 49. True | 72. (c) | 73. (b) |
| 74. (d) | 75. (c) | 76. (b) | 77. (b) | 78. (d) | 79. (c) |
| 80. (b) | 81. (a) | 82. (c) | 83. (6) | 84. (8) | |

Explanations

1. (b): $\text{Zn} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$
 2. (b): German silver : Cu – 56%, Zn – 24% and Ni – 20%
 3. (d)
 4. (b) : The electronic configuration of Ni^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$.

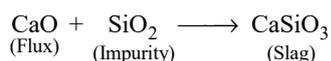
$3d^8 \Rightarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow$ i.e. it has 2 unpaired electrons.

5. (c) : Hypo ($\text{Na}_2\text{S}_2\text{O}_3$) is used in photography to remove the unaffected AgBr in the form of a soluble complex.



6. (d) : Because of formation of a thick protective film of Fe_3O_4 on its surface iron is rendered passive on action with concentrated HNO_3 .

7. (a): $\text{CaCO}_3 \xrightarrow{\text{heat}} \text{CaO} + \text{CO}_2 \uparrow$



8. (b) : Zinc-copper couple can be obtained by coating zinc with copper.

9. (b) : Mn^{2+} (in $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$) has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$, i.e., it has 5 unpaired electrons in 3d-orbitals.

Similarly the number of unpaired electrons in other species are

Cu^{2+} (in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$, i.e., one unpaired electron.

Fe^{2+} (in $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$, i.e., four unpaired electrons.

Ni^{2+} (in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$): $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$, i.e., two unpaired electrons.

So, we find minimum number of unpaired electrons (i.e. 1) is in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ so it has the lowest degree of paramagnetism.

10. (b) : The oxidation states of various metals are
 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$; Cr^{3+} i.e. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
 i.e. 3 unpaired electrons
 $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$; Fe^{2+} i.e. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
 i.e. 4 unpaired electrons
 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$; Cu^{2+} i.e. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
 i.e. 1 unpaired electron
 $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$; Zn^{2+} i.e. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
 i.e. no unpaired electron

Thus highest paramagnetism will be shown by $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ in which we have 4 unpaired d-electrons (maximum number of unpaired electrons).

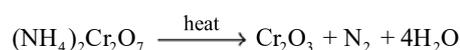
11. (c) : Solder is an alloy. It is made up of Sn = 67% and Pb = 33%.

12. (a) : $2\text{KMnO}_4 + 16\text{HCl} \rightarrow 2\text{KCl} + 2\text{MnCl}_2 + 8\text{H}_2\text{O} + 5\text{Cl}_2$

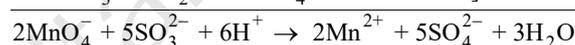
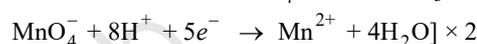
13. (a) : HgS does not dissolve in hot dil HNO_3 .

14. (c) : We get a yellow filtrate (due to presence of CrO_4^{2-} ion in it) and a brown residue of $\text{Fe}(\text{OH})_3$.

15. (b) : The green coloured compound blown in air is Cr_2O_3 .



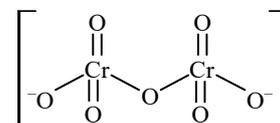
16. (a) : In acidic medium MnO_4^- oxidises SO_3^{2-} to SO_4^{2-} .



Hence, 2 moles of $\text{MnO}_4^- \equiv 5$ moles of SO_3^{2-}

or $\frac{2}{5}$ moles of $\text{MnO}_4^- \equiv 1$ mole of SO_3^{2-}

17. (b) : The structure of $\text{Cr}_2\text{O}_7^{2-}$ is



In it all the six normal Cr — O bonds are equivalent and two bridged Cr — O bonds are equivalent. The normal Cr — O bonds (161 pm) are different from bridged Cr — O bonds (180 pm).

18. (d) : First, added carbon with haematite ore is oxidised to form CO and CO_2 then, CO acts as reducing agent to reduce haematite ore.

19. (b): $2\text{Fe} + 3\text{Cl}_2 \longrightarrow 2\text{FeCl}_3$
 (Dry) (Anhydrous)

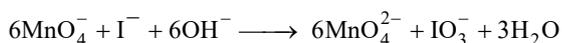
20. (a) : In alkaline medium the stable oxidation state of Mn is +6. Hence MnO_2 is oxidised to K_2MnO_4 (purple green) by atmospheric oxygen in KOH medium.

21. (a) : $2\text{Au} + 4\text{CN}^- + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2[\text{Au}(\text{CN})_2]^- + 2\text{OH}^-$
 $2[\text{Au}(\text{CN})_2]^- + \text{Zn} \rightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{Au}$

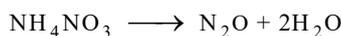
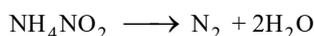
22. (c) : In $\text{Hg}[\text{Co}(\text{SCN})_4]$, the oxidation state of Co is +2. In Co^{2+} ; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$, we have three unpaired electrons so its spin magnetic moment will be

$$\mu = \sqrt{3(3+2)} \text{ B.M.} = \sqrt{3 \times 5} \text{ B.M.} = \sqrt{15} \text{ B.M.}$$

23. (a) : In alkaline medium the stable oxidation state of Mn is +6. Thus MnO_4^- is reduced to MnO_4^{2-} and Γ^- is oxidised to IO_3^- ,

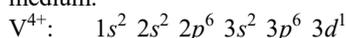


24. (a) : $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{heat}} \text{Cr}_2\text{O}_3 + \text{N}_2 + 4\text{H}_2\text{O}$

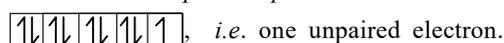
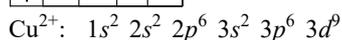
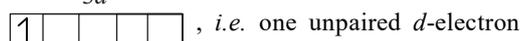


N_2 gas is liberated by heating $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and the same gas (*i.e.* N_2) is liberated by heating NH_4NO_2 . In all other cases N_2 is not a product.

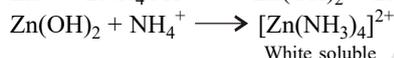
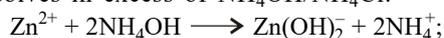
25. (b) : In transition metal salts the appearance of colour is due to $d-d$ transitions of unpaired electrons of d -orbitals. Metal ions having similar number of unpaired electrons in d -orbitals show similar colour in aqueous medium.



3d



26. (a) : When the solution containing Zn^{2+} ions is treated with $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$, first a white precipitate appears which dissolves in excess of $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$.



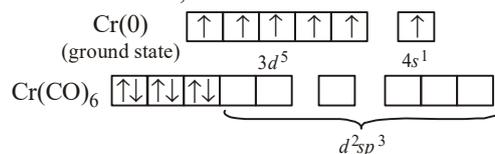
27. (b) : $[\text{CuSO}_4 + 2\text{KCN} \rightarrow \text{Cu}(\text{CN})_2 + \text{K}_2\text{SO}_4] \times 2$
 $2\text{Cu}(\text{CN})_2 \rightarrow \text{Cu}_2(\text{CN})_2 + (\text{CN})_2$
 $\text{Cu}_2(\text{CN})_2 + 6\text{KCN} \rightarrow 2\text{K}_3\text{Cu}(\text{CN})_4$
 $\hline 2\text{CuSO}_4 + 10\text{KCN} \rightarrow 2\text{K}_3\text{Cu}(\text{CN})_4 + 2\text{K}_2\text{SO}_4 + (\text{CN})_2$

28. (d) : $[\text{V}(\text{CO})_6]^-$, the anionic carbonyl complex can delocalise more electron density to antibonding π -orbital ($d\pi-p\pi$ back bonding) of CO and thus lowers the bond order.

29. (b) : Metallic silver dissolves in sodium cyanide solution in the presence of oxygen to form water soluble complex *i.e.*, sodium argentocyanide.

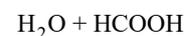
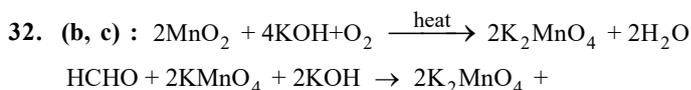


30. (a) : In $\text{Cr}(\text{CO})_6$, CO is a neutral ligand, so Cr is in zero oxidation state, but since it is a strong field ligand, it causes pairing of all the electrons,



$$\therefore n \text{ (no. of unpaired } e^-) = 0 \Rightarrow \mu = \sqrt{n(n+2)} = 0.$$

31. (a) : The colour of aqueous solution of CuSO_4 is blue green. Thus it absorbs orange-red colour and exhibit the complementary colour.



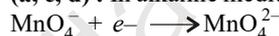
33. (c, d) : Co^{2+} [in aqueous solution of $\text{Co}(\text{NO}_3)_2$] and Cr^{3+} (in CrCl_3) have the outer configuration as d^7 and d^3 respectively. Since both Co^{2+} and Cr^{3+} have incompletely filled d -orbitals so the aqueous solutions of $\text{Co}(\text{NO}_3)_2$ and CrCl_3 are coloured ($d-d$ transitions are possible).

34. (b, c) : Brass contains 60 - 80% Cu and 40 - 20% Zn. Gun metal contains 87% Cu and 3% Zn and 10% Sn.

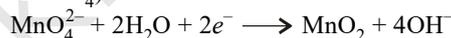
35. (a, c) : The addition of Mn makes steel harder and increases its elasticity and tensile strength.

Mn also acts as a deoxidiser. MnO reacts with S present in cast iron to form SO_2 and thus it can remove oxygen and sulphur.

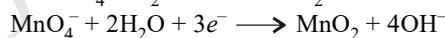
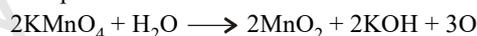
36. (a, c, d) : In alkaline medium.



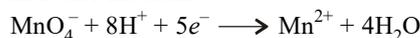
But MnO_4^{2-} is further reduced to MnO_2 (in case of aqueous KMnO_4).



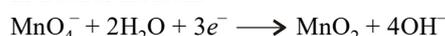
Complete reaction :



In acidic medium



In neutral medium

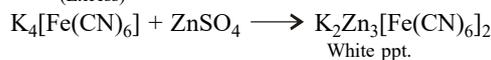


Hence, number of electrons lose in acidic and neutral medium are 5 and 3 electrons respectively.

37. (a, c, d) : $2\text{KI} + 2\text{K}_3[\text{Fe}(\text{CN})_6] \xrightarrow{\text{dil. H}_2\text{SO}_4} 2\text{K}_4[\text{Fe}(\text{CN})_6] + \text{I}_2$... (i)



(Excess)



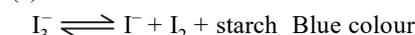
Brownish Colourless solution

yellow filtrate

(a) is correct as in reaction (i), $\Gamma^- (-1)$ is being oxidised to $\text{I}_2(0)$ and Fe^{3+} is being reduced to Fe^{2+} .

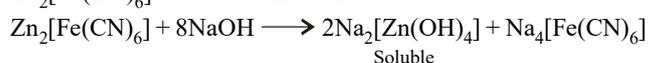
(b) is incorrect as white precipitate is of $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ or $\text{Zn}_2[\text{Fe}(\text{CN})_6]$

(c) is correct as



Filtrate

(d) is correct as white precipitate of $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ or $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ is soluble in NaOH as



The Transition Elements

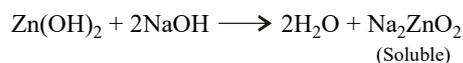
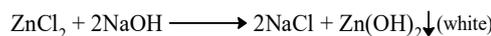
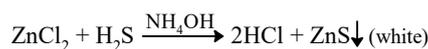
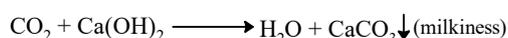
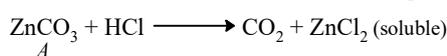
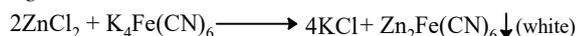
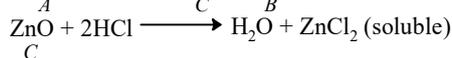
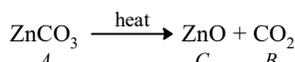
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38. (a, b, c) : (a) Cr^{2+} is a reducing agent, it gets oxidised to Cr^{3+} ($3d^3$ or t_{2g}^3 , stable half-filled configuration).
 (b) Mn^{3+} is an oxidizing agent, it gets reduced to Mn^{2+} ($3d^5$, most stable, half-filled configuration).
 (c) Cr (24) : $3d^4 4s^2$ Mn (25) : $3d^5 4s^2$
 Cr^{2+} : $3d^4$ Mn^{3+} : $3d^4$
 Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration.
 (d) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^3 electronic configuration.

39. PbO_2 .
 40. Zinc; Galvanising is a process of depositing a thin layer of Zn over the surface of Fe.
 41. Hydration energy.
 42. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; Compounds having same lattice type and crystal structure are called isostructural.
 43. Paramagnetism; In $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, the oxidation state of Mn is +2. The arrangement of electrons in this state is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$. There are five unpaired electrons in $3d$ -orbital so it is paramagnetic.
 44. H_2S ; Air contaminated with H_2S covers silver with an adherent film of black silver sulphide.
 45. False
 Fe^{2+} cannot be reduced by copper metal in acidic medium.
 46. True
 Hydration energy > Lattice energy for AgF .
 47. True
 AgCl forms complex with concentrated NaCl and is thus soluble.
 48. False
 In Zn^{2+} , the electronic arrangement is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$. Since it has no unpaired electrons so it is diamagnetic and not paramagnetic.
 49. True
 Cu^+ can be oxidised to Cu^{2+} and it can also be reduced to Cu, thus in solution Cu^+ disproportionates to Cu^{2+} and Cu.

50. (A) - ZnCO_3 (Zinc carbonate)
 (B) - CO_2 (Carbon dioxide)
 (C) - ZnO (Zinc oxide)
 (D) - ZnS (Zinc sulphide)
 (E) - $\text{Zn}(\text{OH})_2$ (Zinc hydroxide)

Reactions :



51. A - ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)
 B - sulphur dioxide (SO_2)
 C - sulphur trioxide (SO_3)
 D - ferric oxide (Fe_2O_3)
 E - iron (Fe)

Ferrous sulphate has a light green colour. It dissolves in water containing sulphuric acid. In the absence of acid, ferrous sulphate being a salt of weak base and strong acid gets hydrolysed to ferrous hydroxide which is insoluble in water, therefore, the solution will not be clear.

Ferrous sulphate is a reducing agent therefore, it decolourises the KMnO_4 solution. On strongly heating ferrous sulphate, both SO_2 (B) and SO_3 (C) are evolved. Sulphur dioxide being a reducing agent turns a dichromate solution green and forms sulphuric acid in the solution. Moreover, the SO_3 dissolves in water to give sulphuric acid. That is why the solution gives a white precipitate (BaSO_4) with a solution of $\text{Ba}(\text{NO}_3)_2$. On heating in a charcoal cavity in a residue flame reduces ferric oxide (D) reduces to iron (Fe) which is a magnetic substance.

52. Reactions involved



$$\begin{aligned} \text{Milliequivalent of FeSO}_4 \text{ in } 30 \text{ ml of } 0.1\text{N FeSO}_4 \\ = 30 \times 0.1 = 3 \end{aligned}$$

$$25 \text{ ml of } \text{KMnO}_4 \text{ reacts with } = 3 \text{ meq of FeSO}_4$$

$$\begin{aligned} \therefore 50 \text{ ml of } \text{KMnO}_4 \text{ reacts with } \frac{3 \times 50}{25} = \text{meq of FeSO}_4 \\ = 6 \text{ meq of FeSO}_4 \end{aligned}$$

$$\begin{aligned} \text{Milliequivalent of } 100 \text{ ml of } 0.1 \text{ N FeSO}_4 \\ = 100 \times 0.1 = 10 \text{ meq.} \end{aligned}$$

$$\begin{aligned} \text{Ferrous sulphate reacted with } \text{Mn}_3\text{O}_4 = 10 - 6 \text{ meq.} \\ = 4 \text{ meq.} \end{aligned}$$

Since millieq. of oxidising agent = millieq. reducing agent
 \therefore milliequivalent of Mn_3O_4 formed = 4 meq.

Since



$$1 \text{ meq.} = 3 \text{ meq}$$

$$\therefore 4 \text{ meq} = 12 \text{ meq.}$$

Equivalent weight of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$

$$= \frac{55 + 32 + (4 \times 16) + (4 \times 18)}{2} = \frac{223}{2}$$

$$\begin{aligned} \text{Weight of } \text{MnSO}_4 \cdot 4\text{H}_2\text{O} \text{ in the sample} &= \frac{12 \times 223}{2} \text{ mg} \\ &= 1.338 \text{ g} \end{aligned}$$

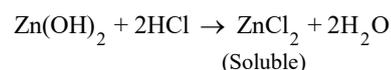
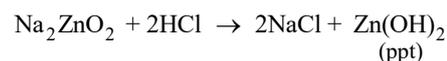
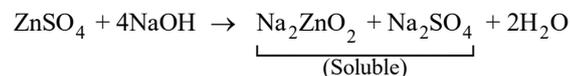
53. $\text{SO}_2 + \text{MnO}_4^- + \text{H}^+ \rightarrow \text{SO}_4^{2-} + \text{Mn}^{2+} + \text{H}_2\text{O}$

54. Since the mixture is soluble in water to give strong alkaline solution so it must contain NaOH as one of the constituents.

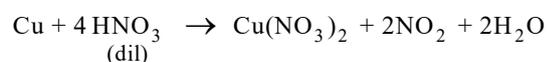
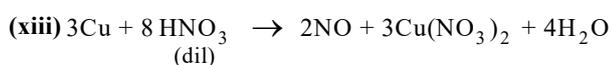
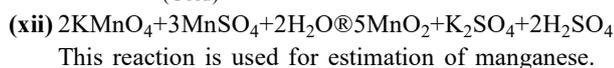
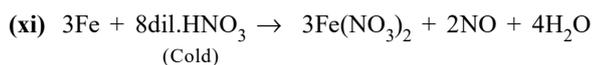
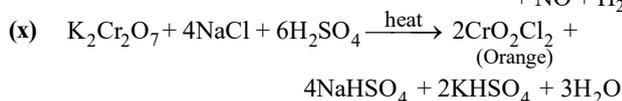
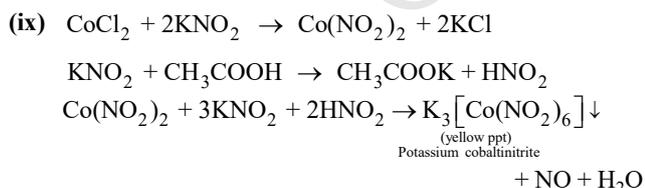
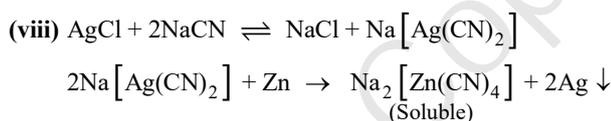
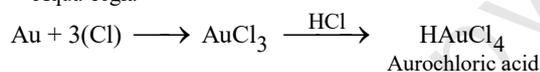
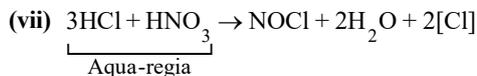
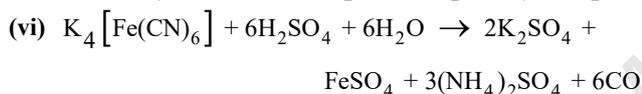
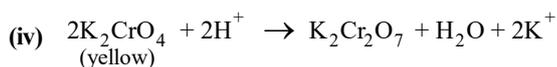
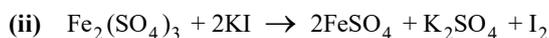
Since a precipitate appears when dil. HCl is added and the precipitate is soluble in excess of dil. HCl so the solution must contain some zinc salt, *i.e.* ZnSO₄.

So NaOH and ZnSO₄ are present in mixture solution.

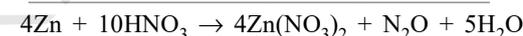
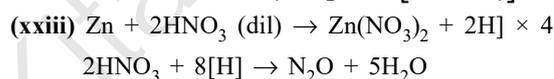
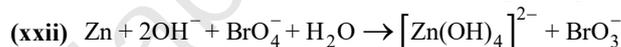
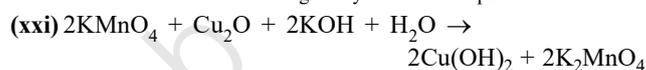
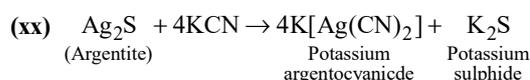
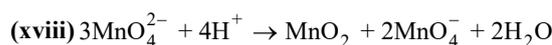
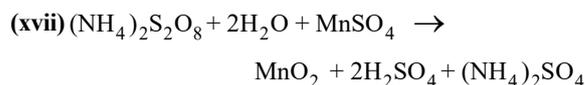
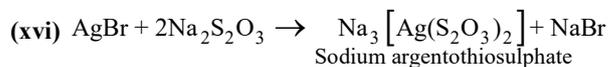
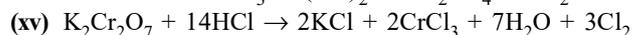
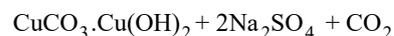
Reactions :



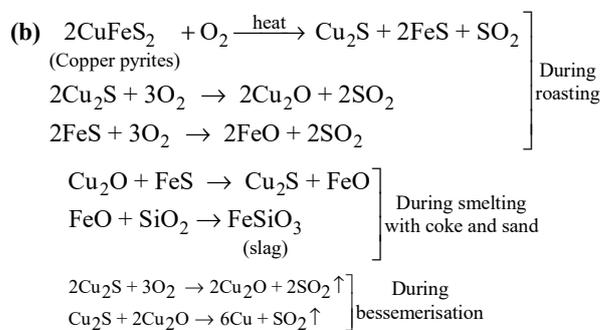
55. (i) : $2\text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O} + 2\text{KCNS} \rightarrow 2\text{Cu(CNS)} + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$
Cuprous thiocyanate



For molar ratio of 2 : 1 of NO and NO₂, we will have
 $7\text{Cu} + 20\text{HNO}_3 \rightarrow 7\text{Cu(NO}_3)_2 + 4\text{NO} + 2\text{NO}_2 + 10\text{H}_2\text{O}$



56. (a) : $\text{Ag}_2\text{S} + 4\text{NaCN} \rightleftharpoons 2\text{Na}[\text{Ag(CN)}_2] + \text{Na}_2\text{S}$
 $4\text{Na}_2\text{S} + 5\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{SO}_4 + 4\text{NaOH} + 7\text{S}$
 $2\text{Na}[\text{Ag(CN)}_2] + \text{Zn} \rightarrow \text{Na}_2[\text{Zn(CN)}_4] + 2\text{Ag} \downarrow$
(Soluble)



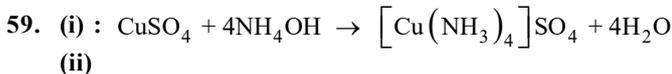
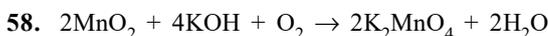
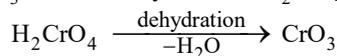
57. (i) Silver bromide is used in photography because of its sensitivity to sunlight. In light AgBr reduces to metallic silver.
 (ii) The colour of transition metal compounds is due to the presence of incompletely filled *d*-orbitals in transition metal ions/atoms, because of this *d-d* transition can occur in them. The colour is due to *d-d* transition for which the energy is absorbed from visible region. The visible colour of a compound is the complementary colour of the absorbed light.
 (iii) Zinc is a cheaper and stronger reducing agent as compared to copper.
 (iv) Mercurous chloride (white) changes to black on treatment with ammonia because of the formation of finely divided mercury (grey).

The Transition Elements

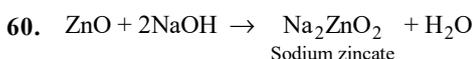
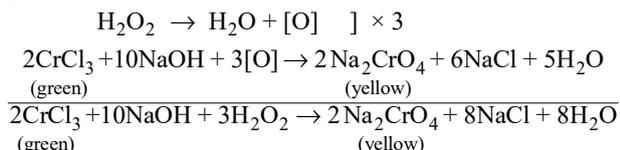
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(v) Cu^{2+} is reduced to Cu^+ by I^- and thus CuI_2 gets converted to Cu_2I_2 . This change cannot be brought about by Cl^- .

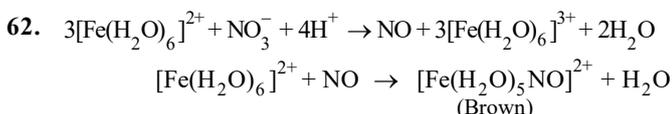
(vi) CrO_3 is acid anhydride of H_2CrO_4 (chromic acid).



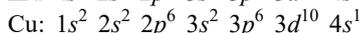
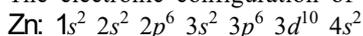
(ii)



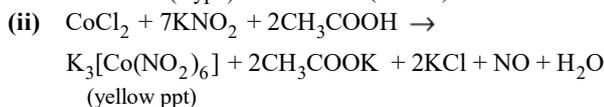
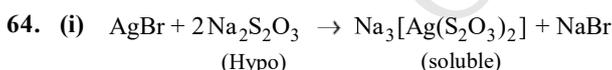
61. Carbon monoxide (CO) is the actual reducing agent of haematite in blast furnace.



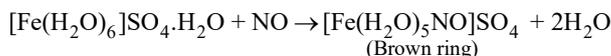
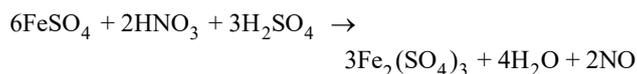
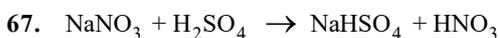
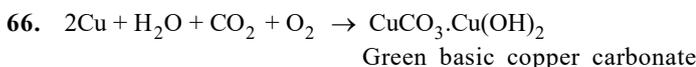
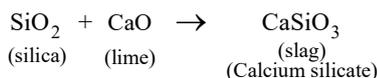
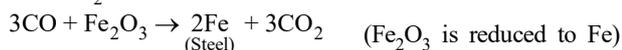
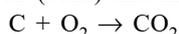
63. The electronic configuration of Zn and Cu are:



From the above configuration it is clear that first ionisation energy of Zn is greater than that of Cu (because of $4s^2$ and $4s^1$ configuration of Zn and Cu respectively). More energy is needed to remove an electron of $4s^2$ than that of $4s^1$. The second I.E. of Cu is higher than that of Zn because for Cu^{2+} the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ and for Zn^+ the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$, it is easier to remove $4s^1$ electron of Zn^+ than a $3d$ -electron from $3d^{10}$ (stable configuration).

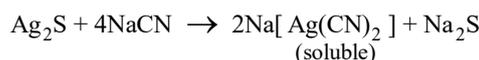


65. Following reactions occur when haematite is burnt with carbon (coke) and lime at 2000°C .



68. (i) Argentite (Ag_2S) ore is concentrated by froth floatation process.

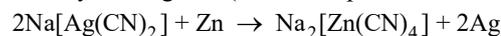
The concentrated ore is finely divided and dissolved in dilute solution of sodium cyanide (NaCN).



It is called leaching.

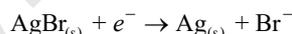
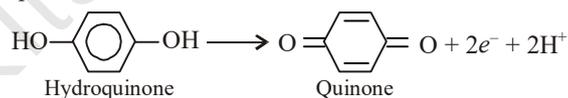
Na_2S is oxidised by air to Na_2SO_4 and it prevents the backward reaction to occur.

Metallic silver (Ag) is then precipitated out from the solution by adding Zn (an electropositive metal).



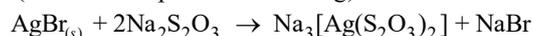
Note : Zinc is more electropositive than Ag.

(ii) During the process of development of the photographic film, the activated AgBr grains are preferentially reduced by mild reducing agent such as hydroquinone.



(Reduction of AgBr to metallic Ag)

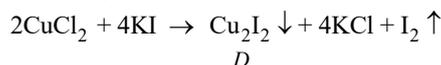
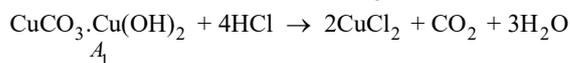
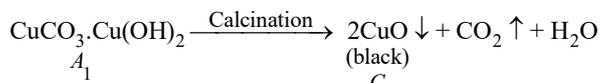
The photographic film is then permanently fixed by immediately washing any non-activated AgBr grains in hypo (This is the process of fixing).



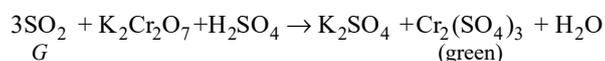
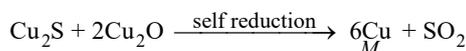
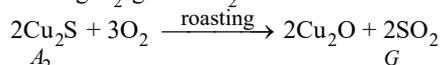
69. The formation of carbon dioxide when ore A_1 is calcined indicates that ore A_1 is a carbonate.

Since ore A_1 when treated with HCl and KI , evolves I_2 so A_1 would be a hydroxide.

From these observation we get the possible formula of ore A_1 as $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. The reactions can be explained as follows:-



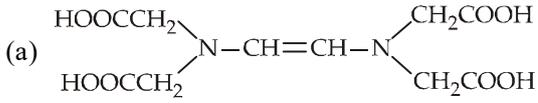
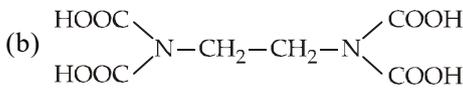
Ore A_2 when roasted gives gas G which gives green colour with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ i.e. the gas G is SO_2 . Since on roasting A_2 gives SO_2 so it should be a sulphide of copper.

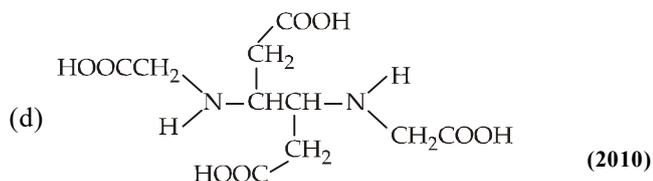
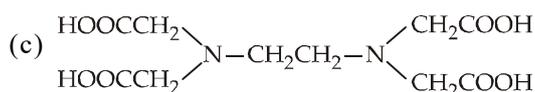


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Coordination Compounds

Multiple Choice Questions with ONE Correct Answer

1. Amongst $\text{Ni}(\text{CO})_4$, $[\text{Ni}(\text{CN})_4]^{2-}$ and NiCl_4^{2-}
 (a) $\text{Ni}(\text{CO})_4$ and NiCl_4^{2-} are diamagnetic $[\text{Ni}(\text{CN})_4]^{2-}$ is paramagnetic
 (b) NiCl_4^{2-} and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $\text{Ni}(\text{CO})_4$ is paramagnetic
 (c) $\text{Ni}(\text{CO})_4$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and NiCl_4^{2-} is paramagnetic.
 (d) $\text{Ni}(\text{CO})_4$ is diamagnetic and NiCl_4^{2-} and $[\text{Ni}(\text{CN})_4]^{2-}$ are paramagnetic. (1991)
2. Which compound is formed when excess of KCN is added to aqueous solution of copper sulphate?
 (a) $\text{Cu}(\text{CN})_2$ (b) $\text{K}_2[\text{Cu}(\text{CN})_4]$
 (c) $\text{K}[\text{Cu}(\text{CN})_2]$ (d) $\text{K}_3[\text{Cu}(\text{CN})_4]$ (1996)
3. Among the following, the compound that is both paramagnetic and coloured is
 (a) $\text{K}_2\text{Cr}_2\text{O}_7$ (b) $(\text{NH}_4)_2(\text{TiCl}_6)$
 (c) CoSO_4 (d) $\text{K}_3[\text{Cu}(\text{CN})_4]$ (1997)
4. Which of the following is an organometallic compound?
 (a) Lithium methoxide (b) Lithium acetate
 (c) Lithium dimethylamide (d) Methyl lithium. (1997)
5. The geometry of $\text{Ni}(\text{CO})_4$ and $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ are
 (a) both square planar
 (b) tetrahedral and square planar respectively
 (c) both tetrahedral
 (d) square planar and tetrahedral respectively (1999)
6. The complex ion which has no *d* electrons in the central metal atom is
 (a) $[\text{MnO}_4]^-$ (b) $[\text{Co}(\text{NH}_3)_6]^{3+}$
 (c) $[\text{Fe}(\text{CN})_6]^{3-}$ (d) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (2001)
7. The species having tetrahedral shape is
 (a) $[\text{PdCl}_4]^{2-}$ (b) $[\text{Ni}(\text{CN})_4]^{2-}$
 (c) $[\text{Pd}(\text{CN})_4]^{2-}$ (d) $[\text{NiCl}_4]^{2-}$ (2004)
8. The pair of the compounds in which both the metals are in the highest possible oxidation state is
 (a) $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$
 (b) CrO_2Cl_2 , MnO_4^-
 (c) TiO_3 , MnO_2
 (d) $[\text{Co}(\text{CN})_6]^{3-}$, MnO_3 (2004)
9. Which kind of isomerism is exhibited by octahedral $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}$?
 (a) Geometrical and Ionization
 (b) Geometrical and Optical
 (c) Optical and Ionization
 (d) Geometrical only (2005)
10. Among the following, the coloured compound is
 (a) CuCl (b) $\text{K}_3[\text{Cu}(\text{CN})_4]$
 (c) CuF_2 (d) $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (2008)
11. Both $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes, respectively, are
 (a) sp^3 , sp^3 (b) sp^3 , dsp^2
 (c) dsp^2 , sp^3 (d) dsp^2 , dsp^2 (2008)
12. The IUPAC name of $[\text{Ni}(\text{NH}_3)_4][\text{NiCl}_4]$ is
 (a) tetrachloronickel(II)-tetraamminenickel(II)
 (b) tetraamminenickel(II)-tetrachloronickel(II)
 (c) tetraamminenickel(II)-tetrachloronickelate(II)
 (d) tetrachloronickel(II)-tetraamminenickelate(0) (2008)
13. The ionization isomer of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$ is
 (a) $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$
 (b) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$
 (c) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$
 (d) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)]\cdot\text{H}_2\text{O}$ (2010)
14. The correct structure of ethylenediaminetetraacetic acid (EDTA) is
 (a) 
 (b) 



15. The complex showing a spin-only magnetic moment of 2.82 B.M. is

- (a) $\text{Ni}(\text{CO})_4$ (b) $[\text{NiCl}_4]^{2-}$
(c) $\text{Ni}(\text{PPh}_3)_4$ (d) $[\text{Ni}(\text{CN})_4]^{2-}$ (2010)

16. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^- , CN^- and H_2O , respectively, are

- (a) octahedral, tetrahedral and square planar
(b) tetrahedral, square planar and octahedral
(c) square planar, tetrahedral and octahedral
(d) octahedral, square planar and octahedral. (2011)

17. Among the following complexes (*K-P*),

- $\text{K}_3[\text{Fe}(\text{CN})_6]$ (*K*), $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (*L*),
 $\text{Na}_3[\text{Co}(\text{oxalate})_3]$ (*M*), $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (*N*),
 $\text{K}_2[\text{Pt}(\text{CN})_4]$ (*O*) and $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (*P*) the diamagnetic
(a) *K, L, M, N* (b) *K, M, O, P*
(c) *L, M, O, P* (d) *L, M, N, O* (2011)

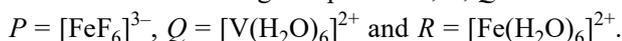
18. As per IUPAC nomenclature, the name of the complex $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$ is

- (a) tetraaquadiamminecobalt(III) chloride
(b) tetraaquadiamminecobalt(III) chloride
(c) diaminetetraaquacobalt(III) chloride
(d) diamminetetraaquacobalt(III) chloride (2012)

19. $\text{NiCl}_2\{\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively

- (a) tetrahedral and tetrahedral
(b) square planar and square planar
(c) tetrahedral and square planar
(d) square planar and tetrahedral (2012)

20. Consider the following complex ions, *P*, *Q* and *R*.



The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is

- (a) $R < Q < P$ (b) $Q < R < P$
(c) $R < P < Q$ (d) $Q < P < R$ (2013)

Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

21. In nitroprusside ion, the iron and NO exist as Fe^{II} and NO^+ rather than Fe^{III} and NO. These forms can be differentiated by

- (a) estimating the concentration of iron
(b) measuring the concentration of CN
(c) measuring the solid state magnetic moment
(d) thermally decomposing the compound (1998)

22. The compound(s) that exhibit(s) geometrical isomerism is(are)

- (a) $[\text{Pt}(\text{en})\text{Cl}_2]$ (b) $[\text{Pt}(\text{en})_2]\text{Cl}_2$
(c) $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$ (d) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. (2009)

23. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are)

- (a) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
(b) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ and $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$
(c) $[\text{CoBr}_2\text{Cl}_2]^{2-}$ and $[\text{PtBr}_2\text{Cl}_2]^{2-}$
(d) $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$ (2013)

Fill in the Blanks

24. AgCl dissolves in excess KCN solution to give the complex compound

(1980)

25. The IUPAC name of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is

(1994)

True / False

26. Both potassium ferrocyanide and potassium ferricyanide are diamagnetic.

(1989)

Subjective Problems

27. Identify the complexes which are expected to be coloured. Explain.

- (i) $[\text{Ti}(\text{NO}_3)_4]$ (ii) $[\text{Cu}(\text{NCCH}_3)_4]^+\text{BF}_4^-$
(iii) $[\text{Cr}(\text{NH}_3)_6]^{3+}3\text{Cl}^-$ (iv) $\text{K}_3[\text{VF}_6]$ (1994)

28. Write down the IUPAC names of the following compounds :

- (i) $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ (1995)
(ii) $\text{K}_3[\text{Cr}(\text{CN})_6]$ (1995)
(iii) $[\text{Cr}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$ (1996)

29. Write the IUPAC name of the compound $[\text{Cr}(\text{NH}_3)_5(\text{NCS})][\text{ZnCl}_4]$. Is this compound coloured? (1997)

30. Write the formulae of the following complexes:

- (i) Pentaamminechlorocobalt(III)
(ii) Lithium tetrahydroaluminate(III). (1997)

Coordination Compounds

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31. *A*, *B* and *C* are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ion as ligands. Complex *A* does not react with concentrated H_2SO_4 , whereas complexes *B* and *C* lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated H_2SO_4 . Identify *A*, *B* and *C*. (1999)
32. Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case. (2000)
33. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms (*A*) and (*B*). The form (*A*) reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (*B*) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (*A*) and (*B*) and state the hybridization of chromium in each. Calculate their magnetic moments (spin-only value). (2001)
34. Deduce the structure of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species. (2002)
35. Write the IUPAC nomenclature of the given complex along with its hybridisation and structure.
 $K_2[Cr(NO)(NH_3)(CN)_4]$, $\mu = 1.73$ BM (2003)
36. Nickel chloride, when treated with dimethylglyoxime in presence of ammonium hydroxide, a bright red precipitate is obtained. Answer the following.
 (a) Draw the structure of the complex showing H-bonds.
 (b) Give oxidation state of nickel and its hybridisation.
 (c) Predict the magnetic behaviour of the complex. (2004)
37. $Fe^{3+} \xrightarrow[\text{excess}]{SCN^-} (A) \xrightarrow[\text{excess}]{F^-} (B)$
 Blood red colouration Colourless
- What are (*A*) and (*B*)? Give IUPAC name of (*A*). Find the spin only magnetic moment of (*B*). (2005)

Matrix Match Type

38. Match the complexes in Column I with their properties listed in Column II.

Column I

- (A) $[Co(NH_3)_4(H_2O)_2]Cl_2$
 (B) $[Pt(NH_3)_2Cl_2]$
 (C) $[Co(H_2O)_5Cl]Cl$
 (D) $[Ni(H_2O)_6]Cl_2$

Column II

- (p) geometrical isomers
 (q) paramagnetic
 (r) diamagnetic
 (s) metal ion with +2 oxidation state

(2007)

39. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists.
 $\{en = H_2NCH_2CH_2NH_2$; atomic numbers :
 $Ti = 22$; $Cr = 24$; $Co = 27$; $Pt = 78\}$

List-I

- (P) $[Cr(NH_3)_4Cl_2]Cl$
 (Q) $[Ti(H_2O)_5Cl](NO_3)_2$
 (R) $[Pt(en)(NH_3)Cl]NO_3$
 (S) $[Co(NH_3)_4(NO_3)_2]NO_3$

List-II

1. Paramagnetic and exhibits ionisation isomerism
 2. Diamagnetic and exhibits *cis-trans* isomerism
 3. Paramagnetic and exhibits *cis-trans* isomerism
 4. Diamagnetic and exhibits ionisation isomerism

Code :

	P	Q	R	S
(a)	4	2	3	1
(b)	3	1	4	2
(c)	2	1	3	4
(d)	1	3	4	2

(2014)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

40. **Statement-1** : $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.
Statement-2 : The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons. (2008)

41. **Statement-1** : The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.
Statement-2 : Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry. (2008)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension - 1

The coordination number of Ni^{2+} is 4.
 $NiCl_2 + KCN$ (excess) $\rightarrow A$ (cyano complex)
 $A + \text{conc. HCl}$ (excess) $\rightarrow B$ (chloro complex)

42. The IUPAC name of *A* and *B* are
 (a) potassium tetracyanonickelate(II),
 potassium tetrachloronickelate(II)

- (b) tetracyanopotassiumnickelate(II),
tetrachloropotassiumnickelate(II)
(c) tetracyanonickel(II), tetrachloronickel(II)
(d) potassiumtetracyanonickel(II),
potassiumtetrachloronickel(II).

43. Predict the magnetic nature of *A* and *B*.

- (a) Both are diamagnetic
(b) *A* is diamagnetic and *B* is paramagnetic with one unpaired electron
(c) *A* is diamagnetic and *B* is paramagnetic with two unpaired electrons
(d) Both are paramagnetic.

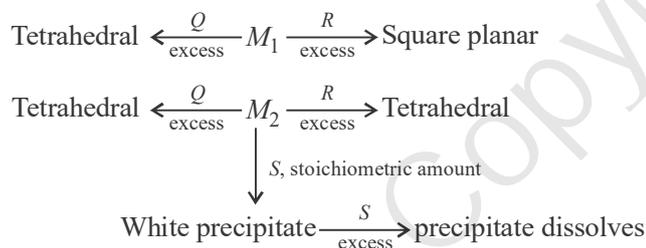
44. The hybridisation of *A* and *B* are

- (a) dsp^2 , sp^3 (b) sp^3 , sp^3
(c) dsp^2 , dsp^2 (d) sp^3d^2 , d^2sp^3 . (2006)

Comprehension-2

An aqueous solution of metal ion M_1 reacts separately with reagents *Q* and *R* in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion M_2 always forms tetrahedral complexes with these reagents. Aqueous solution of M_2 on reaction with reagent *S* gives white precipitate which dissolves in excess of *S*. The reactions are summarized in the scheme given below :

SCHEME :



45. M_1 , *Q* and *R*, respectively are

- (a) Zn^{2+} , KCN and HCl (b) Ni^{2+} , HCl and KCN
(c) Cd^{2+} , KCN and HCl (d) Co^{2+} , HCl and KCN

46. Reagent *S* is

- (a) $K_4[Fe(CN)_6]$ (b) Na_2HPO_4
(c) K_2CrO_4 (d) KOH (2014)

Integer Answer Type

47. The number of water molecule(s) directly bonded to the metal centre in $CuSO_4 \cdot 5H_2O$ is (2009)

48. Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is (2010)

49. $EDTA^{4-}$ is ethylenediaminetetraacetate ion. The total number of N—Co—O bond angles in $[Co(EDTA)]^{1-}$ complex ion is (2013)

50. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is [Atomic number of Fe = 26] (2015)

51. In the complex acetyl bromidodicarbonylbis(triethylphosphine)iron(II), the number of Fe—C bond(s) is (2015)

52. Among the complex ions, $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3-}$, $[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]^-$, $[Co(NH_2CH_2CH_2NH_2)_2(NH_3)Cl]^{2+}$ and $[Co(NH_3)_4(H_2O)Cl]^{2+}$, the number of complex ion(s) that show(s) *cis-trans* isomerism is (2015)

ANSWER KEY

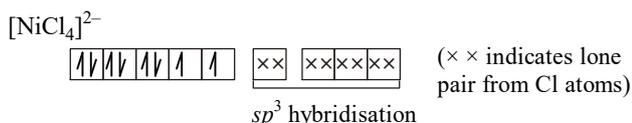
- | | | | | | |
|-------------------------------------|-----------|--|------------|------------|-------------------|
| 1. (c) | 2. (d) | 3. (c) | 4. (d) | 5. (c) | 6. (a) |
| 7. (d) | 8. (b) | 9. (a) | 10. (c) | 11. (b) | 12. (c) |
| 13. (b) | 14. (c) | 15. (b) | 16. (b) | 17. (c) | 18. (d) |
| 19. (c) | 20. (b) | 21. (c) | 22. (c, d) | 23. (b, d) | 24. $K[Ag(CN)_2]$ |
| 25. Hexaamminecobalt (III) chloride | 26. False | 38. (A) → p, q, s; (B) → p, r, s; (C) → q, s; (D) → q, s | 42. (a) | 43. (c) | 44. (a) |
| 39. (b) | 40. (a) | 41. (a) | 45. (b) | 46. (d) | 47. (4) |
| 45. (b) | 46. (d) | 47. (4) | 48. (3) | 49. (8) | 50. (4) |
| 51. (3) | 52. (6) | | | | |

Explanations

1. (c): The electronic configurations in various species are:
 $[\text{NiCl}_4]^{2-}$, the oxidation state of Ni is +2, i.e., Ni^{2+} .
 The electronic configuration of Ni^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$



In Ni^{2+} there are 2 unpaired electrons

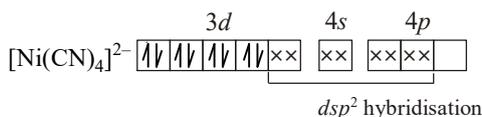


Because of presence of 2 unpaired electrons $[\text{NiCl}_4]^{2-}$ is paramagnetic.

In $[\text{Ni}(\text{CN})_4]^{2-}$ the O.S. of Ni is +2, i.e., Ni^{2+} (d^8)



In presence of CN^- ligand pairing of electrons take place and the hybridisation is dsp^2 .

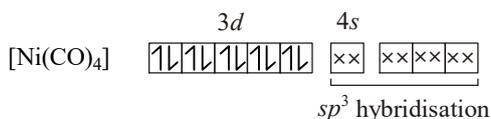


In $[\text{Ni}(\text{CN})_4]^{2-}$ there is no unpaired electrons so it is diamagnetic.

In $[\text{Ni}(\text{CO})_4]$, Ni is in zero state. Its configurations is



In $[\text{Ni}(\text{CO})_4]$, electrons get shifted from 4s to 3d and then sp^3 hybridisation occurs.



Since there are no unpaired electrons in $[\text{Ni}(\text{CO})_4]$, so it is diamagnetic.

So (c) is the correct answer.

2. (d): $\text{CuSO}_4 + 2\text{KCN} \rightarrow \text{Cu}(\text{CN})_2 + \text{K}_2\text{SO}_4$
 $2\text{Cu}(\text{CN})_2 \rightarrow \text{Cu}_2(\text{CN})_2 + \text{C}_2\text{N}_2$ (Cyanogen)
 $\text{Cu}_2(\text{CN})_2 + 6\text{KCN} \rightarrow 2\text{K}_3[\text{Cu}(\text{CN})_4]$
3. (c): In $(\text{NH}_4)_2\text{TiCl}_6$, the O.S. of Ti is +4, i.e., Ti^{4+} . The configuration of Ti^{4+} is $3d^0 4s^0$, i.e., it has no unpaired electron, hence it is diamagnetic and colourless (because of absence of d -electrons).
 In $\text{K}_2\text{Cr}_2\text{O}_7$, O.S. of Cr is +6 i.e. Cr^{6+} , the electronic configuration of Cr^{6+} is $(3d^0 4s^0)$ i.e. it has no unpaired

electron. Thus it is diamagnetic and colourless (absence of d -electrons).

In $\text{Co}(\text{SO}_4)$, the O.S. of Co is +2 i.e. Co^{2+} . Its configuration is $3d^7$ i.e. it has unpaired electrons in $3d$ -orbitals, so it is paramagnetic. Because of incompletely filled d -orbitals it is coloured, i.e. (c) is correct answer.

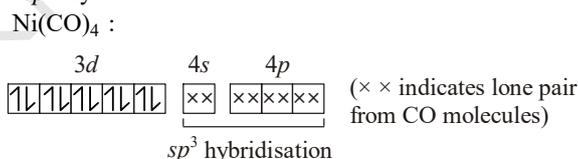
In $\text{K}_3[\text{Cu}(\text{CN})_4]$, the O.S. of Cu is +1, i.e., Cu^+ . Its configuration is $3d^{10} 4s^0$. It has no unpaired electron so it is diamagnetic.

4. (d): Those compounds in which metal atom is directly bonded to carbon atom are called organometallic compounds.

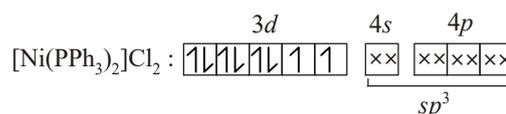
5. (c): In $\text{Ni}(\text{CO})_4$, oxidation state of Ni is zero. Its configuration is $3d^8 4s^2$.



In $\text{Ni}(\text{CO})_4$, the unpaired electrons in $3d$ and $4s$ pair up and $3d$ orbitals are filled up and there is no electron in $4s$ -orbital. Then sp^3 hybridisation occurs.

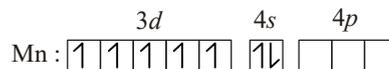


In $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$, O.S. of Ni is +2, i.e., Ni^{2+} so its electronic configuration is $3d^8$ with 2 unpaired electrons PPh_3 cannot pair up electrons in $3d$ -orbitals, thus in $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$, sp^3 hybridisation occurs.

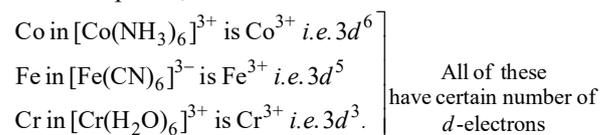


Because of sp^3 hybridization, it is tetrahedral.

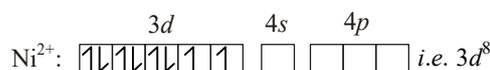
6. (a): In MnO_4^- , the O.S. of Mn is +7 i.e. Mn^{7+} .



In other species, we have



7. (d): The electronic configuration of Ni^{2+} present in $[\text{NiCl}_4]^{2-}$ is



With Ni, Cl^- behaves as a weak field/high spin ligand. Due to this no pairing of electrons takes place and sp^3 hybridisation is involved in the formation of $[\text{NiCl}_4]^{2-}$. Because of sp^3 hybridisation its shape is tetrahedral.

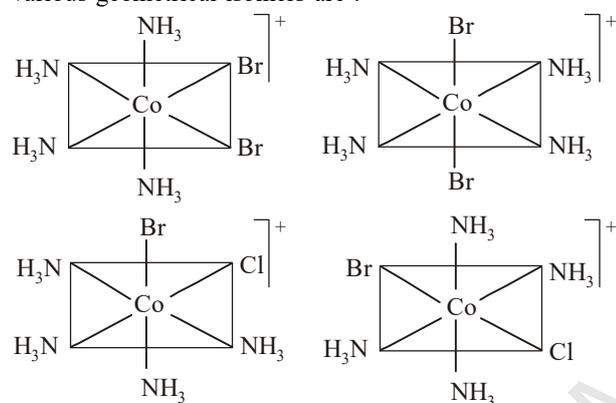
8. (b): The oxidation states of various metals :

- (a) Fe = +3, Co = +3
 (b) Cr = +6, Mn = +7
 (c) Ti = +6, Mn = +4
 (d) Co = +3, Mn = +6

Thus we find that in (b) both Cr and Mn are in their highest oxidation states of +6 and +7 respectively.

9. (a): $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}$ will show both geometrical isomerism and ionisation isomerism.

Ionisation isomers : $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}$ and $[\text{Co}(\text{NH}_3)_4\text{BrCl}]\text{Br}$. Various geometrical isomers are :

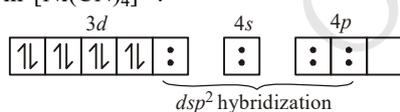


10. (c) : Most of the cuprous compounds are colourless and diamagnetic as $3d$ -shell is completely filled.

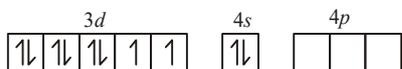
Cupric compounds like CuF_2 contains Cu^{2+} , having d^9 configuration therefore coloured due to $d-d$ transition.

11. (b) : In $[\text{Ni}(\text{CN})_4]^{2-}$, CN^- is strong field ligand.

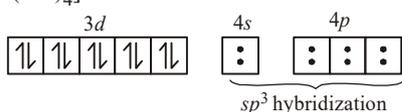
Ni^{2+} in $[\text{Ni}(\text{CN})_4]^{2-}$:



$\therefore [\text{Ni}(\text{CN})_4]^{2-}$ is a square planar complex.
 In $[\text{Ni}(\text{CO})_4]$, CO is strong field ligand.



Ni in $[\text{Ni}(\text{CO})_4]$:



It is a tetrahedral complex.

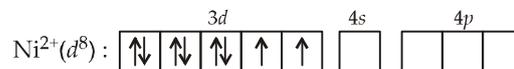
12. (c) : The given complex shows co-ordination isomerism. The IUPAC name of the complex is tetraamminenickel(II) - tetrachloronickelate(II).

13. (b) : Ionization isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

Thus option (b), i.e., $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$ is the ionization isomer of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$.

14. (c)

15. (b) : In $[\text{NiCl}_4]^{2-}$, nickel is in +2 oxidation state.



Since chlorine is a weak field ligand, it does not cause pairing of electrons in the $3d$ orbital and hence Ni^{2+} undergoes sp^3 hybridisation.

$\therefore n = \text{no. of unpaired } e^- = 2$

$$\Rightarrow \mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.82 \text{ BM.}$$

16. (b) : $\text{Ni}^{2+} + \text{Cl}^- \longrightarrow [\text{Ni}(\text{Cl})_4]^{2-}$

tetrahedral due to sp^3 hybridisation

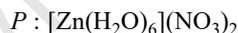


due to dsp^2 hybridisation, it is square planar.



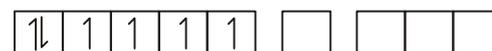
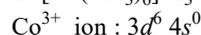
due to sp^3d^2 hybridisation, it is octahedral.

17. (c) : Following compounds are diamagnetic.

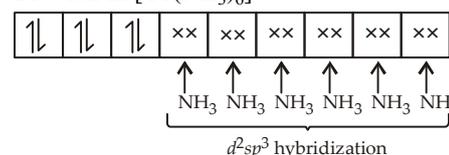


(i) In $\text{K}_3[\text{Fe}(\text{CN})_6]$ the Fe^{3+} is d^2sp^3 hybridised and it has one unpaired electron. It is paramagnetic.

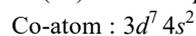
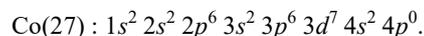
(ii) In $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ Co^{3+} is d^2sp^3 hybridised.



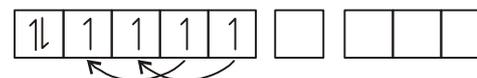
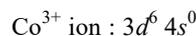
Co^{3+} ion in $[\text{Co}(\text{NH}_3)_6]^{3+}$



(iii) $[\text{Co}(\text{ox})_3]^{3-}$: Tris(oxalato)cobalt(III) ion : In this complex oxidation state of cobalt is +3.

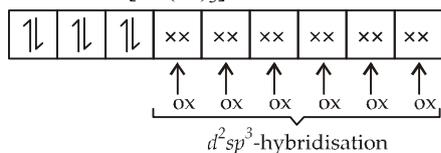


According to magnetic study this ion complex is diamagnetic in nature. In the formation of this ion two electrons of two e_g set of $3d$ orbitals pair up with the three electrons of t_{2g} set of orbitals. Resultant e_g set of orbitals become vacant and are used in hybridisation.



Coordination Compounds

205

Co³⁺ ion in [Co(ox)₃]³⁻

It is inner orbital octahedral complex, diamagnetic in nature as all the electrons are paired.

(iv) In octahedral complex [Ni(H₂O)₆]Cl₂, Ni²⁺ is paramagnetic.

(v) K₂[Pt(CN)₄]

[Pt(CN)₄]²⁻: In this complex oxidation state of Pt is +2.

Pt (78): 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p⁶ 4d¹⁰ 4f¹⁴ 5s² 5p⁶ 5d⁹ 6s¹ 6p⁰

Pt-atom: 5d⁹ 6s¹, Pt²⁺: 6s⁰ 5d⁸

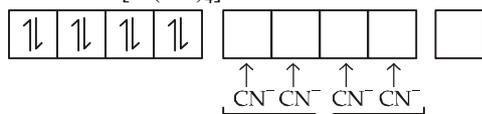


CN⁻ being strong ligand causes pairing and so it is inner orbital and low spin complex.

Pt²⁺ ion: 5d⁸ 6s⁰



Pt²⁺ ion in [Pt(CN)₄]²⁻



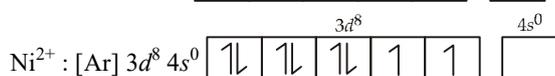
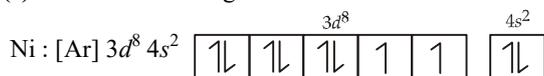
dsp^2 hybridisation:
Square planar geometry
of [Pt(CN)₄]²⁻ ion

Geometry is square planar and complex is diamagnetic as all the electrons are paired.

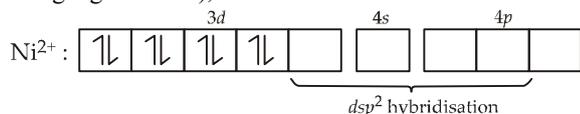
(vi) Octahedral and tetrahedral complex of Zn²⁺ are diamagnetic.

18. (d) : Diamminetetraaquacobalt(III) chloride

19. (c) : Electronic configuration of



Paramagnetic behaviour is possible when pairing does not take place. *i.e.*, 3d will not participate in bonding and hybridisation will be sp^3 including 4s and 4p, thus structure is tetrahedral. When pairing takes places (in presence of strong ligand field),

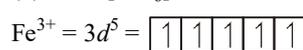


dsp^2 hybrid orbitals arrange in square planar structure.

Ni²⁺: paramagnetic, sp^3 , tetrahedral

Ni²⁺: diamagnetic, dsp^2 , square planar

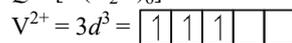
20. (b): $P = [FeF_6]^{3-}$



No. of unpaired electrons = 5

$$\begin{aligned} \text{Magnetic moment } (\mu) &= \sqrt{n(n+2)} \text{ B.M.} \\ &= \sqrt{5(5+2)} \text{ B.M.} = \sqrt{35} \\ &= 5.92 \text{ B.M.} \end{aligned}$$

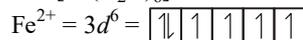
$Q = [V(H_2O)_6]^{2+}$



No. of unpaired electrons = 3

$$\begin{aligned} \text{Magnetic moment } (\mu) &= \sqrt{3(3+2)} \text{ B.M.} \\ &= \sqrt{15} = 3.87 \text{ B.M.} \end{aligned}$$

$R = [Fe(H_2O)_6]^{2+}$



No. of unpaired electrons = 4

$$\begin{aligned} \text{Magnetic moment } (\mu) &= \sqrt{4(4+2)} \text{ B.M.} \\ &= \sqrt{24} = 4.90 \text{ B.M.} \end{aligned}$$

The correct order of spin-only magnetic moment values is $Q < R < P$.

21. (c) : Magnetic moment μ is given by $\mu = \sqrt{n(n+2)}$ B.M.

Where n is the number of unpaired electrons.

Number of unpaired electrons in various species are

Fe^{2+} : It is $3d^6$ *i.e.* 4 unpaired electrons

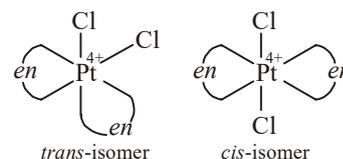
Fe^{3+} : It is $3d^5$ *i.e.* 5 unpaired electrons

^+NO or $^+N \equiv \ddot{O}:$, in this all the electrons are paired.

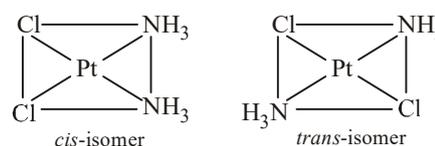
NO or $\ddot{x}N \equiv \ddot{O}:$, we have a three electron bond so it has an odd (unpaired electron). *i.e.* $n = 1$

Since they (*i.e.* ^+NO and NO) have different number of unpaired electrons so they can be differentiated by the measurement of the solid state magnetic moment of nitroprusside ion.

22. (c, d) : Octahedral complexes having symmetrical bidentate ligand, of the type $M(AA)_2X_2$ like $[Pt(en)_2Cl_2]^{2+}$ exhibit geometrical isomerism.



Square planar complexes of the type MA_2X_2 also exhibit geometrical isomerism.



23. (b,d) : Complex ions $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$ both will show geometrical isomerism. $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$ both will show ionisation isomerism.

24. $K[Ag(CN)_2]$

25. Hexaamminecobalt (III) chloride

26. False

Octahedral complexes of Fe(III) (like $[\text{Fe}(\text{CN})_6]^{3-}$) are low spin (d^2sp^3 hybridisation) with one unpaired electron so their magnetic moment is about 1.9 B.M. The complexes of Fe (like $[\text{Fe}(\text{CN})_6]^{2-}$) are low spin complexes (d^2sp^3 hybridisation) and has no unpaired electrons so they are diamagnetic.

27. The electronic configurations are

$[\text{Ti}(\text{NO}_3)_4]$; In it Ti is Ti^{4+} with configuration $3d^0 4s^0$
 $[\text{Cu}(\text{NCCH}_3)_4]^+[\text{BF}_4]^-$; In it the O.S. of Cu is +1 i.e. Cu^+
 The electronic configuration of Cu^+ is $3d^{10} 4s^0$.

In $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$, Cr is in Cr^{3+} with configuration $3d^3 4s^0$
 In $\text{K}_3[\text{VF}_6]$, V is in +3 state or V^{3+} with configuration $3d^2 4s^0$.
 Of the given complexes only two i.e. $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$ and $\text{K}_3[\text{VF}_6]$ have incompletely filled d -orbitals and so they are coloured (due to $d-d$ transitions).

28. (i) Pentaamminenitritocobalt(III) chloride
 (ii) Potassium hexacyanochromate(III)
 (iii) Pentaamminecarbonatochromium(III) chloride

29. Pentaammineisothiocyanatochromium(III) tetrachlorozincate.
 In this compound the oxidation state of Cr is +3 i.e. Cr^{3+} with configuration $3d^3$. Because of incompletely filled d -orbitals this complex will be coloured. ($d-d$ transitions can occur).

30. (i) $[\text{CoCl}(\text{NH}_3)_5]^{2+}$
 (ii) LiAlH_4

31. Since there is no action of concentrated H_2SO_4 on compound A so it can be assumed that all molecules of water in A are coordinated with Cr^{3+} ion. Its structure would be $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$.

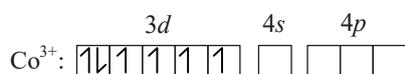
Compound B loses 6.75% of its original mass on being treated with concentrated H_2SO_4 . The loss in mass is due to removal of water molecules that are not directly coordinate to Cr^{3+} ion. From this we can calculate the mass of water molecules removed per mole of the complex B

$$\text{Mass of water lost from } B \text{ per mole} = \frac{6.75}{100} \times 266.5 \text{ g} \\ = 17.98 \text{ g} \quad [\text{Molar mass} = 266.5]$$

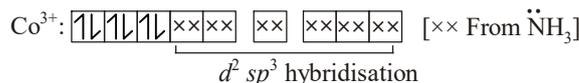
This loss of mass corresponds to loss of 1 molecule of water. Therefore the structure of complex B is $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}](\text{H}_2\text{O})\text{Cl}_2$.

In compound C the mass lost is 13.5%, when C is treated with concentrated H_2SO_4 . The loss in mass is 2 times ($2 \times 6.75 = 13.5$) the loss in mass in case of B . This loss corresponds to 2 molecules of water. So the structure of C is $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{H}_2\text{O})_2\text{Cl}$.

32. $[\text{Co}(\text{NH}_3)_6]^{3+}$: The O.S. of Co is +3 i.e. Co^{3+} i.e. $3d^6 4s^0$

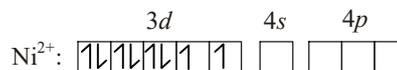


In presence of NH_3 , maximum pairing occurs.

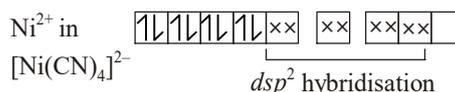


So $[\text{Co}(\text{NH}_3)_6]^{3+}$ is octahedral ($d^2 sp^3$ hybridisation).

$[\text{Ni}(\text{CN})_4]^{2-}$: The O.S. of Ni is +2 i.e. Ni^{2+} ($3d^8$).

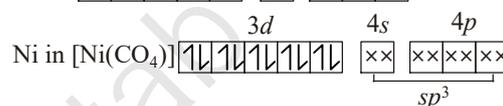
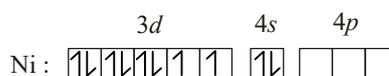


In presence of CN^- the maximum possible pairing occurs.

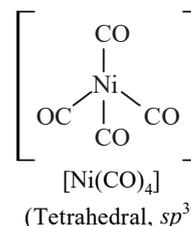
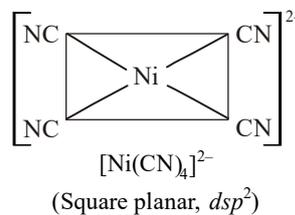
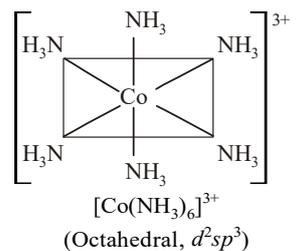


In $[\text{Ni}(\text{CN})_4]^{2-}$, $d^2 sp^2$ hybridisation occurs so it is square planar.

In $[\text{Ni}(\text{CO})_4]$, Ni is in zero state i.e. $3d^8 4s^2$.



In it sp^3 hybridisation occurs, so it is tetrahedral.

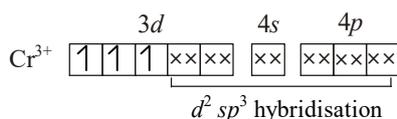


33. Since A when treated with AgNO_3 forms a white ppt (of AgCl) which is readily soluble in dil. $\text{NH}_3(aq)$ so A has at least one Cl^- ion (ionisable chlorine atom). Moreover since the coordination number of chromium is 6 so the formula of the compound is $[\text{Cr}(\text{NH}_3)_4\text{BrCl}]\text{Cl}$.

Since compound B when treated with AgNO_3 forms a pale yellow ppt (of AgBr) soluble in concentrated $\text{NH}_3(aq)$ so B has a Br^- (ionisable bromine atom) in the ionisation sphere. So the formula of B is $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$. Cr in both A and B is in +3 state i.e. Cr^{3+} .

Coordination Compounds

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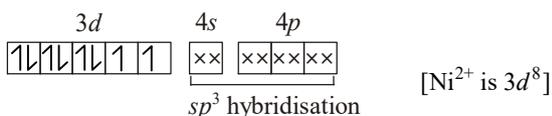
In both cases $d^2 sp^3$ hybridisation occurs

Spin magnetic moment of A or B :

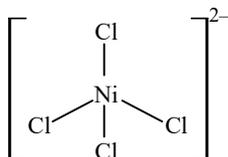
In both cases $n = 3$ ($n =$ number of unpaired electrons)

$$\begin{aligned} \therefore \text{spin magnetic moment} &= \sqrt{n(n+2)} \\ &= \sqrt{3(3+2)} = \sqrt{3 \times 5} \\ &= \sqrt{15} \text{ or } 3.87 \text{ BM} \end{aligned}$$

34. Cl^- is a weak field ligand and so it is not in a position to pair the electrons in Ni^{2+} , so in $[\text{NiCl}_4]^{2-}$ we have

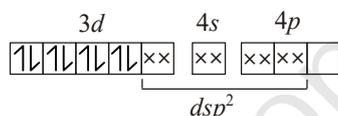


Because of sp^3 hybridisation, it is tetrahedral.

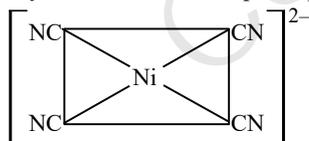


$$\begin{aligned} \text{Magnetic moment of } [\text{NiCl}_4]^{2-} &= \sqrt{2(2+2)} \quad [\because n=2] \\ &= \sqrt{2 \times 4} = \sqrt{8} \text{ or } 2.83 \text{ BM.} \end{aligned}$$

In $[\text{Ni}(\text{CN})_4]^{2-}$, CN^- is a strong field ligand and in this case pairing of electrons occurs in Ni^{2+} .



Because of dsp^2 hybridisation it is square planar.



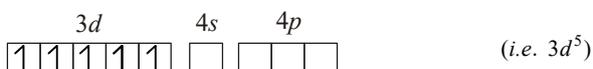
$$\begin{aligned} \text{Magnetic moment of } [\text{Ni}(\text{CN})_4]^{2-} &= \sqrt{0(0+2)} \quad [\because n=0] \\ &= 0.0 \text{ BM.} \end{aligned}$$

35. The spin magnetic moment (m) of complex = 1.73 BM
Using spin magnetic moment = $\sqrt{n(n+2)}$, we get
 $\sqrt{n(n+2)} = 1.73$ or $n \approx 1$

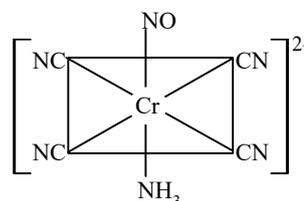
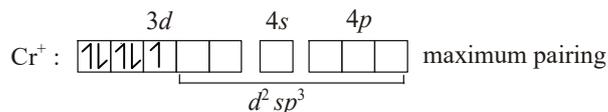
This indicates that in nucleus of the complex, chromium has one unpaired electron. Thus the ligand NO is unipositively charged.

IUPAC name : Potassium amminetetracyanonitrosonium chromate(I).

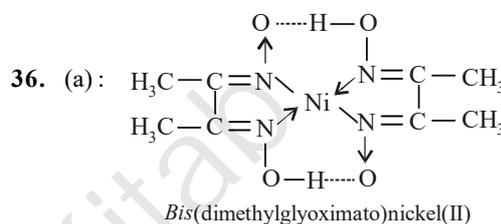
- (a) Electronic configuration of Cr^{3+} :



- (b) **Electronic configuration of Cr^{3+} under the influence of strong field CN^- :**



Hybridisation = $d^2 sp^3$
Shape = Octahedral.



- (b) Charge on Ni in the complex is +2. Hybridisation involved is dsp^2 .
(c) Since, in Ni^{2+} , there is no unpaired electron, so the complex is diamagnetic.
37. (A) = $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$; (B) = $[\text{FeF}_6]^{3-}$
IUPAC name of A is : pentaquathiocyanatoferrate (III) ion
Spin magnetic moment of (B) = $\sqrt{n(n+2)} = \sqrt{5(5+2)}$
 $= \sqrt{5 \times 7}$ or 5.92 BM. [$\because n = 5$ in Fe^{3+}]

38. (A) \rightarrow p, q, s; (B) \rightarrow p, r, s; (C) \rightarrow q, s; (D) \rightarrow q, s
In all the complexes, the oxidation state of central metal ion is +2. Any complex with molecular formula MA_2B_2 shows geometrical isomerism. Moreover, valence shell electron configuration of Co^{2+} in $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$, $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$ and Ni^{2+} in $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (all are attached to weak field ligands) suggest that there are unpaired electrons (paramagnetic) whereas Pt^{2+} do not have any unpaired electrons, hence, it is diamagnetic.

39. (b) : P : Cr^{3+} has $3d^3$ configuration, with 3 unpaired electrons. Hence, it shows paramagnetic behaviour. Complex of the type Ma_4b_2 shows *cis-trans* isomerism.

Q : Ti^{3+} has $3d^1$ configuration, hence shows paramagnetic behaviour. Complex gives Cl^- and NO_3^- ions in solution hence, shows ionisation isomerism.

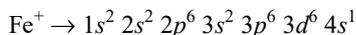
R : Pt^{2+} has $3d^8$ configuration but ligands are strong field ligands hence, it forms square planar complex. Thus, all electrons are paired and it also exhibits ionisation isomerism.

S : Co^{3+} has $3d^6$ configuration. But, ligands present are strong enough to cause electron pairing, hence, it shows diamagnetic behaviour and exhibits *cis-trans* isomerism as it is Ma_4b_2 type complex.

40. (a) : In compound $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ oxidation state of Fe is
 $x + 5 \times 0 + 1 = +2$

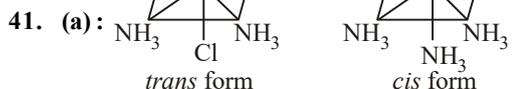
$$\therefore x = +1$$

Here Fe has +1 oxidation state



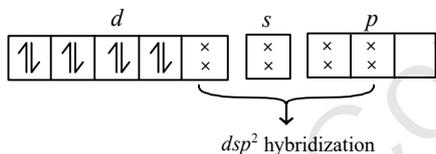
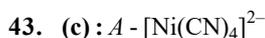
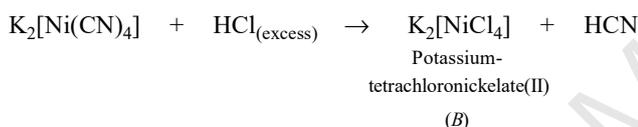
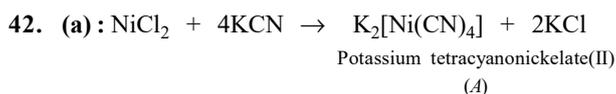
Due to strong field ligand one electron shifted from 4s to 3d thus showing d^7 configuration.

Fe^+

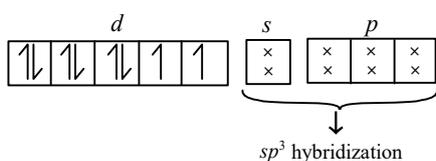


Octahedral complexes of the type Ma_4b_2 exhibit geometrical isomerism.

Geometrical isomer of the complex $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$ are optically inactive. Axis of symmetry causes optical inactivity.

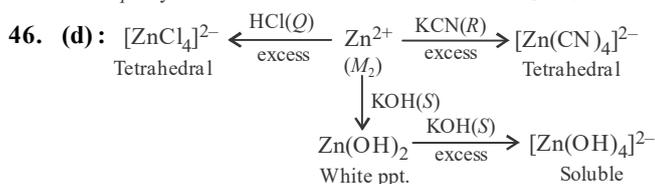
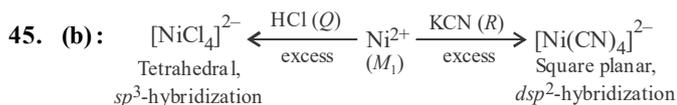


Diamagnetic (no unpaired electrons)



Paramagnetic (due to presence of 2 unpaired electrons).

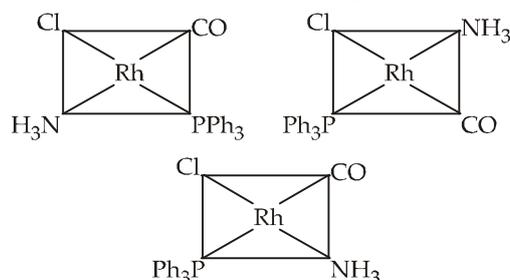
44. (a)



47. (4) : Hydrated copper sulphate or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue in colour and this colour is attributed to the presence of hydrated $\text{Cu}(\text{II})$ ion, i.e., $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$. Thus the number of water molecules directly attached to Cu^{2+} or present within the coordination sphere are 4.

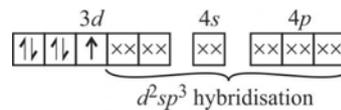
$\therefore \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ can be written as $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$.

48. (3) : The complex $[\text{Rh}(\text{Cl})(\text{CO})(\text{PPh}_3)(\text{NH}_3)]$ is of the type $[\text{M}(a)(b)(c)(d)]$, and thus shows three geometrical isomers.



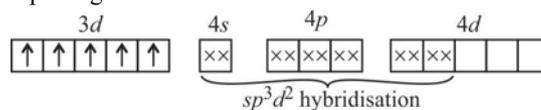
50. (4) : Fe (26) : $3d^6 4s^2$
 $\text{Fe}^{3+} : 3d^5$

In $[\text{Fe}(\text{CN})_6]^{3-}$, CN^- is a strong field ligand which causes pairing of electrons.



$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.732 \text{ BM}$$

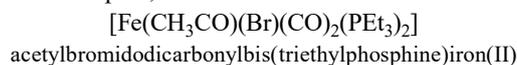
In $[\text{Fe}(\text{SCN})_6]^{3-}$, SCN^- being a weak field ligand does not cause pairing of electrons.



$$\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.916 \text{ BM}$$

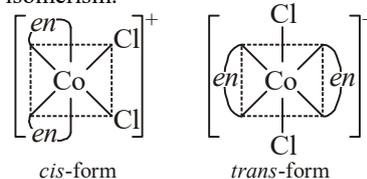
$$\text{Difference} = 5.916 - 1.732 = 4.184 \approx 4 \text{ BM}$$

51. (3) : In the complex,



There are two $M \leftarrow \text{CO}$ bonds and one $M \leftarrow \text{C}=\text{O}-\text{CH}_3$ bond (where $M = \text{Fe}$).

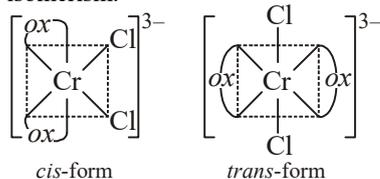
52. (6) : $[\text{Co}(\text{en})_2\text{Cl}_2]^+ - [\text{M}(\text{AA})_2\text{B}_2]$ type complex, shows geometrical isomerism.



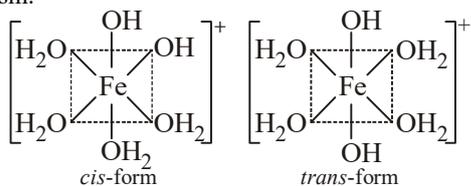
Coordination Compounds

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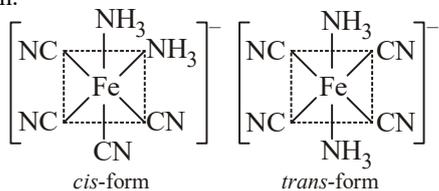
$[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$ – $[\text{M}(\text{AA})_2\text{B}_2]$ type complex, shows geometrical isomerism.



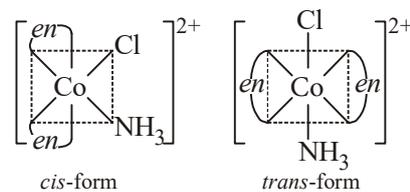
$[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ – $[\text{M}\text{A}_4\text{B}_2]$ type complex, shows geometrical isomerism.



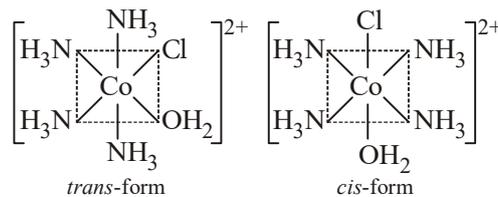
$[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$ – $[\text{M}\text{A}_4\text{B}_2]$ type complex, shows geometrical isomerism.



$[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ – $[\text{M}(\text{AA})_2\text{BC}]$ type complex, shows geometrical isomerism.



$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ – $[\text{M}\text{A}_4\text{BC}]$ type complex, shows geometrical isomerism.



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Analytical Chemistry

Multiple Choice Questions with ONE Correct Answer

- 27 g of Al will react completely with how many gram of oxygen?
(a) 8 g (b) 16 g (c) 32 g (d) 24 g
(1978)
- The reddish-brown coloured gas formed when nitric oxide is oxidised by air is
(a) N_2O_5 (b) N_2O_4 (c) NO_2 (d) N_2O_3
(1979)
- The ion that cannot be precipitated by both HCl and H_2S is
(a) Pb^{2+} (b) Cu^+ (c) Ag^+ (d) Sn^{2+}
(1982)
- Which one among the following pairs of ions cannot be separated by H_2S in dilute hydrochloric acid?
(a) Bi^{3+} , Sn^{4+} (b) Al^{3+} , Hg^{2+}
(c) Zn^{2+} , Cu^{2+} (d) Ni^{2+} , Cu^{2+}
(1986)
- An aqueous solution contains Hg_2^{2+} , Hg_2^{2+} , Pb^{2+} and Cd^{2+} . The addition of HCl of (6 N) will precipitate
(a) Hg_2Cl_2 only (b) PbCl_2 only
(c) PbCl_2 and Hg_2Cl_2 (d) PbCl_2 and HgCl_2
(1995)
- The only cations present in a slightly acidic solution are Fe^{3+} , Zn^{2+} and Cu^{2+} . The reagent that when added in excess to this solution would identify the separate Fe^{3+} in one step is
(a) 2 M HCl (b) 6 M NH_3
(c) 6 M NaOH (d) H_2S gas (1997)
- Identify the correct order of solubility of Na_2S , CuS and ZnS in aqueous medium.
(a) $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$ (b) $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$
(c) $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$ (d) $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$
(2002)
- An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a
(a) Hg_2^{2+} salt (b) Cu^{2+} salt
(c) Ag^+ salt (d) Pb^{2+} salt (2002)
- A gas X is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of colourless gas Y. Identify X and Y.
(a) $X = \text{CO}_2$, $Y = \text{Cl}_2$ (b) $X = \text{Cl}_2$, $Y = \text{CO}_2$
(c) $X = \text{Cl}_2$, $Y = \text{H}_2$ (d) $X = \text{H}_2$, $Y = \text{Cl}_2$
(2003)
- $[X] + \text{H}_2\text{SO}_4 \longrightarrow [Y]$ a colourless gas with irritating smell, $[Y] + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \longrightarrow$ green solution. [X] and [Y] are
(a) SO_3^{2-} , SO_2 (b) Cl^- , HCl
(c) S^{2-} , H_2S (d) CO_3^{2-} , CO_2 (2003)
- A solution which is 10^{-3} M each in Mn^{2+} , Fe^{2+} , Zn^{2+} is treated with 10^{-6} M sulphide ion. If K_{sp} of MnS , FeS , ZnS and HgS are 10^{-15} , 10^{-23} , 10^{-20} and 10^{-54} respectively, which one will precipitate first?
(a) FeS (b) MgS (c) HgS (d) ZnS
(2003)
- A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI is converted into orange colour solution. The cation of the metal nitrate is
(a) Hg^{2+} (b) Bi^{3+} (c) Pb^{2+} (d) Cu^{2+}
(2005)
- A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt(II) thiocyanate gives rise to deep blue crystalline precipitate. The metal ion is
(a) Pb^{2+} (b) Hg^{2+} (c) Cu^{2+} (d) Co^{2+} .
(2007)

Analytical Chemistry

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14. Passing H_2S gas into a mixture of Mn^{2+} , Ni^{2+} , Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates
- (a) CuS and HgS (b) MnS and CuS
 (c) MnS and NiS (d) NiS and HgS (2011)

15. Upon treatment with ammoniacal H_2S , the metal ion that precipitates as a sulfide is
- (a) Fe(III) (b) Al(III)
 (c) Mg(II) (d) Zn(II) (2013)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

16. The reagents, NH_4Cl and aqueous NH_3 will precipitate
- (a) Ca^{2+} (b) Al^{3+} (c) Bi^{3+} (d) Mg^{2+} (1991)

17. Which of the following statements(s) is (are) correct when a mixture of NaCl and $\text{K}_2\text{Cr}_2\text{O}_7$ is gently warmed with concentrated H_2SO_4 ?
- (a) A deep red vapour is evolved.
 (b) The vapours when passed into NaOH solution gives a yellow solution of Na_2CrO_4 .
 (c) Chlorine gas is evolved.
 (d) Chromyl chloride is formed. (1998)

18. Which of the following statements(s) is (are) correct with reference to the ferrous and ferric ions?
- (a) Fe^{3+} gives brown colour with potassium ferricyanide.
 (b) Fe^{2+} gives blue precipitate with potassium ferricyanide.
 (c) Fe^{3+} gives red colour with potassium thiocyanate.
 (d) Fe^{2+} gives brown colour with ammonium thiocyanate. (1998)

19. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are)
- (a) NH_4NO_3 (b) NH_4NO_2
 (c) NH_4Cl (d) $(\text{NH}_4)_2\text{SO}_4$ (2008)

20. The equilibrium $2\text{CuI} \rightleftharpoons \text{Cu}^0 + \text{Cu}^{\text{II}}$ in aqueous medium at 25°C shifts towards the left in the presence of
- (a) NO_3^- (b) Cl^-
 (c) SCN^- (d) CN^- (2011)

21. The pair(s) of ions where BOTH the ions are precipitated upon passing H_2S gas in presence of dilute HCl , is(are)

- (a) Ba^{2+} , Zn^{2+} (b) Bi^{3+} , Fe^{3+}
 (c) Cu^{2+} , Pb^{2+} (d) Hg^{2+} , Bi^{3+}

(2015)

Fill in the Blanks

22. If metal ions of group III are precipitated by NH_4Cl and NH_4OH without prior oxidation by concentrated HNO_3 is not completely precipitated. (1984)
23. The formula of the deep red vapours formed on warming dichromate with KCl in concentrated sulphuric acid is (1993)

True / False

24. Addition of ammonium chloride to a solution containing ferric and magnesium ions is essential for selective precipitation of ferric hydroxide by aqueous ammonia. (1985)
25. From the solution containing copper (+2) and zinc (+2) ions, copper can be selectively precipitated using sodium sulphide. (1987)

Subjective Problems

26. Igniting MnO_2 converts it quantitatively to Mn_3O_4 . A sample of pyrolusite is of the following composition : MnO_2 80%, SiO_2 and other inert constituents 15%, rest being water. The sample is ignited in air to constant weight. What is the percentage of Mn in the ignited sample? [$\text{O} = 16$, $\text{Mn} = 54.9$]. (1978)
27. One gram of an alloy containing aluminium and magnesium when treated with excess of dil. HCl forms magnesium chloride, aluminium chloride and hydrogen. The evolved hydrogen, collected over mercury at 0°C has a volume of 1.20 litres at 0.92 atm pressure. Calculate the composition of the alloy. [$\text{H} = 1$, $\text{Mg} = 24$, $\text{Al} = 27$] (1978)
28. The precipitation of second group sulphides in qualitative analysis is carried out with hydrogen sulphide in presence of hydrochloric acid and not nitric acid. Explain. (1979)
29. Explain the following in not more than two sentences. A solution of FeCl_3 in water gives a brown precipitate on standing. (1980)
30. A mixture contains NaCl and an unknown chloride $M\text{Cl}$. (i) 1 gm of this is dissolved in water. Excess of acidified AgNO_3 solution is added to it. 2.567 g of a white precipitate

- is formed. (ii) 1 gm of the original mixture is heated to 300°C. Some vapours come out which are absorbed in acidified AgNO_3 solution. 1.341 gm a white precipitate is obtained. Find the molecular weight of the unknown chloride. (1980)
31. When 16.8 g of white solid X were heated, 4.4 g of acid gas A that turned lime water milky was driven off together with 1.8 g of a gas B which condensed to a colourless liquid. The solid that remained, Y , dissolved in water to give an alkaline solution, which with excess barium chloride solution gave a white precipitate Z . The precipitate effervesced with acid giving off carbon dioxide. Identify A , B and Y and write down the equation for the thermal decomposition of X . (1984)
32. A mixture of two salts was treated as follows:
- The mixture was heated with manganese dioxide and concentrated sulphuric acid when yellowish green gas was liberated.
 - The mixture on heating with sodium hydroxide solution gave a gas which turned red litmus blue.
 - Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with ammonium thiocyanate.
 - The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K_2HgI_4 to give brown precipitate.
- Identify the two salts. Give ionic equations for reactions involved in the tests (i), (ii), (iii). (1987)
33. A hydrated metallic salt A , light green in colour, on careful heating gives a white anhydrous residue B . B is soluble in water and its aqueous solution reacts with NO to give a dark brown compound C . B on strong heating gives a brown residue D and a mixture of two gases E and F . The gaseous mixture when passed through acidified permanganate, discharges the pink colour and when passed through acidified BaCl_2 solution gave a white precipitate. Identify A , B , C , D , E and F . (1988)
34. When 20.02 g of a white solid X is heated 4.4 g of an acid gas A and 1.8 g of a neutral gas B are evolved, leaving behind a solid residue Y of weight 13.8 g. A turns lime water milky and B condenses into a liquid which changes anhydrous copper sulphate blue. The aqueous solution of Y is alkaline to litmus and gives 19.7 g of white precipitate Z with barium chloride solution. Z gives carbon dioxide with an acid. Identify A , B , X , Y and Z . (1989)
35. The gas liberated on heating a mixture of two salts with NaOH , gives a reddish brown precipitate with an alkaline solution of K_2HgI_4 . The aqueous solution of the mixture on treatment with BaCl_2 gives a white precipitate which is sparingly soluble in concentrated HCl . On heating the mixture with $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 , red vapours of A are produced. The aqueous solution of the mixture gives a deep blue colouration B with potassium ferricyanide solution. Identify the radicals in the given mixture and write the balanced equations for the formation of A and B . (1991)
36. A light bluish green crystalline compound responds to the following tests:
- Its aqueous solution gives a brown precipitate or colour with alkaline $\text{K}_2[\text{HgI}_4]$ solution.
 - Its aqueous solution gives a blue colour with $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution.
 - Its solution in hydrochloric acid gives a white precipitate with BaCl_2 solution.
- Identify the ions present and suggest the formula of the compound. (1992)
37. An orange solid (A) on heating gave a green residue (B), a colourless gas (C) and water vapour. The dry gas (C) on passing over heated Mg gave a white solid (D). (D) on reaction with water gave a gas (E) which formed dense white fumes with HCl . Identify (A) to (E) and give reactions involved. (1993)
38. A is binary compound of a univalent metal. 1.422 g of A reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid B , that forms a hydrated double salt, C with $\text{Al}_2(\text{SO}_4)_3$. Identify A , B and C . (1994)
39. A scarlet compound A is treated with concentrated HNO_3 to give a chocolate brown precipitate B . The precipitate is filtered and the filtrate is neutralised with NaOH . Addition of KI to the resulting solution gives a yellow precipitate C . The precipitate B on warming with concentrated HNO_3 in the presence of $\text{Mn}(\text{NO}_3)_2$ produces a pink-coloured solution due to the formation of D . Identify A , B , C and D . Write the reaction sequence. (1995)
40. Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (A) and alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds A and B . (1996)

41. A colourless inorganic salt (*A*) decomposes completely at about 250°C to give only two products, (*B*) and (*C*), leaving no residue. The oxide (*C*) is a liquid at room temperature and neutral to moist litmus paper while the gas (*B*) is a neutral oxide. White phosphorus burns in excess of (*B*) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process. (1996)
42. During the qualitative analysis of a mixture containing Cu^{2+} and Zn^{2+} ions, H_2S gas is passed through an acidified solution containing these ions in order to test Cu^{2+} alone. Explain briefly. (1998)
43. A white solid is either Na_2O or Na_2O_2 . A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.
- Identify the substance and explain with balanced equation.
 - Explain what would happen to the red litmus if the white solid was the other compound. (1999)
44. An aqueous solution containing one mole of HgI_2 and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl . Explain with equations. (1999)
45. An aqueous blue coloured solution of a transition metal sulphate reacts with H_2S in acidic medium to give a black precipitate *A*, which is insoluble in warm aqueous solution of KOH . The blue solution on treatment with KI in weakly acidic medium, turns yellow and produces a white precipitate *B*. Identify the transition metal ion. Write the chemical reactions involved in the formation of *A* and *B*. (2000)
46. Write the chemical reactions associated with the 'borax bead test' of cobalt (II) oxide. (2000)
47. A white substance (*A*) reacts with dilute H_2SO_4 to produce a colourless gas (*B*) and a colourless solution (*C*). The reaction between (*B*) and acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution produces a green solution and a slightly coloured precipitate (*D*). The substance (*D*) burns in air to produce a gas (*E*) which reacts with (*B*) to yield (*D*) and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or NaOH to (*C*) produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify (*A*), (*B*), (*C*), (*D*) and (*E*). Write the equations of the reactions involved. (2001)
48. When a white crystalline compound *X* is heated with $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 , a reddish brown gas *A* is evolved. On passing *A* into caustic soda solution, a yellow coloured solution of *B* is obtained. Neutralizing the solution *B* with acetic acid and on subsequent addition of lead acetate, a yellow precipitate *C* is obtained. When *X* is heated with NaOH solution, a colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish brown precipitate *D* is formed. Identify *A*, *B*, *C*, *D* and *X*. Write the equations of reactions involved. (2002)
49. A mixture consists of *A* (yellow solid) and *B* (colourless solid) which gives lilac colour in flame.
- Mixture gives black precipitate *C* on passing $\text{H}_2\text{S}_{(g)}$ through its aqueous solution.
 - C* is soluble in aqua-regia and on evaporation of aqua-regia and adding SnCl_2 gives greyish black precipitate *D*.
- The salt solution with alkaline ammonia gives a brown precipitate.
- The sodium extract of the salt with $\text{CCl}_4/\text{FeCl}_3$ gives a violet layer.
 - The sodium extract gives yellow precipitate with AgNO_3 solution which is insoluble in NH_3 . Identify *A* and *B*, and the precipitates *C* and *D*. (2003)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 - Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 - Statement-1 is true, statement-2 is false.
 - Statement-1 is false, statement-2 is true.
50. **Statement-1** : A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing hydrogen sulphide.

Statement-2 : Solubility product of CdS is less than that of NiS. (1989)

51. Statement-1 : Sulphate is estimated as BaSO₄ and not as MgSO₄.

Statement-2 : Ionic radius of Mg²⁺ is smaller than that of Ba²⁺. (1998)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension - 1

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (*P*) and a filtrate (*Q*). The precipitate *P* was found to dissolve in hot water. The filtrate (*Q*) remained unchanged, when treated with H₂S in a dilute mineral acid medium. However, it gave a precipitate

(*R*) with H₂S in an ammoniacal medium. The precipitate *R* gave a coloured solution (*S*), when treated with H₂O₂ in an aqueous NaOH medium.

52. The coloured solution *S* contains

- (a) Fe₂(SO₄)₃ (b) CuSO₄
(c) ZnSO₄ (d) Na₂CrO₄

53. The precipitate *P* contains

- (a) Pb²⁺ (b) Hg₂²⁺
(c) Ag⁺ (d) Hg²⁺ (2013)

Integer Answer Type

54. Among PbS, CuS, HgS, MnS, Ag₂S, NiS, CoS, Bi₂S₃ and SnS₂, the total number of BLACK coloured sulphides is (2014)

ANSWER KEY

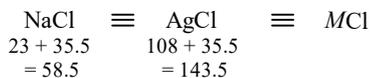
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|------------|---------------|------------|----------------------|--------------------------------------|------------|
| 1. (d) | 2. (c) | 3. (d) | 4. (a) | 5. (c) | 6. (b) |
| 7. (d) | 8. (d) | 9. (c) | 10. (a) | 11. (c) | 12. (b) |
| 13. (b) | 14. (a) | 15. (d) | 16. (b, c) | 17. (a, b, d) | 18. (b, c) |
| 19. (a, b) | 20. (b, c, d) | 21. (c, d) | 22. Fe ³⁺ | 23. CrO ₂ Cl ₂ | 24. True |
| 25. True | 50. (a) | 51. (b) | 52. (d) | 53. (a) | 54. (7) |

Explanations

- (d):** $2\text{Al} + 3/2\text{O}_2 \longrightarrow \text{Al}_2\text{O}_3$
 $2 \times 27 \text{ g of Al reacts completely with } 3 \times 16 \text{ g of O}_2$
 $\therefore 27 \text{ g of Al reacts completely with } \frac{3 \times 16}{2} = 24 \text{ g of O}_2$
- (c):** $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$
- (d):** Sn^{2+} can be precipitated by H_2S but not by HCl .
- (a):** Both Bi^{3+} and Sn^{4+} will get precipitated by H_2S .
- (c):** The group reagent for group I is dil HCl . Only PbCl_2 and Hg_2Cl_2 will get precipitated as Pb^{2+} and Hg_2^{2+} as both are group I basic radicals. Their solubility product is less than that of other radicals.
- (b):** Fe^{3+} is a basic radical of group III. The group reagent for group III of basic radicals is $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$. Thus if 6M NH_3 is added in slightly acidic (HCl) solution, it will lead to precipitation of Fe^{3+} as $\text{Fe}(\text{OH})_3$ (a brown ppt.).

$$\text{Fe}^{3+} + \text{Zn}^{2+} + \text{Cu}^{2+} \xrightarrow{6\text{M-NH}_3} \text{Fe}(\text{OH})_3 \downarrow + [\text{Zn}(\text{NH}_3)_4]^{2+} + [\text{Cu}(\text{NH}_3)_4]^{2+}$$
- (d):** Salts of sodium, potassium and ammonium are generally highly soluble. Cu^{2+} is precipitated as CuS in group II of basic radicals. Zn^{2+} is precipitated as ZnS in group IV of basic radicals. K_{sp} of $\text{ZnS} > K_{sp}$ of CuS . ZnS is precipitated after CuS .
- (d):** $\text{Pb}^{2+} + 2\text{HCl} \longrightarrow \text{PbCl}_2 \xrightarrow{\text{H}_2\text{S}} \text{PbS}$
(White ppt.) (black ppt.)
Soluble in hot water
- (c):** Because a saturated solution of (X) gives white ppt. with AgNO_3 solution, so X may be Cl_2 .
 $\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{HCl} + \text{HClO}$
 X
 $\text{HCl} + \text{AgNO}_3 \longrightarrow \text{AgCl} \downarrow + \text{HNO}_3$
(White ppt.)
 $2\text{HCl} + \text{Mg} \longrightarrow \text{MgCl}_2 + \text{H}_2 \uparrow$
Y
 $\therefore Y$ is H_2 and X is Cl_2
- (a):** Both H_2S and SO_2 are reducing agents and they can turn acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution green. SO_2 can be obtained by the action of acid on a sulphite (SO_3^{2-}). H_2S can be obtained by the action of acid on a sulphide (S^{2-}). SO_2 has an odour of burning sulphur which is irritating. H_2S smells like a rotten egg.
- (c):** From amongst the given compounds the K_{sp} of HgS is minimum, so it will get precipitated first.
- (b):** $\text{Bi}(\text{NO}_3)_3(\text{aq}) + 3\text{KI}(\text{aq}) \longrightarrow \text{BiI}_3(\text{s}) + 3\text{KNO}_3(\text{aq})$
Black
 $\text{BiI}_3(\text{s}) + \text{KI}(\text{aq}) \longrightarrow \text{K}[\text{BiI}_4]$
Orange
- (b):** $\text{Hg}^{2+} + 2\text{KI} \rightarrow \text{HgI}_2 \downarrow + 2\text{K}^+$
(scarlet red)
 $\text{HgI}_2 + 2\text{KI} \rightarrow \text{K}_2\text{HgI}_4$
(Nessler's reagent)
 $\text{Hg}^{2+} + \text{Co}^{2+} + 4\text{SCN}^- \rightarrow \text{CoHg}(\text{SCN})_4 \downarrow$
(deep blue crystalline)
- (a):** H_2S in presence of aqueous acidified solution precipitates as sulphide of Cu and Hg apart from Pb^{2+} , Bi^{3+} , Cd^{2+} , As^{3+} , Sb^{3+} and Sn^{2+} .
- (d):** H_2S gas in presence of NH_4Cl and NH_4OH is the group reagent in group IVth radicals *i.e.* Zn^{2+} , Ni^{2+} , Mn^{2+} and Co^{2+} .
- (b, c):** Al^{3+} is a group III basic radical and Bi^{3+} is a group II basic radical. Both of these radicals get precipitated as their hydroxides [*i.e.* $\text{Al}(\text{OH})_3$] and $\text{Bi}(\text{OH})_3$ respectively] with $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ (or *aq.* NH_3) in their respective groups.
- (a, b, d):** $4\text{NaCl} + \text{K}_2\text{Cr}_2\text{O}_7 + 6\text{H}_2\text{SO}_4 \longrightarrow 2\text{CrO}_2\text{Cl}_2$
(Red vapours)
 $+ 4\text{NaHSO}_4 + 2\text{KHSO}_4 + 3\text{H}_2\text{O}$
 $\text{CrO}_2\text{Cl}_2 + 4\text{NaOH} \longrightarrow \text{Na}_2\text{CrO}_4 + 2\text{NaCl} + 2\text{H}_2\text{O}$
(red vapours) (yellow solution)
- (b, c):** Fe^{2+} ions give blue ppt. with $\text{K}_3[\text{Fe}(\text{CN})_6]$. The blue ppt. appears due to the formation of Turnbull's blue; $\text{KFe}[\text{Fe}(\text{CN})_6]$.
 $\text{Fe}^{2+} + \text{K}_3[\text{Fe}(\text{CN})_6] \longrightarrow \text{KFe}[\text{Fe}(\text{CN})_6] + 2\text{K}^+$
Potassium ferro-ferricyanide
(Turnbull's blue)
 The red colouration that appears in case of Fe^{3+} ions on reaction with potassium thiocyanate (KCNS) is due to formation of $[\text{Fe}(\text{CNS})_3]$.
 $\text{Fe}^{3+} + 3\text{KCNS} \longrightarrow [\text{Fe}(\text{CNS})_3] + 3\text{K}^+$
Ferric thiocyanate
(red)
- (a, b):** The colourless salt may be NH_4NO_3 or NH_4NO_2 .
 $\text{NH}_4\text{NO}_3 + \text{NaOH} \longrightarrow \text{NH}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$
Non flammable
gas
 $4\text{Zn} + 7\text{NaOH} + \text{NaNO}_3 \longrightarrow 4\text{Na}_2\text{ZnO}_2 + \text{NH}_3 + 2\text{H}_2\text{O}$
gas evolution
restarts
 $\text{NH}_4\text{NO}_2 + \text{NaOH} \longrightarrow \text{NaNO}_2 + \text{NH}_3 + \text{H}_2\text{O}$
 $3\text{Zn} + 5\text{NaOH} + \text{NaNO}_2 \longrightarrow 3\text{Na}_2\text{ZnO}_2 + \text{NH}_3 + \text{H}_2\text{O}$
- (b, c, d):** Cu^{2+} ion will react with CN^- and SCN^- forming $[\text{Cu}(\text{CN})_4]^{3-}$ and $[\text{Cu}(\text{SCN})_4]^{3-}$ leading the reaction to the backward direction.

30. Total weight of AgCl obtained = 2.567 g
NaCl does not decompose on heating to 300°C. Therefore, amount of AgCl formed due to MCl = 1.341 g
∴ Weight of AgCl formed due to NaCl = 2.567 – 1.341 g
= 1.226 g



143.5 g of AgCl is obtained from NaCl = 58.5 g

$$\therefore 1.226 \text{ g of AgCl is obtained from NaCl} = \frac{58.5}{143.5} \times 1.226 \text{ g} = 0.4948 \text{ g}$$

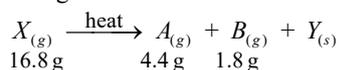
$$\therefore \text{Weight of MCl in 1 g of mixture} = 1.000 - 0.4948 \text{ g} = 0.5052 \text{ g}$$

1.341 g AgCl is obtained from MCl = 0.5052 g

$$143.5 \text{ g AgCl is obtained from MCl} = \frac{0.5052}{1.341} \times 143.5 \text{ g} = 42.029 \text{ g}$$

Molecular weight of MCl = 42.029.

31. From the given facts we can write the following equations:



From the above equation and the facts it can be concluded that:

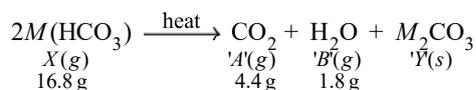
(i) A is CO₂ because it turns lime water milky.

(ii) Y when dissolved in water yields an alkaline solution and the solution on treatment with BaCl₂ solution forms a white ppt, of Z. The compound Z on treatment with acid gives effervescence of CO₂ so Z and hence Y must be a carbonate, CO₃²⁻. We can thus write Y as MCO₃ or M₂CO₃.

(iii) X on being heated yields a carbonate Y, hence CO_{2(g)} i.e. A and another gas B, hence it must be a bicarbonate, HCO₃⁻.

(iv) From these facts we find that B may be water.

In view of these conclusions the above equation may be written as



Molecular weight of M(HCO₃)

4.4 g of CO₂ is given by M(HCO₃) = 16.8 g

44 g of CO₂ is given by M(HCO₃)

$$= \frac{16.8}{4.4} \times 44 = 168 \text{ g}$$

Because 2 molecules of M(HCO₃) are involved in the reaction so molecular weight of M(HCO₃) = 168/2 = 84

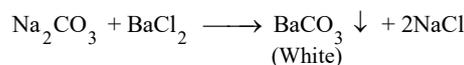
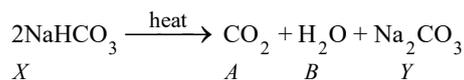
Atomic weight of M: Let the atomic weight be M.

$$\begin{aligned} \text{Molecular weight of } M(\text{HCO}_3) &= M + 1 + 12 + 48 \\ &= M + 61 \end{aligned}$$

$$\therefore M + 61 = 84 \quad \text{or } M = 84 - 61 = 23$$

Thus the metal must be Na and so the given salt X is Na(HCO₃).

These facts confirm to the thermal decomposition of NaHCO₃.



Thus A = CO₂; B = H₂O; Y = Na₂CO₃.

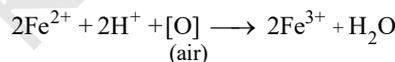
32. (a) From test (i) presence of Cl⁻ in the mixture is indicated because when MnO₂ + H₂SO₄ + salt are heated, Cl_{2(g)} is liberated.

(b) From test (ii) presence of NH₄⁺ ion in the mixture is indicated, because mixture when heated with NaOH gives out NH₃. The red litmus turns blue due to basic nature of NH_{3(g)}.

Presence of NH₄⁺ ion in the mixture is confirmed by test (iv), the brown ppt. with Nessler's reagent is given by NH₃.

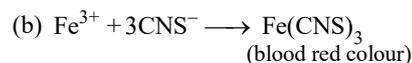
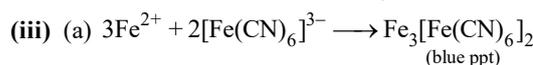
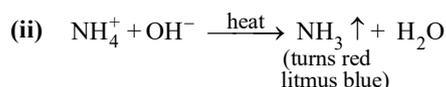
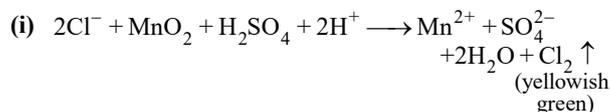
(c) From test (iii) presence of Fe²⁺ ion in the mixture is indicated, Fe²⁺ ions on reaction with K₃[Fe(CN)₆] form blue ppt. The blue ppt. is due to the formation of KFe[Fe(CN)₆], Turnbull's blue.

(d) The formation of red colouration with NH₄CNS indicates the presence of Fe³⁺ ion in the mixture. Fe³⁺ ion might have been formed due to the oxidation by air of Fe²⁺ ion of the mixture.



Thus the mixture contains FeCl₂ and NH₄Cl.

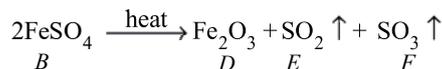
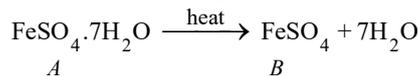
Ionic reactions are:



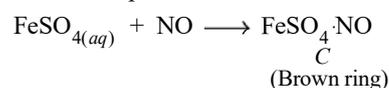
33. (i) Since A, loses water of crystallisation, when heated, so A is a hydrated salt.

(ii) B (anhydrous salt) when heated yields two gases and a brown residue, so B is FeSO₄.

Thus A is FeSO₄·7H₂O

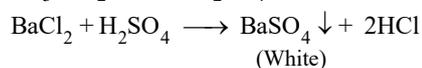
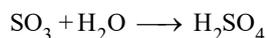


(iii) B is soluble in water and it reacts with NO to form a brown compound.

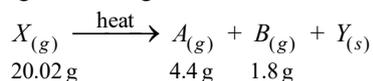


(iv) Gaseous mixture decolourises acidified KMnO_4
 $5\text{SO}_2 + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 2\text{H}_2\text{SO}_4$

(v) Gaseous mixture on passing through BaCl_2 , gives white ppt. of BaSO_4 .



34. Writing down the given facts as chemical equations, we have,



Following facts are evident:

For the facts, please refer answer (27)

Molecular weight of MHCO_3

4.4 g of CO_2 is given by $\text{MHCO}_3 = 20.02$ g

$$44 \text{ g of } \text{CO}_2 \text{ will be given by } \text{MHCO}_3 = \frac{20.02}{4.4} \times 44$$

$$= 200.2 \text{ g}$$

Since two molecules of MHCO_3 take part in the reaction so the molecular weight of $\text{MHCO}_3 = 200.2/2 = 100.1$

Atomic weight of Metal M

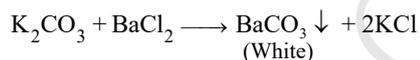
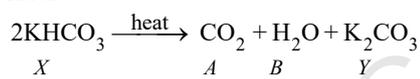
$$\text{Mol. wt. of } \text{MHCO}_3 = M + 1 + 12 + 48 = M + 61$$

$$\therefore 100.1 = M + 61$$

$$\text{or } M = 100.1 - 61 = 38.9$$

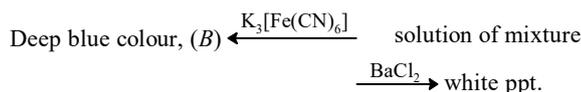
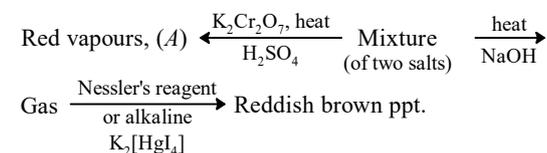
Thus the metal must be K (potassium) and the given salt X is KHCO_3 .

The thermal decomposition of KHCO_3 confirms the above facts.



Hence; $X = \text{KHCO}_3$; $Y = \text{K}_2\text{CO}_3$; $Z = \text{BaCO}_3$; $A = \text{CO}_2$; $B = \text{H}_2\text{O}$.

35. The given facts can be written down in the form of equations as follows:



Following conclusions can be drawn from these facts:

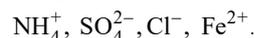
(i) Presence of NH_4^+ , shown by formation of reddish brown ppt. by the gas obtained on heating mixture with NaOH . In this case $\text{NH}_3(g)$ is evolved which gives the reddish brown ppt. with a solution of $\text{K}_2[\text{HgI}_4]$.

(ii) Presence of SO_4^{2-} ; the aqueous solution of mixture when treated with BaCl_2 solution gives a white ppt. (BaSO_4 is insoluble in water, sparingly soluble in concentrated HCl .)

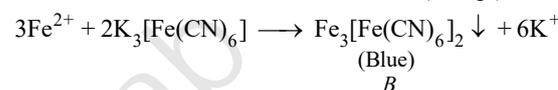
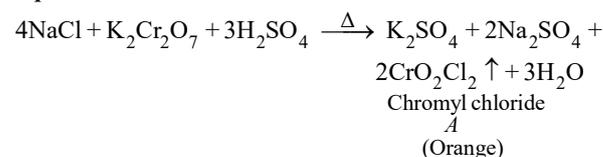
(iii) Presence of Cl^- ; the red vapours of CrO_2Cl_2 (chromyl chloride) are formed when mixture is heated with $\text{K}_2\text{Cr}_2\text{O}_7$ + concentrated H_2SO_4 .

(iv) Since the aqueous solution of mixture reacts with potassium ferricyanide to deep blue colour, so it points to the presence of Fe^{2+} ions in the mixture.

Thus the following ions are present in the mixture



Equations for the formation of A and B



36. Following conclusions can be drawn from the given information:

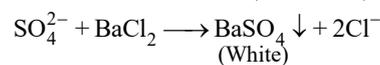
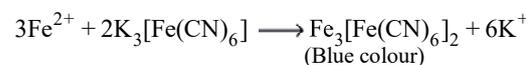
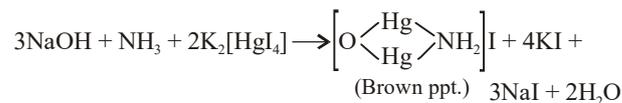
(i) The formation of brown ppt. on reaction with alkaline $[\text{K}_2\text{HgI}_4]$ indicates the presence of NH_4^+ in the compound.

(ii) Appearance of blue colour with $\text{K}_3[\text{Fe}(\text{CN})_6]$ indicates the presence of Fe^{2+} ion in the compound.

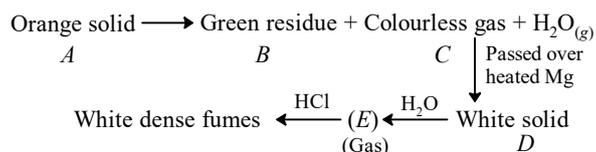
(iii) The solution of compound in dil HCl , on reaction with BaCl_2 solution gives a white ppt., this indicates the presence of SO_4^{2-} in the compound.

(iv) The bluish-green colour of the given crystalline compound containing, NH_4^+ , Fe^{2+} and SO_4^{2-} , suggests that it is Mohr's salt, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

Reactions:



37. We can summarise the given facts as follows:



From the given facts following conclusions can be drawn:

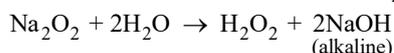
(i) Formation of white dense fumes when gas (E) is passed over HCl indicates that the gas (E) is NH_3 .

(ii) Formation of gas (E) i.e. NH_3 on hydrolysis of white solid D indicates that D is Mg_3N_2 .

The available concentration of S^{2-} in acidic medium is sufficient to cause the precipitation of CuS and is not sufficient to cause the precipitation of ZnS .

$$[K_{sp}(CuS) = 10^{-38}, K_{sp}(ZnS) = 10^{-22}]$$

43. (i): The substance is Na_2O_2 . This when dissolved in water gives an alkaline solution with liberation of H_2O_2 .

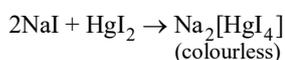


Due to its alkaline nature the solution turns red litmus paper blue, which subsequently changes into white due to the oxidation caused by H_2O_2 .

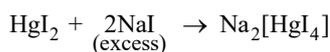
(ii) The substance Na_2O merely produces alkaline solution and so its solution changes red litmus paper to blue



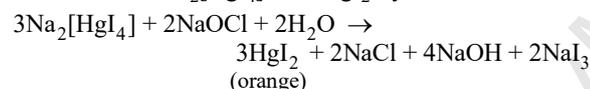
44. The colourless complex $Na_2[HgI_4]$ is formed by the action of NaI with HgI_2 .



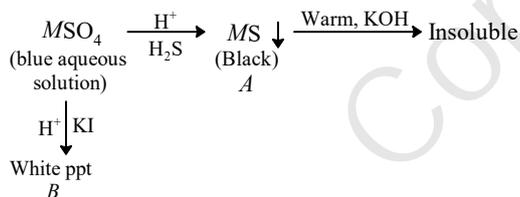
The colour is due to presence of residual HgI_2 . When excess of NaI is added, there is no excess of HgI_2 and so the colour disappears.



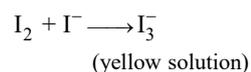
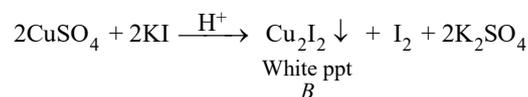
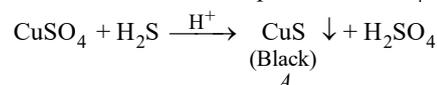
The orange colour of HgI_2 reappears because of the conversion of $Na_2[HgI_4]$ into HgI_2 by $NaClO$.



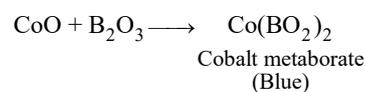
45. The given information can be summarised as follows:



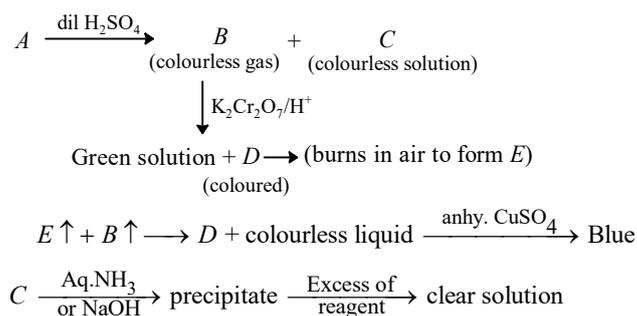
Above reactions correspond to $CuSO_4$



46. $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\text{heat}} Na_2B_4O_7 \xrightarrow{740^\circ C} 2NaBO_2 + B_2O_3$
(Borax)



47. The given facts can be summarised as follows:



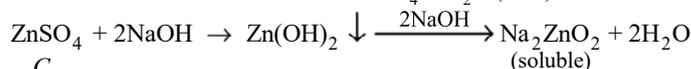
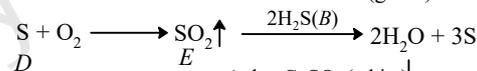
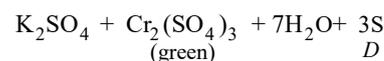
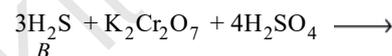
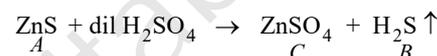
From the given set of information following conclusions can be drawn.

(i) As the gas B is colourless and it turns acidified $K_2Cr_2O_7$ solution green so it is H_2S .

(ii) Since H_2S gas is obtained by the reaction of dilute H_2SO_4 on A so A must be a sulphide.

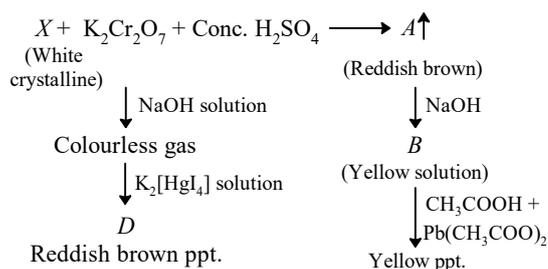
(iii) The colour of sulphide A is white so most probably it is ZnS .

The reactions are:



Thus $A = ZnS$; $B = H_2S$; $C = ZnSO_4$; $D = S$; $E = SO_2$.

48. In the form of a summary the given facts are

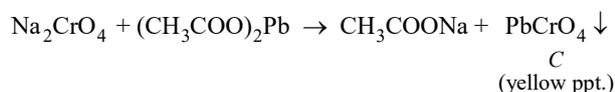
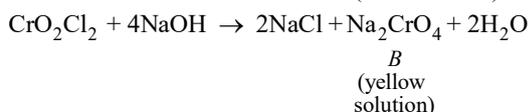
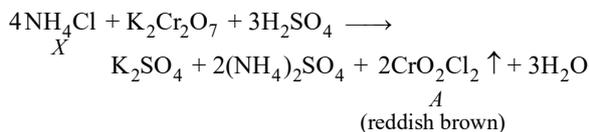
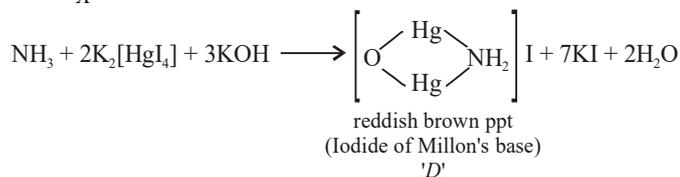
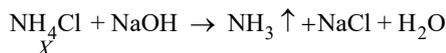


Following conclusions can be drawn

(i) Reactions of X with $NaOH$ solution to produce a colourless gas that gives a reddish brown ppt. with $K_2[Hg_2I_4]$ indicates that X contains NH_4^+ radical. The gas is NH_3 .

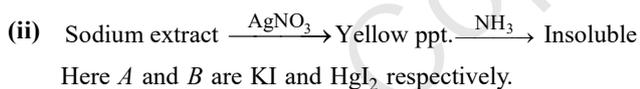
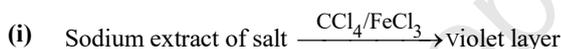
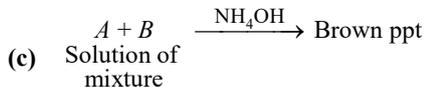
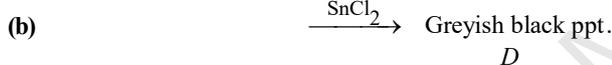
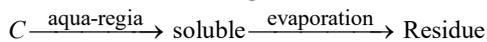
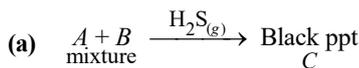
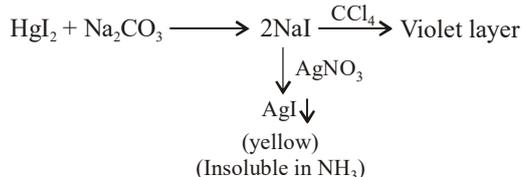
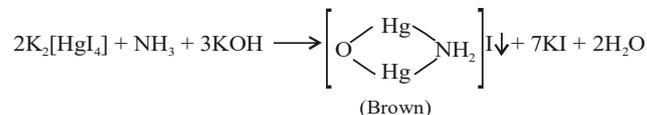
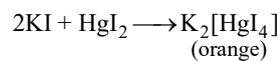
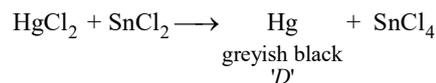
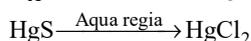
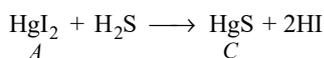
(ii) Reaction of X with acidified $K_2Cr_2O_7$ and subsequent treatment of reddish brown vapours (of CrO_2Cl_2) to form yellow solution (due to CrO_4^{2-} ion) and formation of a yellow ppt. of $PbCrO_4$ indicates that X contains Cl^- radical.

Thus compound X is NH_4Cl .

Reaction:

49. Given facts are:

$A + B \rightarrow$ Lilac colour (light purple colour) in flame

**Reaction:**

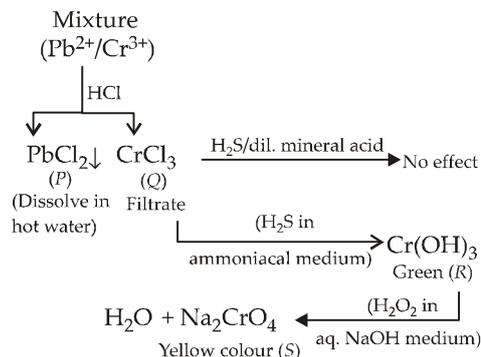
50. (a): Cd^{2+} belongs to group II and Ni^{2+} belongs to group IV of qualitative inorganic analysis. The K_{sp} of $\text{NiS} > K_{sp}$ of CdS . CdS is precipitated as yellow ppt. in group II and NiS is precipitated as black ppt. in group IV.

51. (b): Generally we estimate SO_4^{2-} as BaSO_4 (white ppt.) because BaSO_4 is insoluble in water.

52. (d)

53. (a)

Note :



54. (7) : The black coloured sulphides are PbS , CuS , HgS , Ag_2S , NiS , CoS and Bi_2S_3 . MnS is buff coloured while SnS_2 is yellow in colour.



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General Organic Chemistry

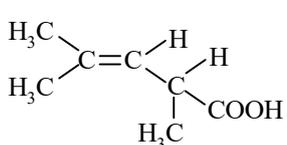
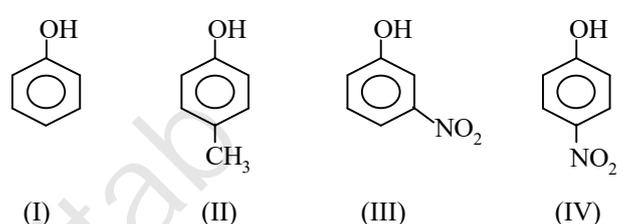
Multiple Choice Questions with ONE Correct Answer

- The bond order of individual carbon-carbon bonds in benzene is
(a) one
(b) two
(c) between one and two
(d) one and two, alternately. (1981)
- Molecule in which the distance between the two adjacent carbon atoms is largest is
(a) ethane
(b) ethene
(c) ethyne
(d) benzene. (1981)
- The compound which is not isomeric with diethyl ether is
(a) *n*-propyl methyl ether
(b) butan-1-ol
(c) 2-methylpropan-2-ol
(d) butanone. (1981)
- Among the following, the compound that can be most readily sulphonated is
(a) benzene
(b) nitrobenzene
(c) toluene
(d) chlorobenzene. (1982)
- The compound 1, 2-butadiene has
(a) only *sp* hybridised carbon atoms
(b) only *sp*² hybridised carbon atoms
(c) both *sp* and *sp*² hybridised carbon atoms
(d) *sp*, *sp*² and *sp*³ hybridised carbon atoms. (1983)
- Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism?
(a) 2-Butene
(b) 2-Butyne
(c) 2-Butanol
(d) Butanal (1983)
- The IUPAC name of the compound having the formula

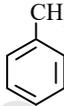
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C} - \text{C} - \text{CH} = \text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$$
 is
(a) 3, 3, 3-Trimethyl-1-propene
(b) 1, 1, 1-Trimethyl-2-propene
(c) 3, 3-Dimethyl-1-butene
(d) 2, 2-Dimethyl-3-butene (1984)
- An isomer of ethanol is
(a) methanol
(b) diethyl ether
(c) acetone
(d) dimethyl ether. (1986)
- Out of the following compounds, which will have a zero dipole moment?
(a) 1,1-dichloroethylene
(b) *cis*-1, 2-dichloroethylene
(c) *trans*-1, 2-dichloroethylene
(d) None of these (1987)
- The bond between carbon atom (1) and carbon atom (2) in compound $\text{N} \equiv \underset{1}{\text{C}} - \underset{2}{\text{CH}} = \text{CH}_2$ involves the hybrids as
(a) *sp*² and *sp*²
(b) *sp*³ and *sp*
(c) *sp* and *sp*²
(d) *sp* and *sp* (1987)
- The IUPAC name of the compound
 $\text{CH}_2 = \text{CH} - \text{CH}(\text{CH}_3)_2$ is
(a) 1,1-dimethyl-2-propene
(b) 3-methyl-1-butene
(c) 2-vinylpropane
(d) 1-isopropyl ethylene (1987)
- The Cl - C - Cl angle in 1, 1, 2, 2-tetrachloroethene 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)
- In $\text{CH}_3\text{CH}_2\text{OH}$, the bond that undergoes heterolytic cleavage most readily is
(a) C - C
(b) C - O
(c) C - H
(d) O - H (1988)
- The compound which has one isopropyl group is
(a) 2, 2, 3, 3-Tetramethylpentane
(b) 2, 2-Dimethylpentane
(c) 2, 2, 3-Trimethylpentane
(d) 2-Methylpentane. (1989)

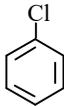
General Organic Chemistry

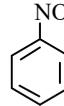
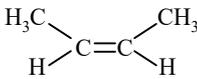
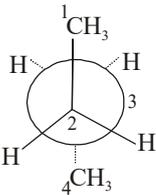
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15. The C—H bond distance is the longest in
(a) C₂H₂ (b) C₂H₄ (c) C₂H₆ (d) C₂H₂Br₂
(1989)
16. The number of sigma and pi-bonds in 1-butene-3-yne are
(a) 5 sigma and 5 pi (b) 7 sigma and 3 pi
(c) 8 sigma and 2 pi (d) 5 sigma and 4 pi.
(1989)
17. The compound which gives the most stable carbonium ion on dehydration is
(a) $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2\text{OH}$
(b) $\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{OH}$
(c) CH₃ - CH₂ - CH₂ - CH₂OH
(d) $\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \text{CH}_3$
(1989)
18. The hybridisation of carbon atoms in C - C single bond of HC ≡ C - CH = CH₂ is
(a) sp³ - sp³ (b) sp² - sp³
(c) sp - sp² (d) sp³ - sp
(1991)
19. The products of combustion of an aliphatic thiol (RSH) at 298 K are
(a) CO_{2(g)}, H₂O_(g) and SO_{2(g)}
(b) CO_{2(g)}, H₂O_(l) and SO_{2(g)}
(c) CO_{2(l)}, H₂O_(l) and SO_{2(g)}
(d) CO_{2(g)}, H₂O_(l) and SO_{2(l)}
(1992)
20. Isomers which can be interconverted through rotation around a single bond are
(a) conformers (b) diastereomers
(c) enantiomers (d) positional isomers
(1992)
21. The structure  shows
(a) geometrical isomerism
(b) optical isomerism
(c) geometrical and optical isomerism
(d) tautomerism.
(1995)
22. Allyl isocyanide has
(a) 2σ and 4π bonds
(b) 8σ and 5π bonds
(c) 9σ, 3π and 2 non-bonded electrons
(d) 8σ, 3π and 4 non-bonded electrons
(1995)
23. Arrange in order of decreasing trend towards S_E reactions: Chlorobenzene (I), Benzene (II), Anilinium chloride (III), Toluene (IV)
(a) II > I > III > IV (b) III > I > II > IV
(c) IV > II > I > III (d) I > II > III > IV
(1995)
24. Most stable carbonium ion is
(a) p - NO₂ - C₆H₄ - CH₂⁺
(b) C₆H₅CH₂⁺
(c) p - Cl - C₆H₄ - CH₂⁺
(d) p - CH₃O - C₆H₄ - CH₂⁺
(1995)
25. In the following compounds

(I) (II) (III) (IV)
The order of acidity is
(a) III > IV > I > II (b) I > IV > III > II
(c) II > I > III > IV (d) IV > III > I > II
(1996)
26. Arrange the following compounds in order of increasing dipole moment :
toluene (I) m-dichlorobenzene (II)
o-dichlorobenzene (III) p-dichlorobenzene (IV)
(a) I < IV < II < III (b) IV < I < II < III
(c) IV < I < III < II (d) IV < II < I < III
(1996)
27. In the following groups
-OAc -OMe -OSO₂Me -OSO₂CF₃
I II III IV
the order of leaving groups ability is
(a) I > II > III > IV (b) IV > III > I > II
(c) III > II > I > IV (d) II > III > IV > I
(1997)
28. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is
(a) MeCOCl (b) MeCHO
(c) MeCOOMe (d) MeCOOCOMe
(1997)
29. How many optically active stereoisomers are possible for butane-2, 3-diol?
(a) 1 (b) 2 (c) 3 (d) 4
(1997)

30. Among the following compounds, the strongest acid is
(a) $\text{HC} \equiv \text{CH}$ (b) C_6H_6 (c) C_2H_6 (d) CH_3OH
(1998)
31. In the compound $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{C} \equiv \text{CH}$ the $\text{C}_2 - \text{C}_3$ bond is of the type
(a) $sp - sp^2$ (b) $sp^3 - sp^3$
(c) $sp - sp^3$ (d) $sp^2 - sp^3$
(1999)
32. The optically active tartaric acid is named as $D - (+) -$ tartaric acid because it has a positive
(a) optical rotation and is derived from D -glucose
(b) pH in organic solvent
(c) optical rotation and is derived from $D - (+) -$ glyceraldehyde
(d) optical rotation only when substituted by deuterium.
(1999)
33. Which of the following compounds will exhibit geometrical isomerism?
(a) 1-Phenyl-2-butene (b) 3-Phenyl-1-butene
(c) 2-Phenyl-1-butene (d) 1,1-Diphenyl-1-propene
(2000)
34. Which of the following has the highest nucleophilicity?
(a) F^- (b) OH^- (c) CH_3^- (d) NH_2^-
(2000)
35. The order of reactivities of the following alkyl halides for a $\text{S}_{\text{N}}2$ reaction is
(a) $\text{RF} > \text{RCl} > \text{RBr} > \text{RI}$ (b) $\text{RF} > \text{RBr} > \text{RCl} > \text{RI}$
(c) $\text{RCl} > \text{RBr} > \text{RF} > \text{RI}$ (d) $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$
(2000)
36. Which of the following has the most acidic hydrogen?
(a) 3-Hexanone (b) 2, 4-Hexanedione
(c) 2, 5-Hexanedione (d) 2, 3-Hexanedione
(2000)
37. The number of isomers for the compound with molecular formula C_2BrClFI is
(a) 3 (b) 4 (c) 5 (d) 6
(2001)
38. An $\text{S}_{\text{N}}2$ reaction at an asymmetric carbon of a compound always gives
(a) an enantiomer of the substrate
(b) a product with opposite optical rotation
(c) a mixture of diastereomers
(d) a single stereoisomer.
(2001)
39. Which of the following compounds exhibits stereoisomerism?
(a) 2-Methylbutene-1 (b) 3-Methylbutyne-1
(c) 3-Methylbutanoic acid (d) 2-Methylbutanoic acid
(2002)
40. Which of the following acids has the smallest dissociation constant?
(a) $\text{CH}_3\text{CHF}\text{COOH}$ (b) $\text{FCH}_2\text{CH}_2\text{COOH}$
(c) $\text{BrCH}_2\text{CH}_2\text{COOH}$ (d) $\text{CH}_3\text{CHBr}\text{COOH}$
(2002)
41. Identify the correct order of boiling points of the following compounds
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
1 2 3
(a) $1 > 2 > 3$ (b) $3 > 1 > 2$
(c) $1 > 3 > 2$ (d) $3 > 2 > 1$ (2002)
42. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds
- 
1


2


3


4
- (a) $1 > 2 > 3 > 4$ (b) $4 > 3 > 2 > 1$
(c) $2 > 1 > 3 > 4$ (d) $2 > 3 > 1 > 4$
(2002)
43. Which of the following hydrocarbons has the lowest dipole moment?
(a)  (b) $\text{CH}_3\text{C} \equiv \text{CCH}_3$
(c) $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$ (d) $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$
(2002)
44. Which of the following represents the given mode of hybridisation $sp^2 - sp^2 - sp - sp$ from left to right?
(a) $\text{H}_2\text{C} = \text{CH} - \text{C} \equiv \text{N}$ (b) $\text{HC} \equiv \text{C} - \text{C} \equiv \text{CH}$
(c) $\text{H}_2\text{C} = \text{C} = \text{C} = \text{CH}_2$ (d) 
(2003)
45. Among the following, the molecule with the highest dipole moment is
(a) CH_3Cl (b) CH_2Cl_2 (c) CHCl_3 (d) CCl_4
(2003)
46. In the given conformation, if C_2 is rotated $\text{C}_2 - \text{C}_3$ bond anticlockwise by an angle of 120° then the conformation obtained is
- 

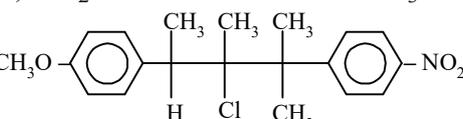
General Organic Chemistry

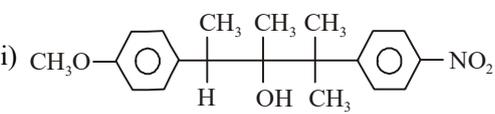
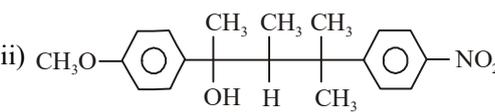
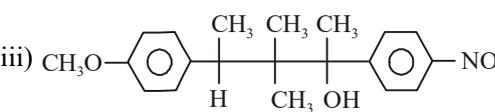
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- (a) fully eclipsed conformation
 (b) partially eclipsed conformation
 (c) gauche conformation
 (d) staggered conformation. (2004)

47. Which of the following resonating structures of 1-methoxy-1,3-butadiene is least stable?

- (a) $\bar{\text{C}}\text{H}_2-\text{CH}=\text{CH}-\text{CH}=\overset{+}{\text{O}}-\text{CH}_3$
 (b) $\text{CH}_2=\text{CH}-\bar{\text{C}}\text{H}-\text{CH}=\overset{+}{\text{O}}-\text{CH}_3$
 (c) $\bar{\text{C}}\text{H}_2-\overset{+}{\text{C}}\text{H}-\text{CH}=\text{CH}-\text{O}-\text{CH}_3$
 (d) $\text{CH}_2=\text{CH}-\bar{\text{C}}\text{H}-\overset{+}{\text{C}}\text{H}-\text{O}-\text{CH}_3$ (2005)

48.  compound on hydrolysis in aqueous acetone will give

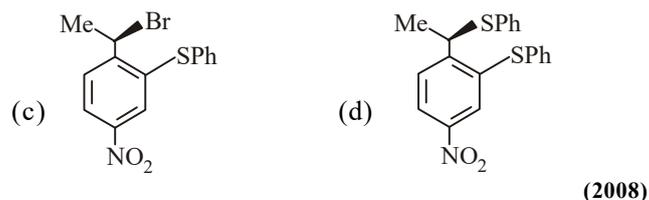
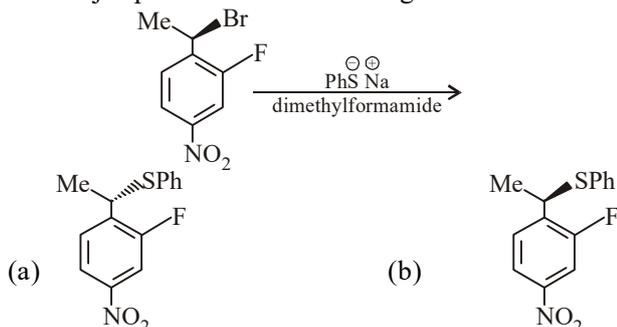
- (i) 
 (ii) 
 (iii) 
 (a) mixture of (i) and (ii) (b) mixture of (i) and (iii)
 (c) only (iii) (d) only (i) (2005)

49. The IUPAC name of $\text{C}_6\text{H}_5\text{COCl}$ is
 (a) benzene chloro ketone
 (b) chlorobenzyl ketone
 (c) chlorophenyl ketone
 (d) benzene carbonyl chloride. (2006)

50. The number of structural isomers for C_6H_{14} is
 (a) 3 (b) 4 (c) 5 (d) 6. (2007)

51. The number of stereoisomers obtained by bromination of *trans*-2-butene is
 (a) 1 (b) 2 (c) 3 (d) 4. (2007)

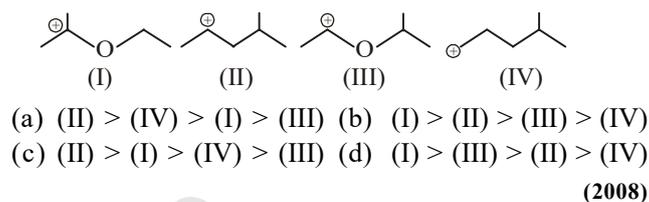
52. The major product of the following reaction is



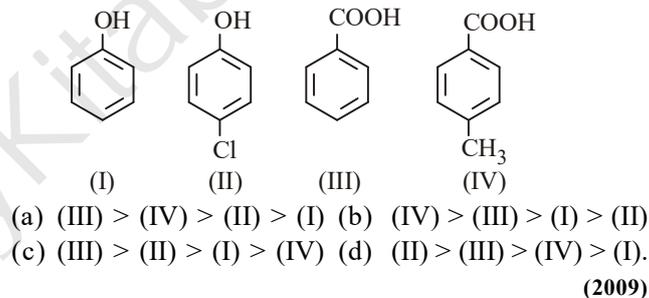
53. Hyperconjugation involves overlap of the following orbitals

- (a) $\sigma - \sigma$ (b) $\sigma - \pi$ (c) $p - p$ (d) $\pi - \pi$ (2008)

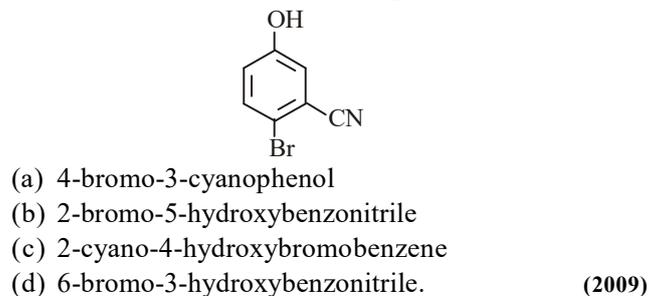
54. The correct stability order for the following species is



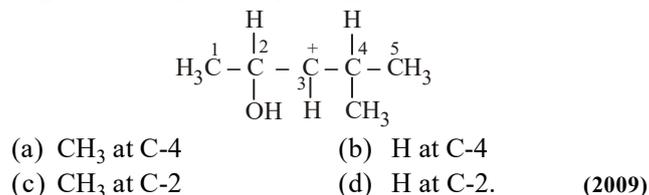
55. The correct acidity order of the following is



56. The IUPAC name of the following compound is



57. In the following carbocation, H/ CH_3 that is most likely to migrate to the positively charged carbon is



58. The correct stability order of the following resonance structures is

- (I) $\text{H}_2\text{C}=\overset{+}{\text{N}}=\bar{\text{N}}$ (II) $\text{H}_2\bar{\text{C}}-\text{N}=\bar{\text{N}}$
 (III) $\text{H}_2\bar{\text{C}}-\overset{+}{\text{N}}\equiv\text{N}$ (IV) $\text{H}_2\bar{\text{C}}-\text{N}=\overset{+}{\text{N}}$

- (a) (I) > (II) > (IV) > (III) (b) (I) > (III) > (II) > (IV)
 (c) (II) > (I) > (III) > (IV) (d) (III) > (I) > (IV) > (II).

(2009)

59. The bond energy (in kcal mol⁻¹) of a C-C single bond is approximately

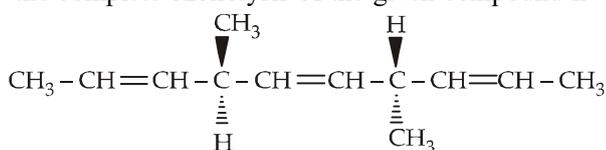
- (a) 1 (b) 10 (c) 100 (d) 1000

(2010)

60. In allene (C₃H₄), the type(s) of hybridisation of the carbon atoms is(are)

- (a) *sp* and *sp*³ (b) *sp* and *sp*²
 (c) only *sp*² (d) *sp*² and *sp*³ (2012)

61. The number of optically active products obtained from the complete ozonolysis of the given compound is



- (a) 0 (b) 1 (c) 2 (d) 4 (2012)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

62. Resonance structures of a molecule should have

- (a) identical arrangements of atoms
 (b) nearly the same energy content
 (c) the same number of paired electrons
 (d) identical bonding. (1984)

63. Phenol is less acidic than

- (a) acetic acid (b) *p*-methoxyphenol
 (c) *p*-nitrophenol (d) ethanol. (1986)

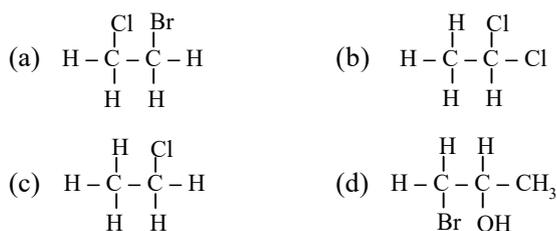
64. Dipole moment is shown by

- (a) 1, 4-dichlorobenzene
 (b) *cis*-1, 2-dichloroethene
 (c) *trans*-1, 2-dichloroethene
 (d) *trans*-1, 2-dichloro-2-pentene. (1986)

65. Only two isomeric monochloro derivatives are possible for

- (a) *n*-butane (b) 2, 4-dimethylpentane
 (c) benzene (d) 2-methylpropane. (1986)

66. Which of the following have asymmetric carbon atom?



(1989)

67. What is the decreasing order of strength of the bases OH⁻, NH₂⁻, H-C≡C⁻ and CH₃-CH₂⁻?

- (a) CH₃-CH₂⁻ > NH₂⁻ > H-C≡C⁻ > OH⁻
 (b) H-C≡C⁻ > CH₃-CH₂⁻ > NH₂⁻ > OH⁻
 (c) OH⁻ > NH₂⁻ > H-C≡C⁻ > CH₃-CH₂⁻
 (d) NH₂⁻ > H-C≡C⁻ > OH⁻ > CH₃-CH₂⁻

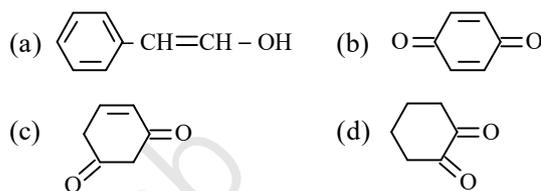
(1993)

68. Which of the following compounds will show geometrical isomerism?

- (a) 2-Butene (b) Propene
 (c) 1-Phenylpropene (d) 2-Methyl-2-butene

(1998)

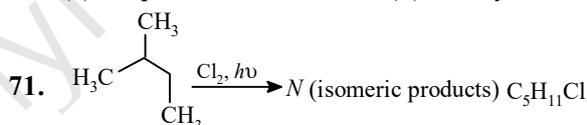
69. Tautomerism is exhibited by



(1998)

70. An aromatic molecule will

- (a) have 4*n* π electrons (b) have (4*n*+2)π electrons
 (c) be planar (d) be cyclic. (1999)

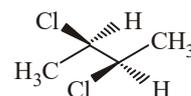


fractional distillation → *M* (isomeric products)

Give the numbers of *N* and *M*?

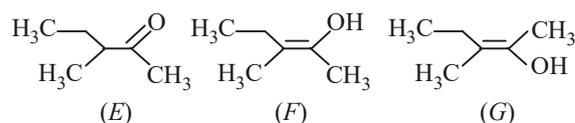
- (a) 6, 6 (b) 6, 4 (c) 4, 4 (d) 3, 3. (2006)

72. The correct statement(s) about the compound given below is (are)



- (a) the compound is optically active
 (b) the compound possesses centre of symmetry
 (c) the compound possesses plane of symmetry
 (d) the compound possesses axis of symmetry. (2008)

73. The correct statement(s) concerning the structures *E*, *F* and *G* is (are)

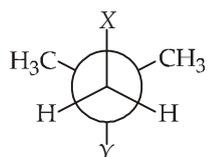


- (a) *E*, *F* and *G* are resonance structures
 (b) *E*, *F* and *E*, *G* are tautomers
 (c) *F* and *G* are geometrical isomers
 (d) *F* and *G* are diastereomers. (2008)

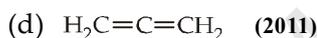
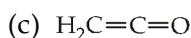
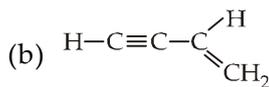
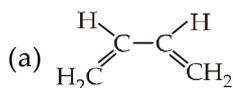
74. The correct statement(s) about the compound $\text{H}_3\text{C}(\text{HO})\text{HC} - \text{CH} = \text{CH} - \text{CH}(\text{OH})\text{CH}_3$ (X) is(are)
- the total number of stereoisomers possible for X is 6
 - the total number of diastereomers possible for X is 3
 - if the stereochemistry about the double bond in X is *trans*, the number of enantiomers possible for X is 4
 - if the stereochemistry about the double bond in X is *cis*, the number of enantiomers possible for X is 2.

(2009)

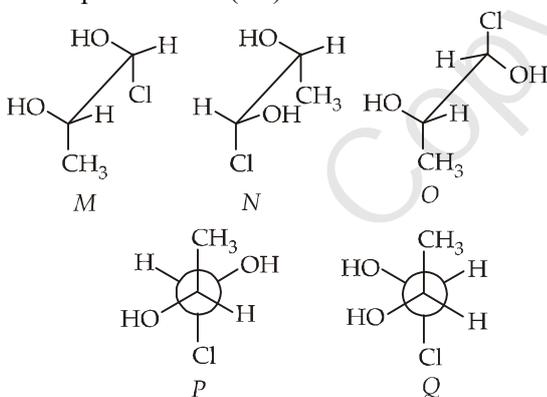
75. In the Newman projection for 2,2-dimethylbutane

 X and Y can respectively be

- H and H
 - H and C_2H_5
 - C_2H_5 and H
 - CH_3 and CH_3
76. Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are)



77. Which of the given statement(s) about N , O , P and Q with respect to M is(are) correct?



- M and N are non-mirror image stereo-isomers.
 - M and O are identical.
 - M and P are enantiomers.
 - M and Q are identical.
78. The hyperconjugative stabilities of *tert*-butyl cation and 2-butene, respectively, are due to
- $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations
 - $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations
 - $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations
 - p (filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations.

(2013)

Fill in the Blanks

79. Among the given cations, is most stable.
(*sec*-butyl carbonium ion; *tert*-butyl carbonium ion; *n*-butyl carbonium ion) (1981)
80. The compound having both sp and sp^2 hybridised carbon atoms is (propene, propane, propadiene) (1981)
81. ring is most strained. (Cyclopropane, Cyclobutane, Cyclopentane) (1981)
82. The terminal carbon atom in butane is hybridised. (1985)
83. A diol has two hydroxyl groups on carbon atoms. (1986)
84. Isomers which are mirror images are known as
(superimposable, non-superimposable, enantiomers, diastereomers, epimers) (1988)
85. The valence atomic orbitals on carbon in silver acetylide is hybridised. (1990)
86. The kind of delocalisation involving sigma bond orbitals is called (1994)
87. The IUPAC name of succinic acid is (1994)
88. Among PCl_3 , CH_3^+ , NH_2^- and NF_3 , is least reactive towards water. (1997)

True / False

89. Iodide is a better nucleophile than bromide. (1985)
90. An electron donating substituent in benzene orients the incoming electrophilic group to the *meta* position. (1987)
91. 2,3,4-Trichloropentane has three asymmetric carbon atoms. (1990)
92. During $\text{S}_{\text{N}}1$ reaction, the leaving group leaves the molecule before the incoming group is attached to the molecule. (1990)

Subjective Problems

93. Write structural formulae for all the isomeric alcohols having the molecular formula $\text{C}_4\text{H}_{10}\text{O}$. (1984)
94. Arrange the following in:
(i) Increasing reactivity towards HCN
 CH_3CHO , CH_3COCH_3 , HCHO , $\text{C}_2\text{H}_5\text{COCH}_3$ (1985)
(ii) *n*-Butane, *n*-butanol, *n*-butyl chloride, isobutane in increasing order of boiling point. (1988)

(iii) Benzene, toluene, methoxybenzene, chlorobenzene in increasing order of reactivity towards sulphonation with fuming sulphuric acid. (1988)

(iv) Increasing order of acid strength: (1991)

ClCH_2COOH (I), $\text{CH}_3\text{CH}_2\text{COOH}$ (II)

$\text{ClCH}_2\text{CH}_2\text{COOH}$ (III), $(\text{CH}_3)_2\text{CHCOOH}$ (IV),

CH_3COOH (V)

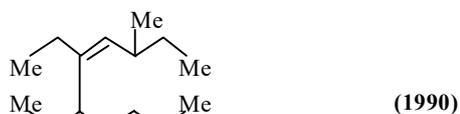
(v) Increasing reactivity in nucleophilic substitution reactions

CH_3F , CH_3I , CH_3Br , CH_3Cl (1992)

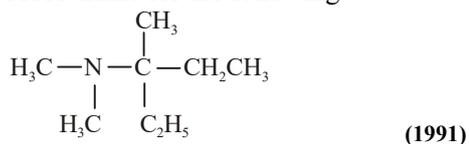
95. (i) Write the IUPAC name of:

$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCOOH}$ (1986)

(ii) Give the IUPAC name of the following compound:



(iii) Write the IUPAC name for the following:



96. For nitromethane molecule, write structure(s)

(i) showing significant resonance stabilisation

(ii) indicating tautomerism. (1986)

97. Write the structural formula of 4-chloro-2-pentene. (1988)

98. Give reasons for the following:

(i) Carbon oxygen bond lengths in formic acid are 1.23\AA and 1.36\AA and both the carbon oxygen bonds in sodium formate have the same value *i.e.* 1.27\AA . (1988)

(ii) Phenyl group is known to exert negative inductive effect. But each phenyl ring in biphenyl ($\text{C}_6\text{H}_5 - \text{C}_6\text{H}_5$) is more reactive than benzene towards electrophilic substitution. (1992)

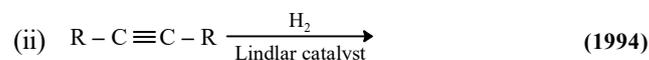
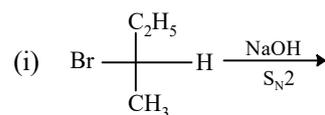
(iii) Aryl halides are less reactive than alkyl halides towards nucleophilic reagents. (1994)

(iv) $\text{CH}_2 = \text{CH}^-$ is more basic than $\text{HC}^- \equiv \text{C}^-$. (1994)

(v) Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds. (1995)

99. Write tautomeric forms for phenol. (1992)

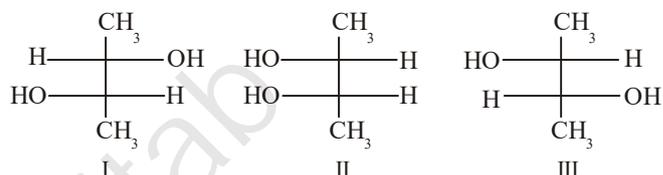
100. Draw the stereochemical structures of the products in the following reaction. (1992)



101. Write down the structures of the stereoisomers formed when *cis*-2-butene is reacted with bromide. (1995)

102. Discuss the hybridisation of carbon atoms in allene (C_3H_4) and show the π -orbital overlaps. (1999)

103. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III.



(2000)

104. Which one is more soluble in diethyl ether-anhydrous AlCl_3 or hydrous AlCl_3 ? Explain in terms of bonding. (2003)

105. Match the K_a values

(a) Benzoic acid K_a 3.3×10^{-5}

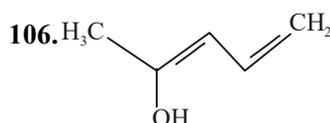
(b) 10.2×10^{-5}

(c) 30.6×10^{-5}

(d) 6.4×10^{-5}

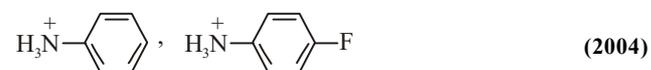
(e) 4.2×10^{-5}

(2003)



Write resonance structure of the given compound. (2003)

107. Which of the following is more acidic and why? (2004)



General Organic Chemistry

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108. (i) $\mu_{\text{obs}} = \sum_i \mu_i x_i$

Where μ_i is the dipole moment of a stable conformer of the molecule, $Z - \text{CH}_2 - \text{CH}_2 - Z$ and x_i is the mole fraction of the stable conformer.

Given: $\mu_{\text{obs}} = 1.0 \text{ D}$ and $x (\text{Anti}) = 0.82$

Draw all the stable conformers $Z - \text{CH}_2 - \text{CH}_2 - Z$ and calculate the value of $\mu_{(\text{Gauche})}$.

(ii) Draw the stable conformer of $Y - \text{CHD} - \text{CHD} - Y$ (meso form), when $Y = \text{CH}_3$ (rotation about $\text{C}_2 - \text{C}_3$) and $Y = \text{OH}$ (rotation about $\text{C}_1 - \text{C}_2$) in Newmann projection.

(2005)

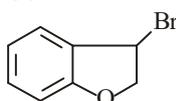
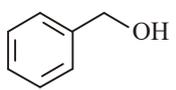
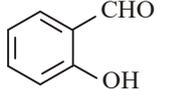
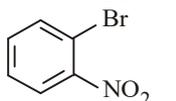
Matrix Match Type

109. Match the following:

Column I	Column II
A. $\text{CH}_3 - \text{CHBr} - \text{CD}_3$ on treatment with alc. KOH gives $\text{CH}_2 = \text{CH} - \text{CD}_3$ as a major product	P. E1 reaction
B. $\text{Ph} - \text{CHBr} - \text{CH}_3$ reacts faster than $\text{Ph} - \text{CHBr} - \text{CD}_3$	Q. E2 reaction
C. $\text{Ph} - \text{CH}_2 - \text{CH}_2\text{Br}$ on treatment with $\text{C}_2\text{H}_5\text{OD}/\text{C}_2\text{H}_5\text{O}^-$ gives $\text{Ph} - \text{CD} = \text{CH}_2$ as the major product	R. E1cB reaction
D. $\text{PhCH}_2\text{CH}_2\text{Br}$ and $\text{PhCD}_2\text{CH}_2\text{Br}$ react with same rate	S. First order reaction.

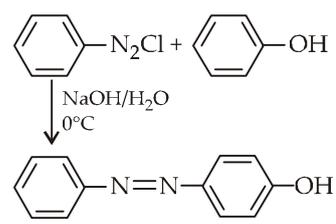
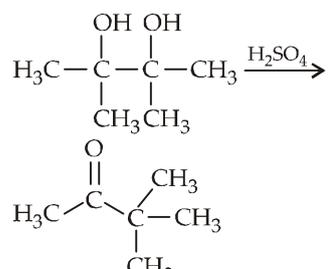
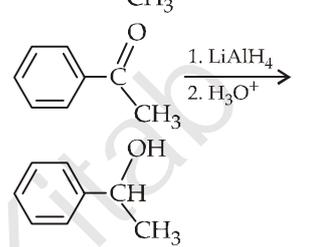
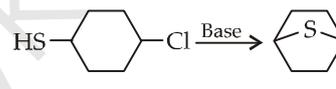
(2006)

110. Match each of the compounds given in column I with the reaction(s), that they can undergo given in column II.

Column I	Column II
(A) 	(p) Nucleophilic substitution
(B) 	(q) Elimination
(C) 	(r) Nucleophilic addition
(D) 	(s) Esterification with acetic anhydride
	(t) Dehydrogenation

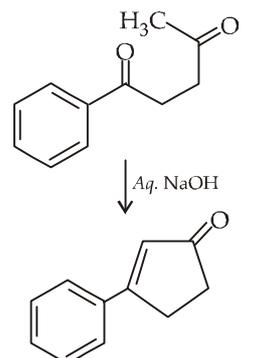
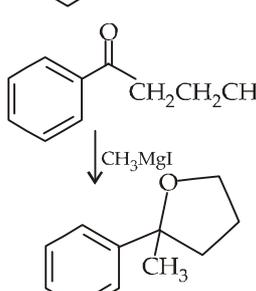
(2009)

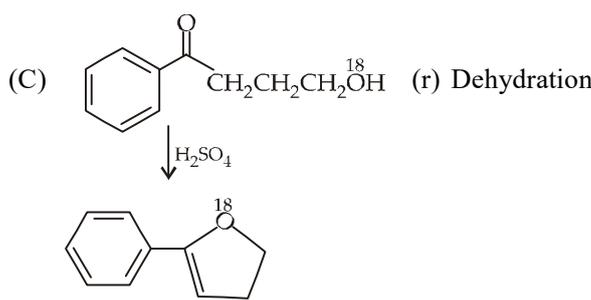
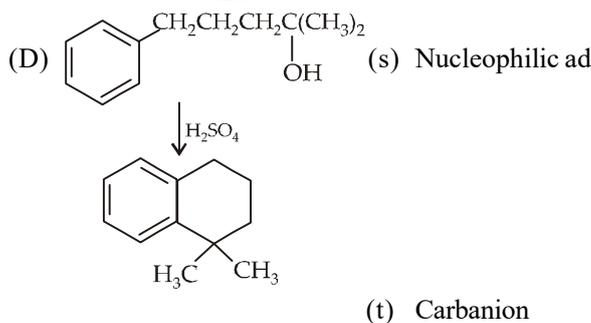
111. Match the reactions in Column I with appropriate options in Column II.

Column I	Column II
(A) 	(p) Racemic mixture
(B) 	(q) Addition reaction
(C) 	(r) Substitution reaction
(D) 	(s) Coupling reaction
	(t) Carbocation intermediate

(2010)

112. Match the reactions in Column I with appropriate types of steps/reactive intermediate involved in these reactions as given in Column II.

Column I	Column II
(A) 	(p) Nucleophilic substitution
(B) 	(q) Electrophilic substitution

- (C)  (r) Dehydration
- (D)  (s) Nucleophilic addition
- (t) Carbanion (2011)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
- (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
- (c) Statement-1 is true, statement-2 is false.
- (d) Statement-1 is false, statement-2 is true.

113. Statement-1 : Aryl halides undergo nucleophilic substitution with ease.

Statement-2 : The carbon-halogen bond in aryl halides has partial double bond character. (1991)

114. Statement-1 : Phenol is more reactive than benzene towards electrophilic substitution reaction.

Statement-2 : In the case of phenol, the intermediate carbocation is more resonance stabilized. (2000)

115. Statement-1 : Molecules that are not superimposable on their mirror images are chiral.

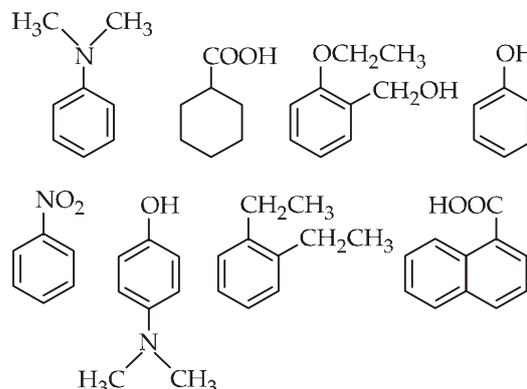
Statement-2 : All chiral molecules have chiral centres. (2007)

Integer Answer Type

116. The total number of cyclic structural as well as stereoisomers possible for a compound with the molecular formula C_5H_{10} is (2009)

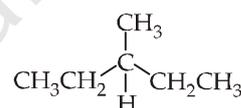
117. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is (2010)

118. Amongst the following, the total number of compounds soluble in aqueous NaOH is



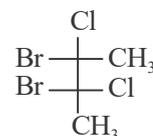
(2010)

119. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound, is



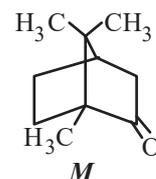
(2011)

120. The total number(s) of stable conformers with non-zero dipole moment for the following compound is (are)



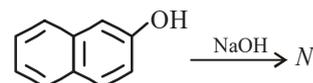
(2014)

121. The total number of stereoisomers that can exist for *M* is



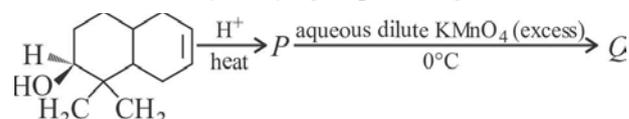
(2015)

122. The number of resonance structures of *N* is



(2015)

123. The number of hydroxyl group(s) in *Q* is



(2015)

ANSWER KEY

- | | | | | | |
|---|---|--------------------------------------|---------------|---------------|------------|
| 1. (c) | 2. (a) | 3. (d) | 4. (c) | 5. (d) | 6. (a) |
| 7. (c) | 8. (d) | 9. (c) | 10. (c) | 11. (b) | 12. (a) |
| 13. (d) | 14. (d) | 15. (c) | 16. (b) | 17. (b) | 18. (c) |
| 19. (b) | 20. (a) | 21. (b) | 22. (c) | 23. (c) | 24. (d) |
| 25. (d) | 26. (b) | 27. (b) | 28. (a) | 29. (b) | 30. (d) |
| 31. (d) | 32. (c) | 33. (a) | 34. (c) | 35. (d) | 36. (b) |
| 37. (d) | 38. (d) | 39. (d) | 40. (c) | 41. (b) | 42. (c) |
| 43. (b) | 44. (a) | 45. (a) | 46. (c) | 47. (c) | 48. (a) |
| 49. (d) | 50. (c) | 51. (a) | 52. (a) | 53. (b) | 54. (d) |
| 55. (a) | 56. (b) | 57. (d) | 58. (b) | 59. (c) | 60. (b) |
| 61. (a) | 62. (a, b, c) | 63. (a, c) | 64. (b, d) | 65. (a, d) | 66. (d) |
| 67. (a) | 68. (a, c) | 69. (a, c, d) | 70. (b, c, d) | 71. (b) | 72. (a, d) |
| 73. (b, c, d) | 74. (a, d) | 75. (b, d) | 76. (b, c) | 77. (a, b, c) | 78. (a) |
| 79. Tertiary-butyl carbonium ion | 80. Propadiene | 81. Cyclopropane | | | |
| 82. sp^3 | 83. Vicinal, adjacent | 84. Non-superimposable, enantiomers. | | | |
| 85. sp | 86. Hyperconjugation | 87. Butanedioic acid | 88. NH_2^- | | |
| 89. False | 90. False | 91. False | 92. True | | |
| 109. (A) \rightarrow Q; (B) \rightarrow Q; (C) \rightarrow R, S; (D) \rightarrow P, S | 110. (A) \rightarrow (p, q, t); B \rightarrow (p, q, s, t); C \rightarrow (r, s); D \rightarrow (p) | | | | |
| 111. (A) \rightarrow (r, s); B \rightarrow (t); C \rightarrow (p, q); D \rightarrow (r) | 112. (A) \rightarrow (r, s, t); B \rightarrow (p, s, t); C \rightarrow (r, s); D \rightarrow (q, r) | | | | |
| 113. (d) | 114. (a) | 115. (c) | 116. (7) | 117. (5) | 118. (4) |
| 119. (8) | 120. (3) | 121. (2) | 122. (9) | 123. (4) | |

Explanations

1. (c): Benzene is a resonance hybrid.

$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms}}{\text{Total number of resonating structures}}$$

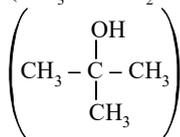
$$\text{C - C bond order in benzene} = \frac{2+1}{2} = 1.5$$

2. (a): The size of sp orbital is shortest and that of sp^3 is longest ($sp^3 > sp^2 > sp$ - order of decreasing size).

The hybridisation involved in ethane is sp^3 , ethene is sp^2 and ethyne is sp .

The C - C bond length is longest (1.54 Å), C = C bond length is 1.34 Å. In benzene C - C bond length is 1.39 Å.

3. (d): Diethylether is $C_4H_{10}O$ ($C_2H_5 - O - C_2H_5$), *n*-propyl methyl ether ($CH_3 - CH_2 - CH_2 - O - CH_3$), butan-1-ol ($CH_3 - CH_2 - CH_2 - CH_2OH$), 2-methylpropan-2-ol



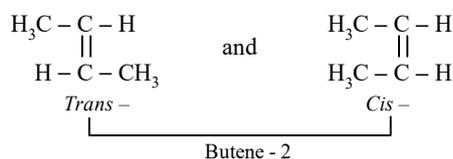
all have molecular formula $C_4H_{10}O$, hence these are isomeric with diethyl ether. The molecular formula of butanone is different, it is C_4H_8O . So these two are not isomers.

4. (c): $-CH_3$ group has +I effect and due to its presence, toluene has highest electron density in the benzene ring. For this reason toluene can be easily sulphonated.

5. (d): $CH_3 - CH = C = CH_2$. From this we find the hybridisation of various carbon atoms as follows:

$$C^1 = sp^2, C^2 = sp, C^3 = sp^2, C^4 = sp^3$$

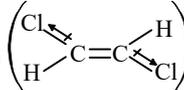
6. (a): *Cis-trans* (geometrical) isomerism is exhibited by those compounds which have same structural formula but different spatial arrangement of groups around C = C (carbon-carbon) double bond.



7. (c): $CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH = CH_2$

The correct name is 3, 3-Dimethylbut-1-ene.

8. (d): Both ethanol (CH_3CH_2OH) and dimethylether ($CH_3 - O - CH_3$) have same molecular formula (C_2H_6O).

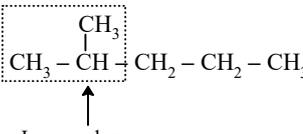
9. (c): In case of *trans*-1, 2-dichloroethylene  the net dipole moment is zero but in case of *cis*-1, 2-dichloroethylene there is some resultant dipole moment.

10. (c): $N \equiv C$ is sp hybrid. A carbon atom bonded to a double bond (C = C) is sp^2 hybrid.

11. (b): $H_2C^1=CH^2-\overset{\overset{CH_3}{|}}{CH^3}-CH_4^4$. Its correct IUPAC name is 3-methyl-1-butene.

12. (a): Since tetrachloroethene is an alkene (substituted) it has sp^2 hybridized C-atoms so Cl - C - Cl bond angle is 120° . Tetrachloromethane is an alkane (substituted) and in it the bond angle is $109^\circ 28'$ (sp^3 hybridisation).

13. (d): O - H bond is most readily cleaved because oxygen is more electronegative and can accommodate the negative charge more effectively after cleavage.

14. (d):  Isopropyl group

15. (c): C_2H_6 is an alkane (sp^3 hybridisation). Among alkanes, alkenes and alkynes and so the C - H bond length will be maximum in case of alkanes.

16. (b): In ($H_2C = CH - C \equiv CH$) there are 7σ - and 3π - bonds.

17. (b): The stability of carbonium ions follows the order: $3^\circ > 2^\circ > 1^\circ$.

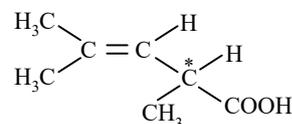
18. (c): In $C \equiv C$ there is sp hybridisation whereas in $C = C$ it is sp^2 .

19. (b): $C_2H_5SH + \frac{9}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} + SO_{2(g)}$

20. (a): Stereo isomers $\left\{ \begin{array}{l} \text{mirror images} \longrightarrow \text{enantiomers} \\ \text{not mirror images} \longrightarrow \text{diastereomers} \end{array} \right.$

Conformers are those isomers which can be interconverted by rotation around a C - C single bond.

21. (b): It has an asymmetric carbon (C^*) so it will show optical isomerism.



It will not show geometric isomerism because two same groups (*i.e.*, CH₃) are attached to double bonded carbon atom.

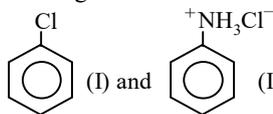
In it tautomerism is not possible because –CO group is not present in it.

22. (c): CH₂=CH–CH₂–N≡C

In it we find 5C–H (σ bonds), 1 C–C (σ bond), 1 C–N (σ bond), 1 C=C (1σ and 1π bonds), 1 N≡C (1σ and 2π bonds) *i.e.* a total of 9σ and 3π bonds.

Two non-bonded electrons are also present on C-atom (of N≡C).

23. (c): An electrophile attacks the region on high electron density. –CH₃ group, having +I effect, increases the electron density in the benzene ring whereas –Cl group having –I effect decreases the electron density in the benzene ring. Among



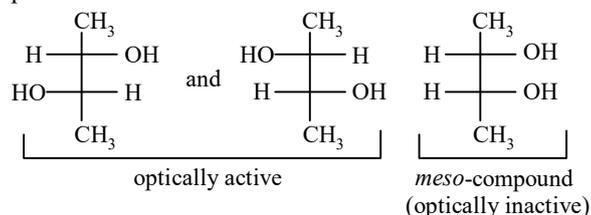
(I) and (II), (I) is deactivating due to –I effect but *o/p*. directing due to +M effect, whereas (II) is deactivating due to –I effect. Hence (II) undergoes electrophilic substitution reaction less readily than (I). Therefore the decreasing order is

Toluene > Benzene > Chlorobenzene > Anilinium chloride.

24. (d): All the carbonium ions are primary but (a) and (c) are not much stable because the NO₂ and Cl groups present intensifies positive charge. In (d) the charge (positive) of benzyl cation is more dispersed because of +M effect of –OCH₃ group.
25. (d): Due to the presence of electron-attracting group (–NO₂) the phenoxide ion is stabilised *i.e.* acid strength of phenol is increased. The presence of substituent in *para* position is more effective than in *meta* position. The presence of an electron-releasing substituent (–CH₃) destabilises the phenoxide ion and so decreases the acid strength of phenol.
26. (b): The dipole moment of *p*-dichlorobenzene is zero as the dipole moment due to the two Cl atoms cancel out. Due to the presence of electronegative Cl atom *o*- and *m*-dichlorobenzene have higher dipole moment than toluene. Again *o*-dichlorobenzene has higher dipole moment than *m*-dichlorobenzene. Hence the increasing order is *p*-dichlorobenzene < toluene < *m*-dichlorobenzene < *o*-dichlorobenzene.
27. (b): Weaker the base better is the leaving ability. Since the conjugate acid of a weak base is stronger therefore the correct arrangement in order of decreasing acidity is HOSO₂CF₃ > HOSO₂Me > HOAc > H₂O
28. (a): Among aldehydes and acid derivatives, acid chlorides are most susceptible to nucleophilic attack because of strong

–I effect and weak +R effect of Cl atom, due to this the carbonyl carbon has highest electron deficiency. Hence the order is MeCOCl > MeCOOCOMe > MeCOOMe > MeCHO.

29. (b): The number of optically active stereoisomers possible for 2, 3-diol is 2, *i.e.*, *d*- and *l*- which are optically active. The *meso*-compound is optically inactive due to internal compensation.



30. (d): The correct order of acidic strength is CH₃OH > CH≡CH > C₆H₆ > C₂H₆. CH₃OH is most acidic because O is more electronegative than C and it can accommodate negative charge as CH₃O[–]. All the given compounds are neutral towards litmus.

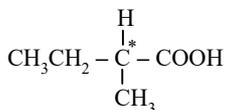
31. (d): ¹CH₂=²CH–³CH₂–⁴CH₂–⁵CH₂–⁶C≡CH
In it the C₂–C₃ bond is formed by overlap of *sp*²–*sp*³ orbitals.
32. (c): Any compound that can be prepared from, or converted into, *D*(+)-glyceraldehyde will belong to *D*-series and any compound that can be prepared from, or converted into, *L*(–) glyceraldehyde will belong to *L*-series.
33. (a): It will show geometrical isomerism because it has the two groups attached to C=C bonded C atoms which are different.
34. (c): Lesser the electronegativity of the donor atom, more is its tendency to donate a pair of electron and stronger is the nucleophile. Electronegativity of C, N, O, F are in the order F > O > N > C. Therefore CH₃[–] is the strongest nucleophilic, *i.e.* it has highest nucleophilicity.
35. (d): In *R*-X the rate of reactions follows the order R–I > R–Br > R–Cl > R–F. (I[–] is the best leaving group among halide ions).

36. (b): In CH₃–C(=O)–CH₂–C(=O)–CH₂–CH₃, CH₂ is flanked on both sides by electron withdrawing groups and so it is most acidic.

37. (d):

38. (d): S_N2 reaction proceeds by inversion of configuration. Since only one product is obtained so we cannot obtain diastereomers.

39. (d): It contains one asymmetric carbon atom (C^*)



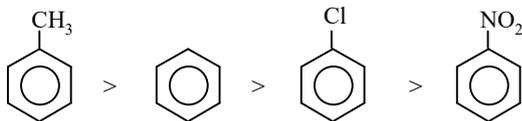
40. (c): The least dissociation constant is for weakest acid *i.e.* $\text{BrCH}_2\text{CH}_2\text{COOH}$. Br is less electronegative than F and Br is two carbon atoms away from $-\text{COOH}$.

41. (b): Higher the molecular weight higher will be the boiling point.

So, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} > \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} > \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$. *i.e.* $3 > 1 > 2$.

Carboxylic acid shows strongest intermolecular H-bonding and aldehyde shows weakest H-bond.

42. (c): The correct order is:

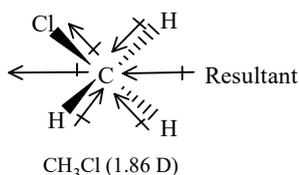
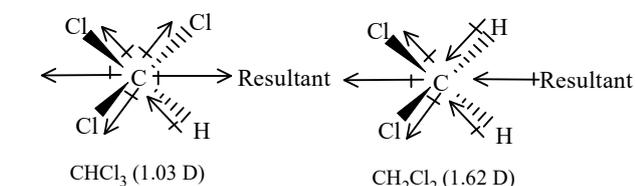


$-\text{CH}_3$ is an activating group because of $+I$ effect, $-\text{Cl}$ is deactivating due to $-I$ effect and $-\text{NO}_2$ is deactivating due to its $-I$ and $-M$ effect.

43. (b): $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$. It is linear and symmetrical so it has the lowest dipole moment.

44. (a): $\overset{sp^2}{\text{H}_2\text{C}} = \overset{sp^2}{\text{CH}} - \overset{sp}{\text{C}} \equiv \overset{sp}{\text{N}}$

45. (a): The dipole moment of a polar molecule depends on its geometry and shape. A symmetrical molecule is non-polar even though it contains polar bonds. CH_4 being symmetrical molecule has zero resultant dipole moment. We know that the bond dipole moment of $\text{C}-\text{H}$ bond and that of $\text{C}-\text{Cl}$ bond reinforce one-another.



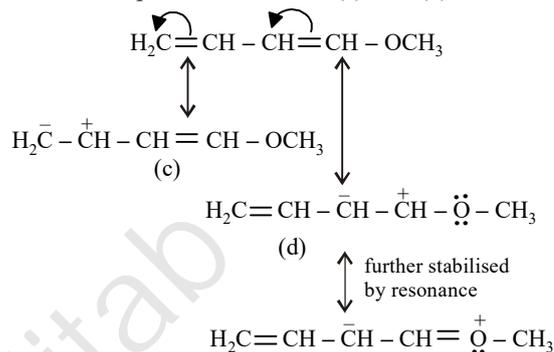
In CHCl_3 , the resultant of $\text{C}-\text{H}$ and $\text{C}-\text{Cl}$ dipoles opposes the resultant of two $\text{C}-\text{Cl}$ dipoles while in CH_2Cl_2 , the resultant of $\text{C}-\text{H}$ dipoles add to the resultant of two $\text{C}-\text{Cl}$ dipoles. In case of CH_3Cl , the resultant of two $\text{C}-\text{H}$ dipoles add to the resultant of $\text{C}-\text{H}$ and $\text{C}-\text{Cl}$ dipoles. Thus

dipole moment of CH_3Cl is highest among the given compounds. The molecule (CCl_4) again becomes symmetrical and dipole moment reduces to zero.

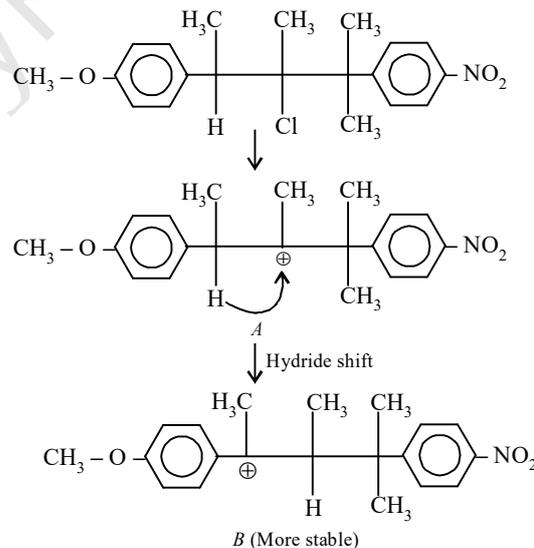
46. (c): The conformation obtained will be gauche conformation.

47. (c): The molecule in which all the atoms have completed octet is more stable than atom which have incomplete octet. More number of resonating structures, more will be the stability.

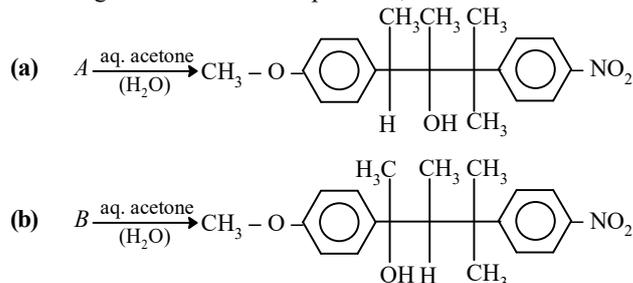
(a) and (b) have complete octet but in (c) and (d) all atoms do not have complete octet. Hence (c) and (d) are unstable.



48. (a): It is S_N1 reaction in which an intermediate carbocation is involved.

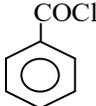


This carbocation is specially stabilised through resonance in which $-\text{O}-\text{CH}_3$ group acts as a good electron donor hence we will get a mixture of two products,

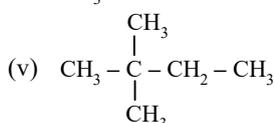
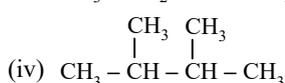
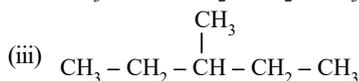
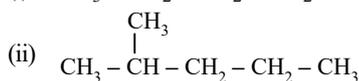
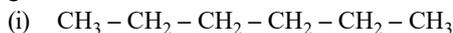


General Organic Chemistry

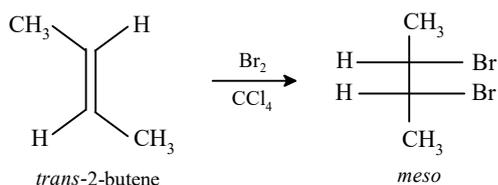
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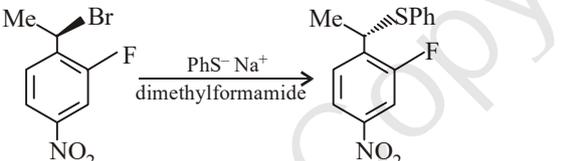
49. (d):  is known as benzene carbonyl (benzoyl) chloride.

50. (c): There are five structural isomers of C_6H_{14} , which are given as



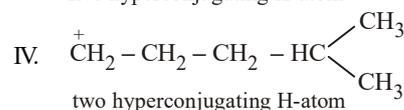
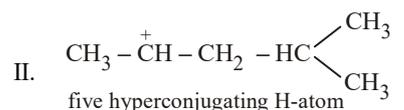
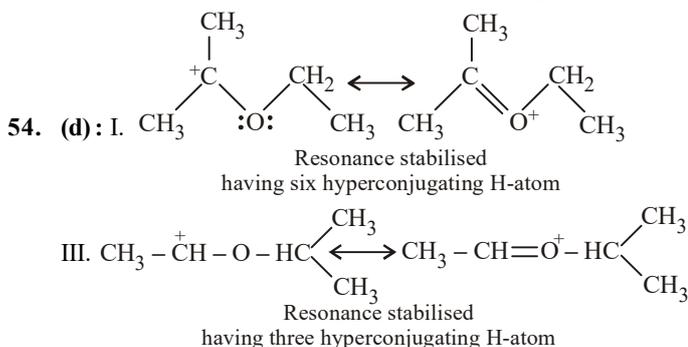
51. (a): Addition of halogens on alkenes is predominantly anti-addition. Anti-addition of Br_2 on *trans* alkene produces *meso* compound.



52. (a): 

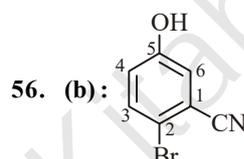
Nucleophilic substitution on alkyl halide is easier than on aryl halides. Substitution reaction is of S_N2 type that leads the formation of inversion product.

53. (b): Hyperconjugation involves delocalization of σ and π bond orbitals. *i.e.*, it undergoes $\sigma - \pi$ conjugation. The kind of delocalization involving sigma electrons of single bond and π -electrons of multiple bond is called hyperconjugation.



Stability of the following species depends upon the no. of α -hydrogen which can undergo hyperconjugation as well as resonance. Higher the no. of α -hydrogen, higher will be the stability of the compound.

55. (a): In general, acids have greater tendency to lose H^+ compared to alcohols. Out of (III) and (IV), (III) is a stronger acid than (IV) due to the presence of CH_3 (+I effect) which makes the release of proton difficult from the latter. Out of (I) and (II), (II) is a stronger acid due to presence of Cl (-I effect) which facilitates the release of proton than by (I). Hence the order is (III) > (IV) > (II) > (I).

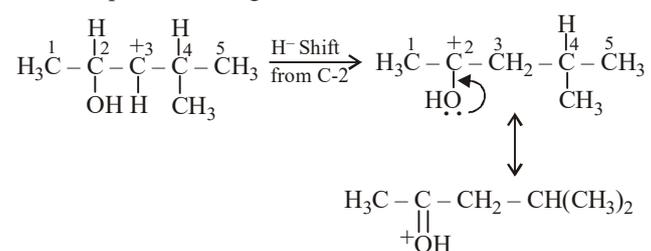


Since -CN has the highest priority, hence the parent compound is a nitrile.

\therefore IUPAC name of the compound is 2-bromo-5-hydroxybenzonitrile.

57. (d): In the carbocation, H^- shift occurs from C-2 to C-3 because:

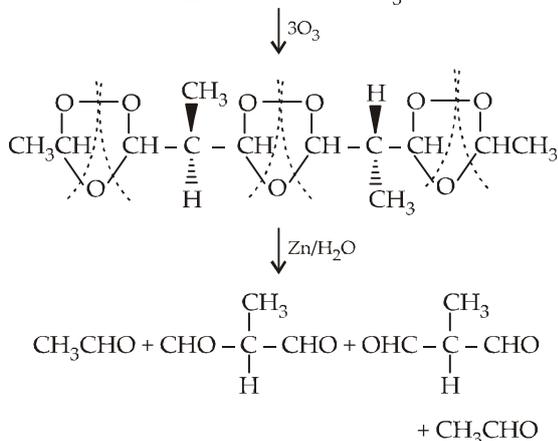
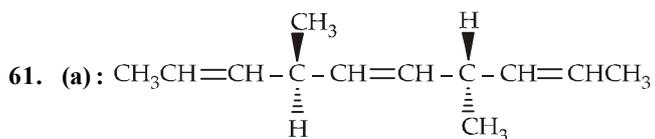
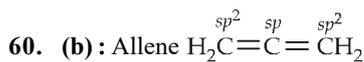
- the positive charge developed on C-2 is in conjugation with the -OH group.
- also the CH_3 group at C-2 shows +I effect and stabilizes the positive charge.



58. (b): The stability order of the structures, (I) > (III) > (II) > (IV) can be explained as follows:

- Number of π -bonds \propto Resonance energy \propto Stability.
- Contributing structures should be such that negative charge resides on an electronegative element and positive charge resides on an electropositive element.
- In contributing structures, like charges should not reside on atoms close to each other and unlike charges should not be widely separated.

59. (c): The approximate bond energy of C—C bond is $100 \text{ kcal mol}^{-1}$.



All are optically inactive.

62. (a, b, c): The arrangement of atomic nuclei must be same in all the resonating structures and all of them must also contain the same number of paired and unpaired electrons. Different resonating structures may differ in the way of distribution of electrons. The energies of all the resonating structures are almost same.

63. (a, c): Phenol is less acidic than acetic acid and *p*-nitrophenol.

64. (b, d): The dipole moments of both *p*-dichlorobenzene and *trans*-1,2-dichloroethene are zero due to their symmetrical structure.

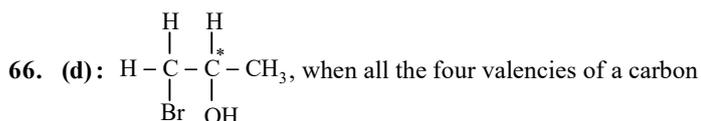
65. (a, d): In case of *n*-butane ($\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$) two isomers will be obtained depending on whether the Cl atom adds on to carbon -2 or carbon -1.

In option (b) *i.e.* $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$, we will get three

isomers with Cl group at either of the $-\text{CH}_3$ groups, second carbon atom and third carbon atom.

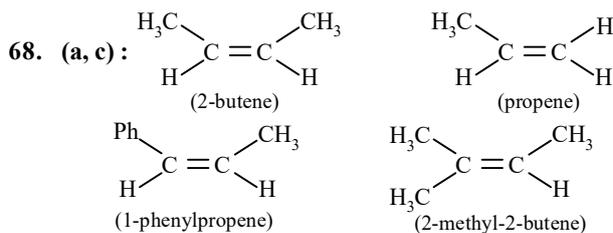
In case of benzene only one derivative is obtained. In option (d) *i.e.* $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$, we will get two isomers with Cl atom

at either one of the $-\text{CH}_3$ groups or on the central C-atom.



atom are satisfied with different atoms or groups, it is called asymmetric carbon atom.

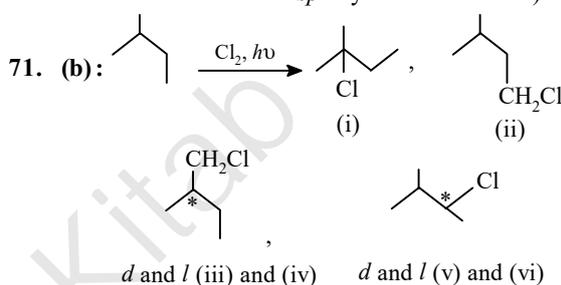
67. (a): The conjugate base of a strong acid is weaker while the conjugate base of a weak acid is stronger.



Of these only 2-butene and 1-phenylpropene can show geometrical isomerism (*cis-trans* isomerism).

69. (a, c, d)

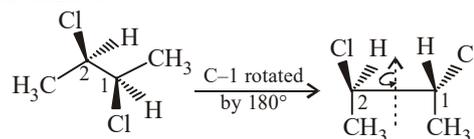
70. (b, c, d): For a compound to be aromatic it should have
($4n + 2$) π electrons (Huckel's Rule)
Planar structure (Because of resonance)
Cyclic structure (Because of the presence of sp^2 hybridised C-atom).



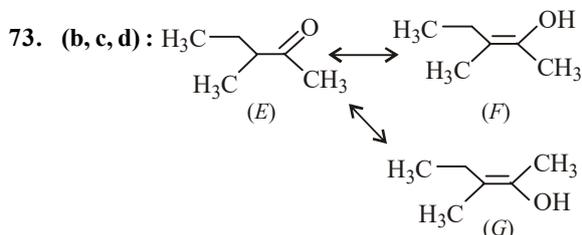
Total 6 isomers will be formed out of which only 4 isomers will be obtained on fractional distillation as (*d* + *l*) mixture will not be separated by distillation.

Methods used for separation of optically active compounds are chromatography, mechanical separation, biochemical separation, chemical separation, etc.

72. (a, d): The compound is optically active as it possesses two chiral centres.



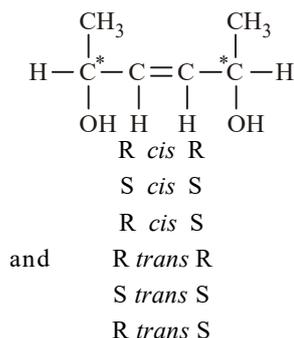
The compound possesses axis of symmetry perpendicular to the C - C bond.



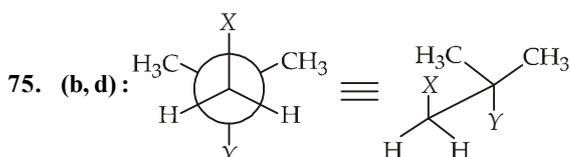
E - *F* and *E* - *G* are tautomers to each other.

F and *G* are geometrical isomers as their methyl group can be *cis* and *trans* position to each other. Also all geometrical isomers are diastereomers to each other.

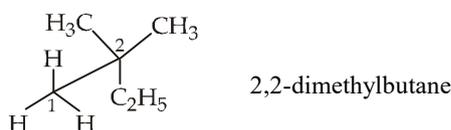
74. (a, d): The given molecule contains 2 stereocentres and one double bond. So, total number of different combination of stereoisomers is 6.



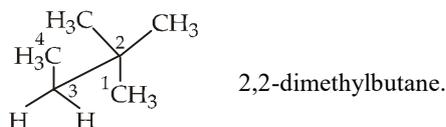
With *cis/trans*, it will give a pair of enantiomers, or two enantiomers.



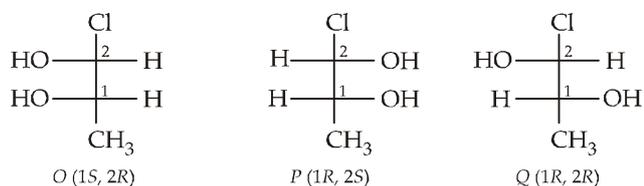
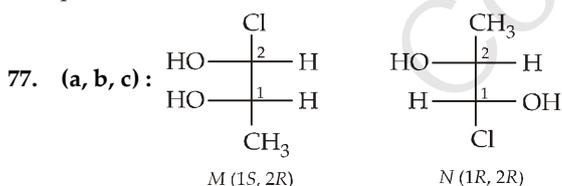
\therefore When X is H and Y is C_2H_5 ,



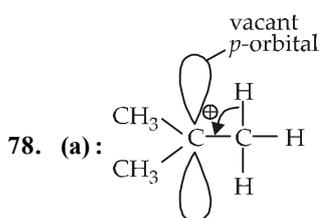
and when X is CH_3 and Y is also CH_3 ,



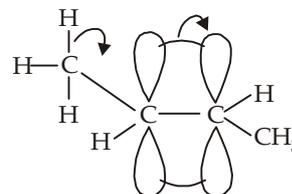
76. (b, c): Along C—C single bond, conformations are possible in butadiene in which all the atoms may not lie in the same plane.



M and N \Rightarrow Diastereomers M and O \Rightarrow Identical
M and P \Rightarrow Enantiomers M and Q \Rightarrow Diastereomers



In *tert*-butyl cation, carbon bearing positive charge has one vacant p -orbital. Hence, it is $\sigma \rightarrow p$ (empty) electron delocalisation.



In 2-butene, it is $\sigma \rightarrow \pi^*$ electron delocalisation.

79. Tertiary-butyl carbonium ion; $-\text{CH}_3$ is an electron repelling group.

80. Propadiene; $\text{H}_2\text{C}=\text{C}=\text{CH}_2$

81. Cyclopropane; In this case the bond angle is 60° . In this case the deviation is maximum from normal bond angle of $109^\circ 28'$.

82. sp^3 ; $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$

83. Vicinal, adjacent

84. Non-superimposable, enantiomers

85. sp ; $\text{HC}\equiv\text{CAg}$

86. Hyperconjugation

87. Butanedioic acid; CH_2COOH
 $\quad \quad \quad |$
 $\quad \quad \quad \text{CH}_2\text{COOH}$

88. NH_2^- ; NH_2^- is a nucleophile and hence least reactive towards water.

89. False

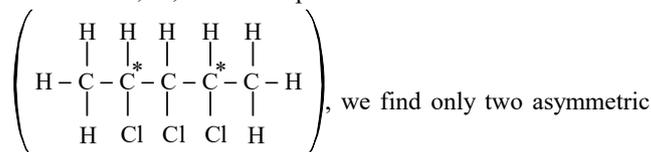
In nucleophiles we generally find a lone pair of electrons. That nucleophile which attacks the substrate (with minimum electron density) faster is a better nucleophile.

90. False

Electron-donating groups are *o*-, *p*-directing.

91. False

In case of 2, 3, 4-trichloropentane



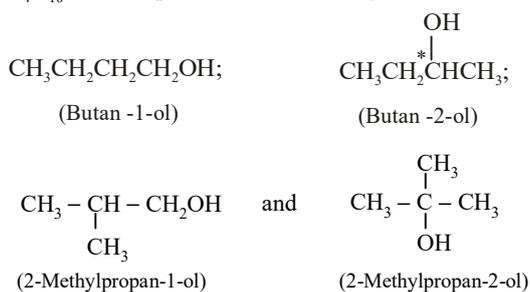
carbon atoms.

92. True

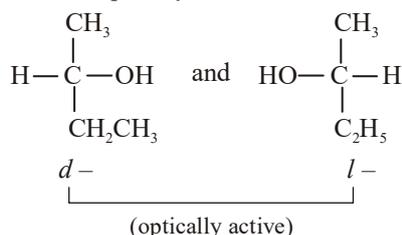
$\text{S}_\text{N}1$ mechanism involves only one species in the rate determining step. It proceeds in following steps:

- A carbocation is formed when leaving group leaves.
- The incoming group adds on to the carbocation formed.

93. $C_4H_{10}O$ can represent the following four alcohols:



Moreover butan-2-ol shows optical isomerism because it has an asymmetric carbon atom. It can exist as *d*- and *l*- isomer and both are optically active.



94. (i) : $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$ (nucleophilic addition reaction).

(ii) From amongst isomeric alkanes (non-polar molecules), the straight chain isomers has higher b.p. as compared to that of a branched chain isomer.

i.e. b.p. of *n*-butane > isobutane.

Since *n*-butyl chloride is a polar molecule so its b.p. is higher than that of alkanes.

Due to intermolecular hydrogen bonding the b.p. of *n*-butanol is highest from amongst given species.

Thus we have

isobutane < *n*-butane < *n*-butylchloride < *n*-butanol.

(iii) Chlorobenzene < benzene < toluene < methoxybenzene. Because of the presence of $-OCH_3$ and $-CH_3$ in methoxybenzene and toluene they get activated. In methoxybenzene the oxygen atom has two lone pairs and due to this mesomeric effect and electromeric effect are operative while in toluene only the inductive effect activates the ring.

Because of the presence of $-Cl$ group in chlorobenzene, the ring gets deactivated and so benzene can be sulphonated more readily than chlorobenzene.

(iv) The halogenated acids are stronger than the parent acid because the strongly electronegative $-Cl$ atom facilitates the removal of proton from the hydroxy group of acid. ($-Cl$ is an electron withdrawing group).

In case of other acids the order is $(CH_3)_2CHCOOH < CH_3CH_2COOH < CH_3COOH$.

The presence of $-CH_3$ group (electron repelling or *+I*) makes the removal of proton difficult.

Hence the arrangement is



(v) $CH_3F < CH_3Cl < CH_3Br < CH_3I$

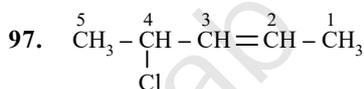
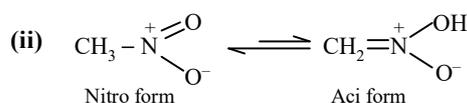
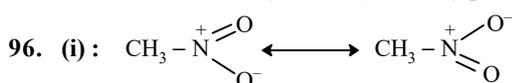
Lower the basicity of X^- , better the leaving group (X^-) and more reactive is the *RX*. The increasing order of basicities of X^- is $I^- < Br^- < Cl^- < F^-$.

95. (i) : Pent-2-en-1-oic acid or 2-pentenoic acid.

(ii) 5, 6-diethyl-3-methyl-4-decene

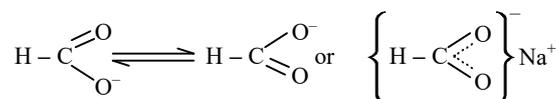
or 5, 6-diethyl-3-methyldec-4-ene.

(iii) 3-(*N,N*-dimethyl amino)-3-methylpentane.



98. (i) : Resonance is not possible in case of formic acid ($HCOOH$)

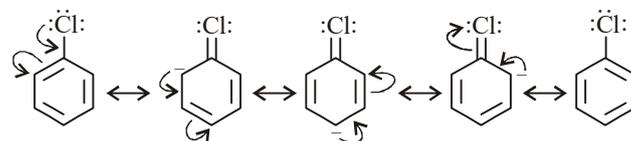
and so it has two types of C-O bonds $\left(\begin{array}{c} O \\ // \\ H - C \\ \backslash \\ OH \end{array} \right)$. In case of sodium formate resonance is possible in formate ion.



(ii) In biphenyl, one of the phenyl groups acts as electron donor and the other phenyl group acts as electron acceptor. Because of this biphenyl becomes more reactive than benzene.

(iii) Like vinyl halides (but unlike alkyl halides), aryl halides do not undergo nucleophilic substitution under ordinary conditions. Therefore the halogen atom of aryl halides is not replaced by $-OH$, $-NH_2$, $-CN$ etc, when aryl halides are treated with aqueous $NaOH$, NH_3 and KCN respectively.

The low reactivity of halogen atom in aryl halides and vinyl halides is due to resonance.



Because of resonance carbon-chlorine bond acquires partial double bond character and so it becomes shorter and stronger and thus cannot be easily replaced by nucleophiles.

(iv) $CH \equiv CH$ is more acidic than $CH_2 = CH_2$ because in $CH \equiv CH$ the hybridisation involved is *sp* and so its conjugate base will be less basic.

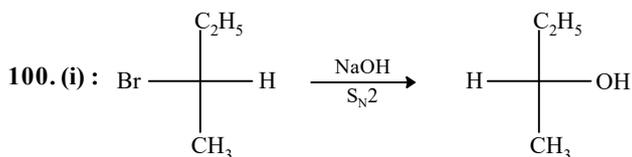
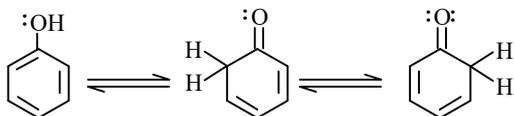
(v) Benzene gives electrophilic substitution reaction than electrophilic addition reaction, because it will result in a product having a stable benzene ring. Benzene and its

General Organic Chemistry

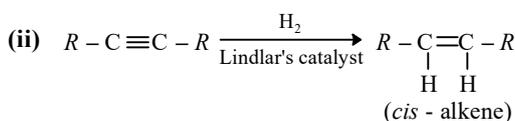
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derivatives are less prone to undergo addition reaction because their special stability arising from aromaticity is lost in addition process.

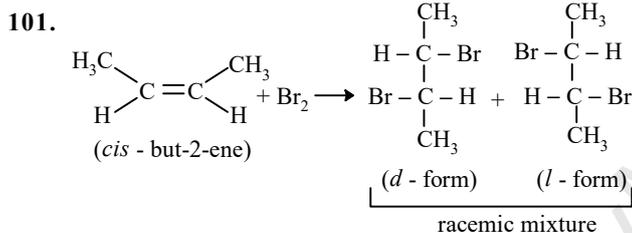
99. The tautomeric forms are:



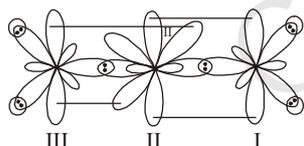
In it optical inversion occurs.



In presence of Lindlar's catalyst, alkynes on partial hydrogenation give *cis*-alkene while in presence of NaNH_2 give *trans*-alkene.

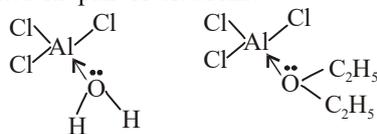


102. $\text{CH}_2=\text{C}=\text{CH}_2$ (Allene)
 $sp^2 \quad sp \quad sp^2$

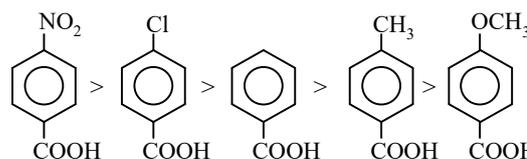


103. (I) and (III) are enantiomers. (I) and (II) are diastereomers.
(II) and (III) are diastereomers.

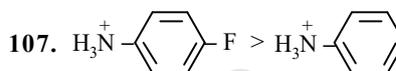
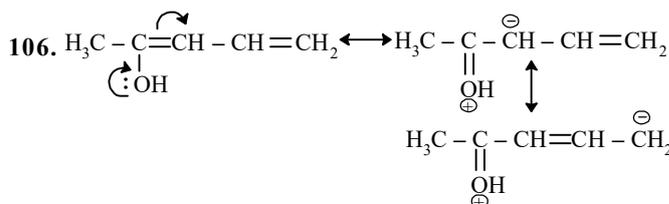
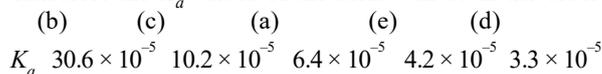
104. Anhydrous AlCl_3 is more soluble in diethyl ether because the oxygen atom of ether can donate its pair of electrons to the vacant orbital of electron deficient AlCl_3 through coordinate bond formation. In hydrated AlCl_3 , aluminium is not electron deficient because oxygen atom of water molecule has already donated its pair of electrons.



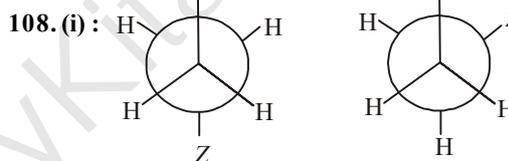
105. The correct order is



Therefore the K_a values of the acids will be in the order



p-fluoroanilium ion is more acidic than anilium ion because of the presence of strongly electronegative F atom.



Given, $\mu_{\text{obs}} = 1.0 \mu$; $m_{\text{anti}} = 0.82$

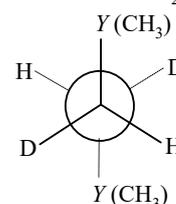
$$\mu_{\text{obs}} = \mu_{\text{anti}} \times x_{\text{anti}} + \mu_{\text{gauche}} \times x_{\text{gauche}}$$

or, $1 = \mu_{\text{anti}} \times 0.82 + \mu_{\text{gauche}} \times (1 - 0.82)$

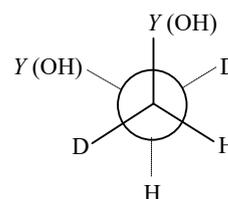
or, $1 = 0 \times 0.82 + \mu_{\text{gauche}} \times 0.18$ [$\therefore \mu_{\text{anti}} = 0$]

or, $\mu_{\text{gauche}} = \frac{1}{0.18} = 5.56 \text{ D}$

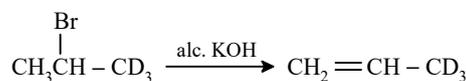
(ii) The stable conformer of $Y-\text{CHD}-\text{CHD}-Y$ (meso form) when $Y = \text{CH}_3$ and rotated about $\text{C}_2 - \text{C}_3$ is



The stable conformer of $Y-\text{CHD}-\text{CHD}-Y$ (meso form) when $Y = \text{OH}$ and rotated about $\text{C}_1 - \text{C}_2$ is



109. $A \rightarrow Q$

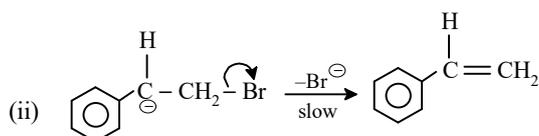
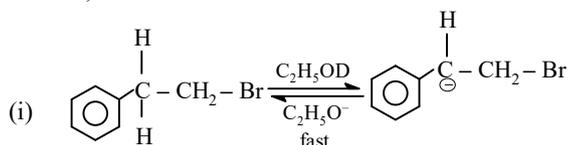


Formation of $\text{CH}_2 = \text{CH} - \text{CD}_3$ can be explained on the basis of the fact that C - D bond is much stronger than C - H bond.

B \rightarrow Q

Reactivity of PhCHBrCH_3 is greater than PhCHBrCD_3 only due to stronger nature of C - D bond in comparison to C - H bond.

C \rightarrow R, S

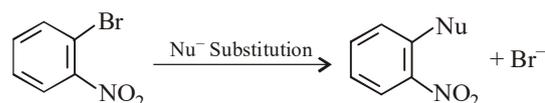
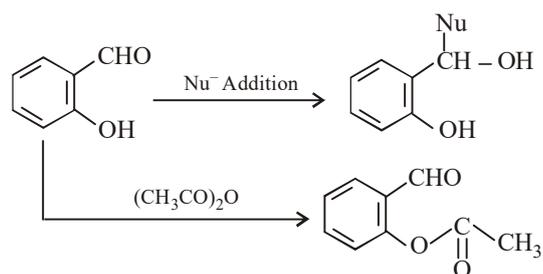
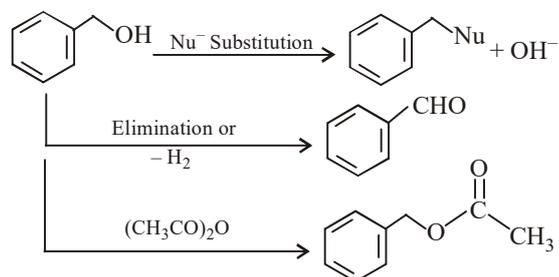
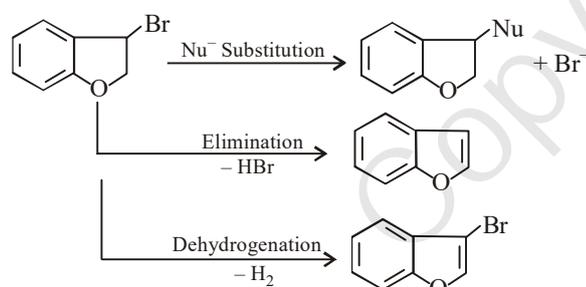


In the (ii) step, a slow unimolecular elimination occurs in the conjugate base (cb) of the reactant and hence this mechanism is called the E1cB or carbanion mechanism. Since the first step must be reversible (acid-conjugate base equilibrium), if ethanol containing EtOD is used as solvent, it would be expected that the original bromide would incorporate deuterium.

Rate = $k[\text{PhCH}_2\text{CH}_2\text{Br}]$ = first order reaction.

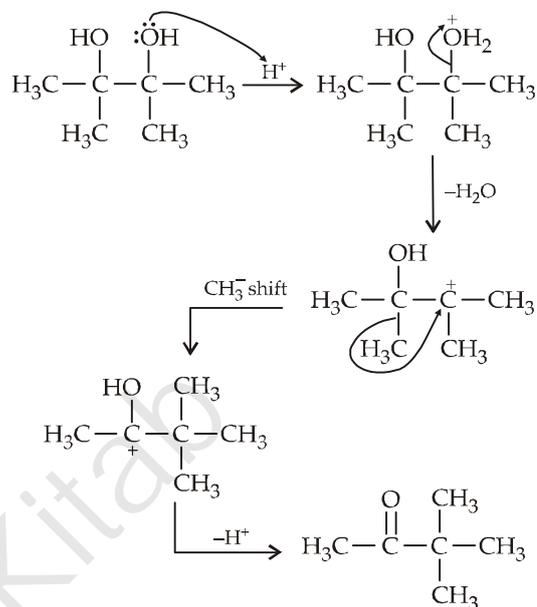
D \rightarrow P, S

110. (A) \rightarrow (p, q, t); (B) \rightarrow (p, q, s, t); (C) \rightarrow (r, s); (D) \rightarrow (p)

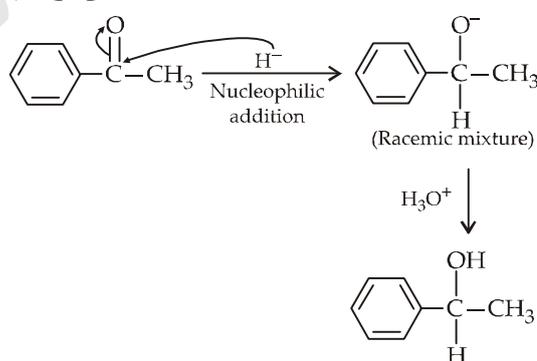


111. (A) \rightarrow (r, s)

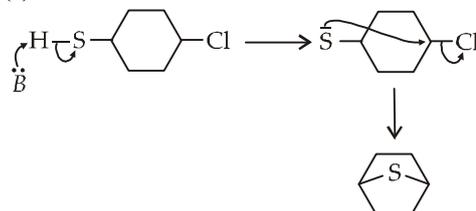
(B) \rightarrow (t)



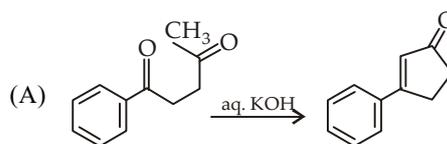
(C) \rightarrow (p, q)



(D) \rightarrow (r)



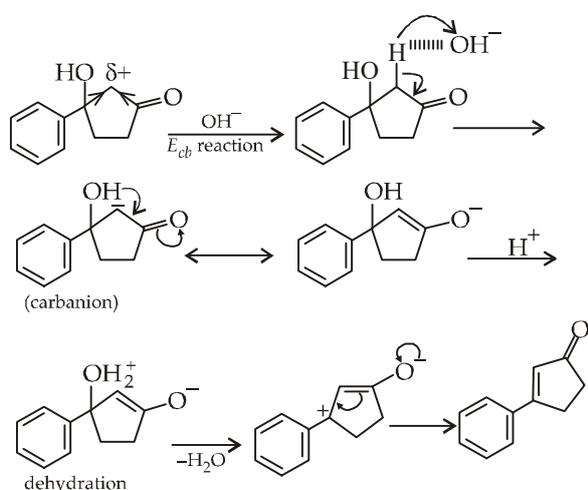
112. (A) \rightarrow (r, s, t); (B) \rightarrow (p, s, t); (C) \rightarrow (r, s); (D) \rightarrow (q, r)



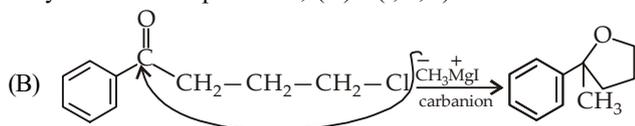
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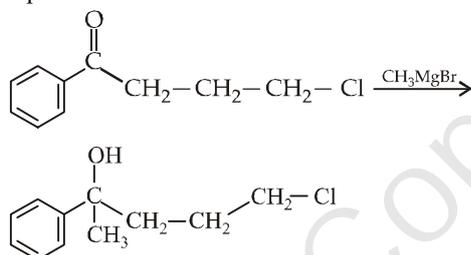
Aldol condensation is example of nucleophilic addition reaction.



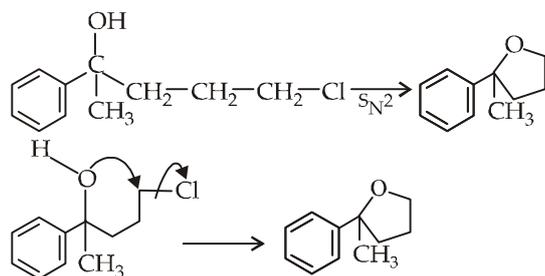
So, nucleophilic addition, formation of carbanion, dehydration takes place. So, (A)→(r, s, t)



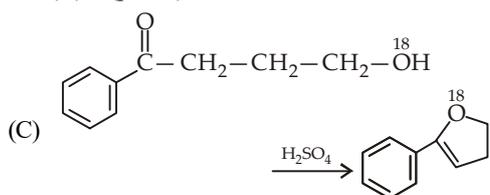
(i) It is an example of nucleophilic addition reaction *i.e.*, reaction between Grignard reagent and *keto* group is nucleophilic addition.



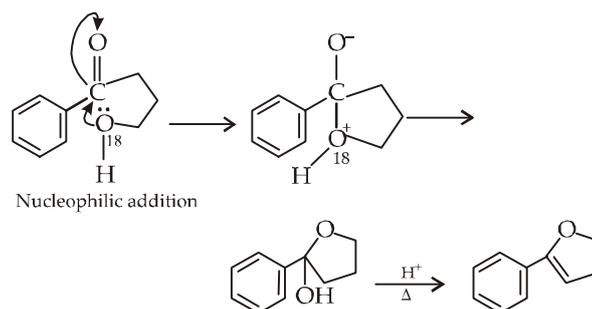
(ii) Now reaction is nucleophilic substitution



So, (B)→(p, s, t)

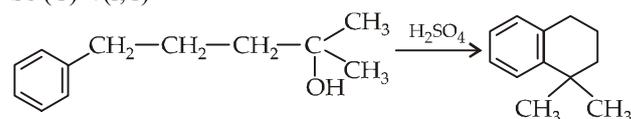


Example : Nucleophilic addition and dehydration.



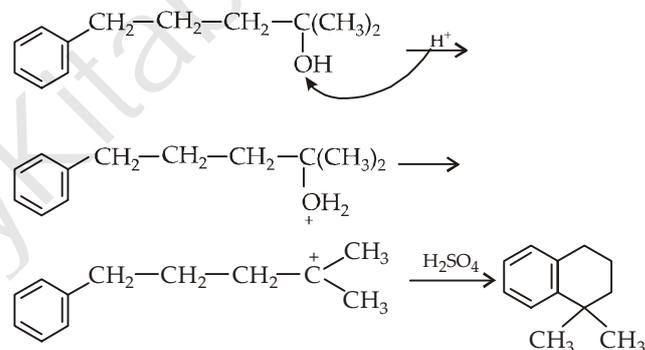
So, it is an example of nucleophilic addition reaction and dehydration.

So (C)→(r, s)



(D)

It is Friedel Craft reaction which is electrophilic substitution.



This reaction is an example of dehydration and electrophilic substitution.

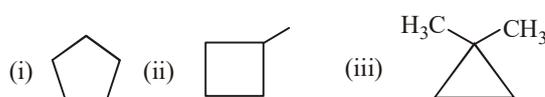
So, (D)→(q, r)

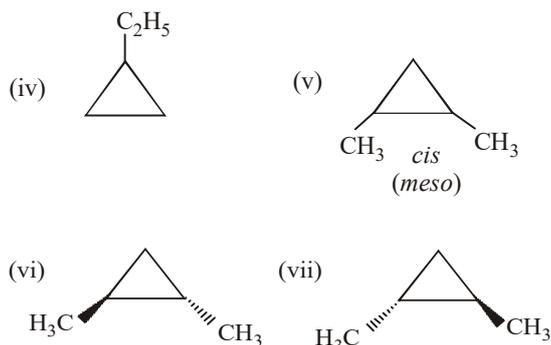
113. (d): Statement-1 is false (Aryl halides do not undergo nucleophilic substitution under ordinary conditions). Statement-2 is correct. The carbon-halogen bond in aryl halides have partial double bond character so it becomes shorter and stronger and cannot be easily replaced by nucleophiles.

114. (a): Because of +R effect of $-\ddot{O}-H$, its intermediate cation is more stable than the one in benzene.

115. (c) : Suitably substituted allenes (2,3-pentadiene) and biphenyls are optically active although they are dissymmetric, *i.e.* don't have asymmetric carbon atom.

116. (7) : For a compound with molecular formula C_5H_{10} , the isomers are as follows :

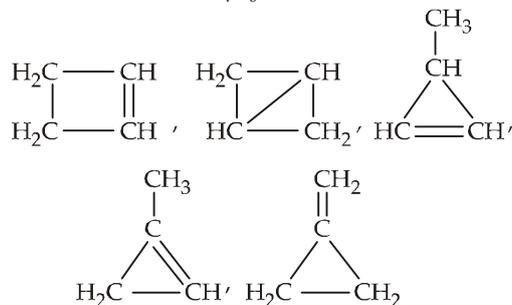




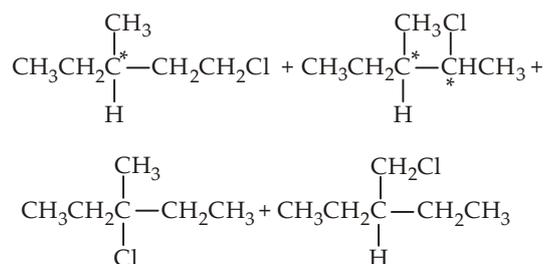
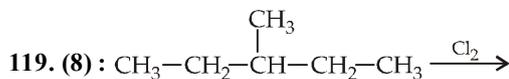
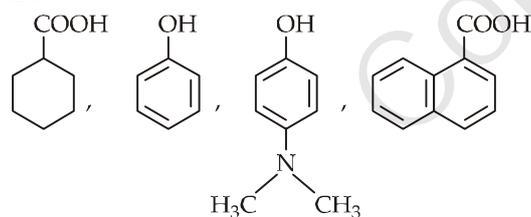
Structures (vi) and (vii) are *trans*-isomers and are same. It can exist in *d,l* form.

So, total no. of cyclic as well as stereoisomers possible is 7.

117. (5) : The possible cyclic isomers of the compound with molecular formula C_4H_6 are :

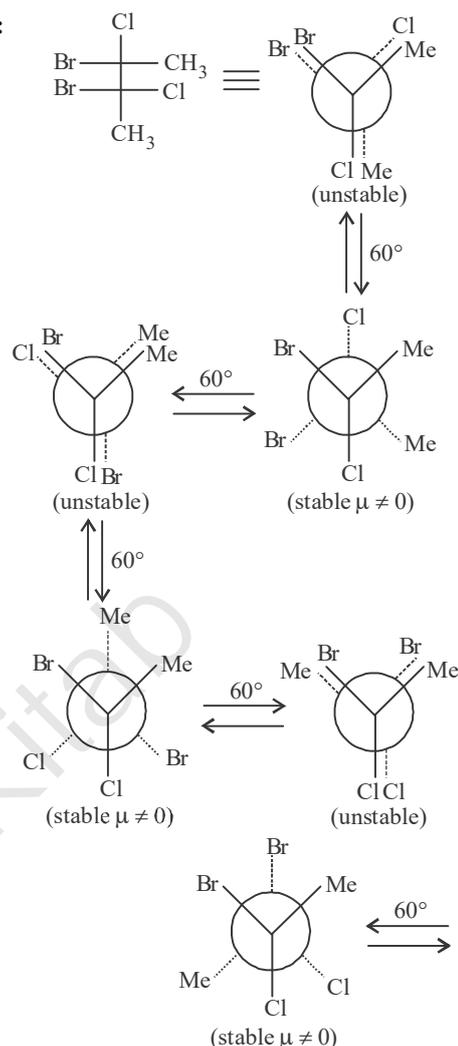


118. (4) : Out of the given compounds, those soluble in aq. NaOH are :

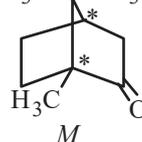


Total = 2 + 4 + 1 + 1 = 8

120. (3) :

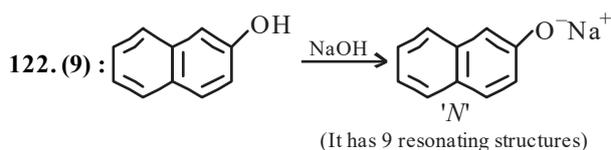


121. (2) : $H_3C-\overset{\overset{CH_3}{|}}{C^*}-\overset{\overset{CH_3}{|}}{C^*}-CH_3$



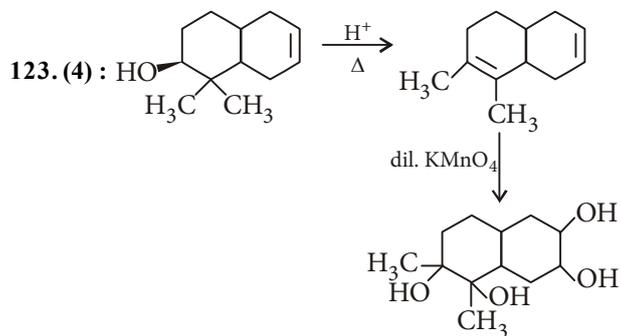
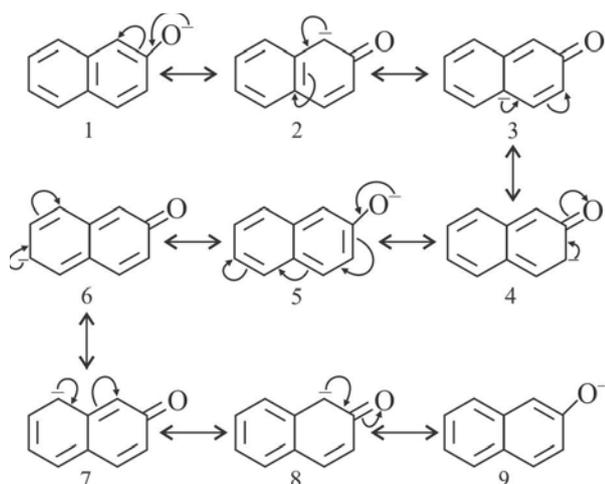
M has two chiral C-atoms thus, no. of stereoisomers = $2^n = 2^2 = 4$.

But due to bridging, rotation is not possible so, only two stereoisomers exist.

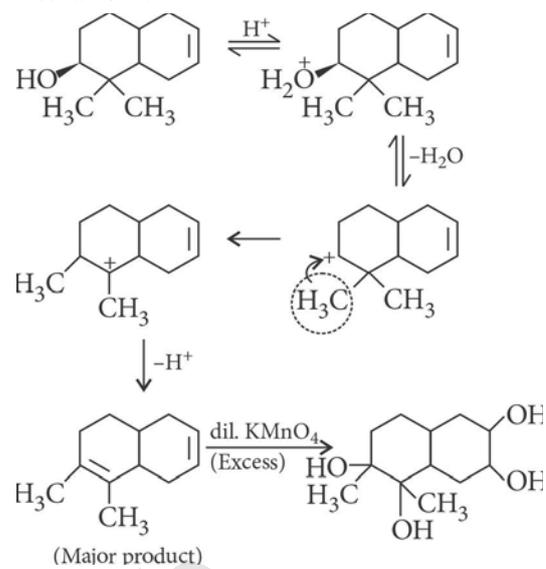


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Mechanism :



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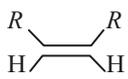
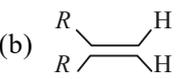
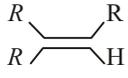
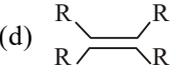
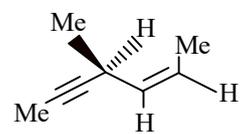
Hydrocarbons

Multiple Choice Questions with ONE Correct Answer

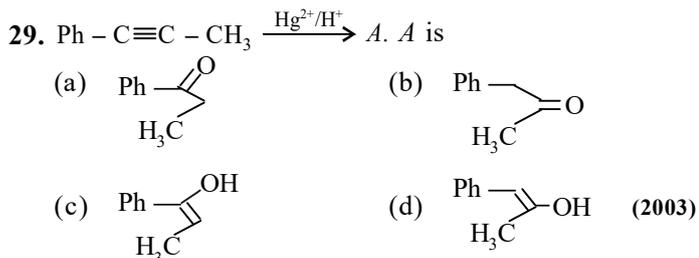
1. Which of the following will decolourise alkaline KMnO_4 solution?
(a) C_3H_8 (b) C_2H_4 (c) CH_4 (d) CCl_4 (1980)
2. Marsh gas mainly contains
(a) C_2H_2 (b) CH_4
(c) H_2S (d) CO (1980)
3. The compound with the highest boiling point is
(a) *n*-hexane (b) *n*-pentane
(c) 2, 2-dimethylpropane (d) 2-methylbutane (1982)
4. The maximum number of isomers for an alkene with the molecular formula C_4H_8 is
(a) 2 (b) 3 (c) 4 (d) 5 (1982)
5. When propyne is treated with aqueous H_2SO_4 in presence of HgSO_4 the major product is
(a) propanal
(b) propyl hydrogen sulphate
(c) acetone
(d) propanol (1983)
6. Which of the following compounds does not dissolve in concentrated H_2SO_4 even on warming?
(a) Ethylene (b) Benzene
(c) Hexane (d) Aniline (1983)
7. Baeyer's reagent is
(a) alkaline permanganate solution
(b) acidified permanganate solution
(c) neutral permanganate solution
(d) aqueous bromine solution (1984)
8. Acidic hydrogen is present in
(a) ethyne (b) ethene
(c) benzene (d) ethane (1985)
9. Anti-Markownikoff addition of HBr is not observed in
(a) propene (b) butene
(c) but-2-ene (d) pent-2-ene (1985)
10. The reaction conditions leading to the best yields of $\text{C}_2\text{H}_5\text{Cl}$ are
(a) C_2H_6 (excess) + $\text{Cl}_2 \xrightarrow{\text{UV light}}$
(b) $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow[\text{room temperature}]{\text{dark}}$
(c) $\text{C}_2\text{H}_6 + \text{Cl}_2$ (excess) $\xrightarrow{\text{UV light}}$
(d) $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{UV light}}$ (1986)
11. The highest boiling point is expected for
(a) iso-octane
(b) *n*-octane
(c) 2, 2, 3, 3-tetramethylbutane
(d) *n*-butane (1986)
12. Which of the following will have least hindered rotation about carbon-carbon bond?
(a) Ethane (b) Ethylene
(c) Acetylene (d) Hexachloroethane (1987)
13. *n*-Propyl bromide on treatment with ethanolic potassium hydroxide produces
(a) propanone (b) propene
(c) propyne (d) propanol (1987)
14. The chief reaction product of reaction between *n*-butane and bromine at 130°C is
(a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ (b) $\text{CH}_3\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\text{Br}$
(c) $\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{Br}}{\text{C}}} - \text{Br}$ (d) none of these (1995)
15. Isobutyl magnesium bromide with dry ether and absolute alcohol gives
(a) $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{MgBr}$

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- (b) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{Mg}(\text{OH})\text{Br}$
- (c) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$, $\text{CH}_2=\text{CH}_2$ and $\text{Mg}(\text{OH})\text{Br}$
- (d) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{OMgBr}$ (1995)
16. During debromination of *meso*-dibromobutane, the major compound formed is
 (a) *n*-butane (b) 1-butene
 (c) *cis*-2-butene (d) *trans*-2-butene (1997)
17. The intermediate during the addition of HCl to propene in the presence of peroxide is
 (a) $\text{CH}_3\overset{+}{\text{C}}\text{HCH}_2\text{Cl}$ (b) $\text{CH}_3\overset{+}{\text{C}}\text{HCH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_3$ (d) $\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{H}_2$ (1997)
18. When cyclohexane is poured on water, it floats, because
 (a) cyclohexane is in 'boat' form
 (b) cyclohexane is in 'chair' form
 (c) cyclohexane is in 'crown' form
 (d) cyclohexane is less dense than water. (1997)
19. $(\text{CH}_3)_3\text{CMgCl}$ on reaction with D_2O produces
 (a) $(\text{CH}_3)_3\text{CD}$ (b) $(\text{CH}_3)_3\text{OD}$
 (c) $(\text{CD}_3)_3\text{CD}$ (d) $(\text{CD}_3)_3\text{OD}$ (1997)
20. The product(s) obtained via oxymercuration ($\text{HgSO}_4 + \text{H}_2\text{SO}_4$) of 1-butyne would be
 (a) $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_3$
 (b) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CHO}$
 (c) $\text{CH}_3 - \text{CH}_2 - \text{CHO} + \text{HCHO}$
 (d) $\text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH}$ (1999)
21. Propyne and propene can be distinguished by
 (a) concentrated H_2SO_4 (b) Br_2 in CCl_4
 (c) dilute KMnO_4 (d) AgNO_3 in ammonia (2000)
22. Which one of the following will react fastest with H_2 under catalytic hydrogenation condition?
 (a)  (b) 
 (c)  (d)  (2000)
23. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff addition to alkenes because
 (a) both are highly ionic
 (b) one is oxidising and the other is reducing
 (c) one of the steps is endothermic in both the cases
 (d) all the steps are exothermic in both the cases (2001)
24. 
 Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives
 (a) an optically active compound
 (b) an optically inactive compound
 (c) a racemic mixture
 (d) a diastereomeric mixture (2001)
25. The reaction of propene with HOCl proceeds via the addition of
 (a) H^+ in the first step
 (b) Cl^+ in the first step
 (c) OH^- in the first step
 (d) Cl^+ and OH^- in a single step (2001)
26. The nodal plane in the π -bond of ethene is located in
 (a) the molecular plane
 (b) a plane parallel to the molecular plane
 (c) a plane perpendicular to the molecular plane which bisects the carbon-carbon σ -bond at right angle.
 (d) a plane perpendicular to the molecular plane which contains the carbon-carbon σ -bond. (2002)
27. Consider the following reaction

$$\text{H}_3\text{C} - \underset{\text{D}}{\underset{|}{\text{CH}}} - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_3 + \overset{\cdot}{\text{Br}} \longrightarrow \text{X} + \text{HBr}$$
 Identify the structure of the major product X.
 (a) $\text{H}_3\text{C} - \underset{\text{D}}{\underset{|}{\text{CH}}} - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \overset{\cdot}{\text{C}}\text{H}_2$ (b) $\text{H}_3\text{C} - \underset{\text{D}}{\underset{|}{\text{CH}}} - \overset{\cdot}{\text{C}} - \text{CH}_3$
 (c) $\text{H}_3\text{C} - \overset{\cdot}{\text{C}} - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_3$ (d) $\text{H}_3\text{C} - \overset{\cdot}{\text{C}}\text{H} - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_3$ (2002)
28. Identify the reagent from the following list which can easily distinguish between 1-butyne and 2-butyne.
 (a) Bromine, CCl_4
 (b) H_2 , Lindlar catalyst
 (c) Dilute H_2SO_4 , HgSO_4
 (d) Ammonical Cu_2Cl_2 solution (2002)



30. Which of the following is used for the conversion of 2-hexyne into *trans*-2-hexene?

- (a) $\text{H}_2/\text{Pd}/\text{BaSO}_4$ (b) H_2, PtO_2
(c) NaBH_4 (d) $\text{Li-NH}_3/\text{C}_2\text{H}_5\text{OH}$ (2003)

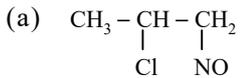
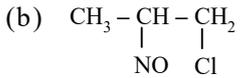
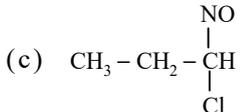
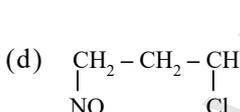
31. On monochlorination of 2-methylbutane, the total number of chiral compounds formed is

- (a) 2 (b) 4 (c) 6 (d) 8 (2004)

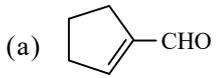
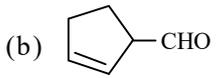
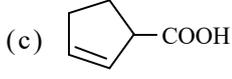
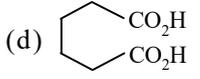
32. When phenyl magnesium bromide reacts with *t*-butanol, the product would be

- (a) benzene (b) phenol
(c) *t*-butyl benzene (d) *t*-butyl phenyl ether (2005)

33. $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{NOCl} \longrightarrow P$. Identify the adduct.

- (a)  (b) 
- (c)  (d)  (2006)

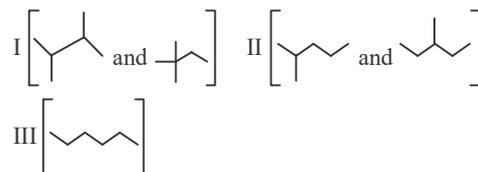
34. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E . Compound E on further treatment with aqueous KOH yields compound F . Compound F is

- (a)  (b) 
- (c)  (d)  (2007)

35. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are

- (a) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
(b) $\text{BrCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$
(c) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{C}\equiv\text{CH}$
(d) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ (2010)

36. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.



The correct order of their boiling point is

- (a) $\text{I} > \text{II} > \text{III}$ (b) $\text{III} > \text{II} > \text{I}$
(c) $\text{II} > \text{III} > \text{I}$ (d) $\text{III} > \text{I} > \text{II}$ (2014)

Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

37. Which one of the following has the smallest heat of hydrogenation per mole?

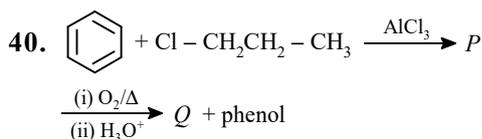
- (a) 1-Butene (b) *Trans*-2-butene
(c) *Cis*-2-butene (d) 1,3-Butadiene (1993)

38. Benzyl chloride ($\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$) can be prepared from toluene by chlorination with

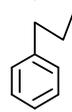
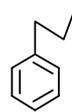
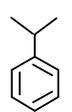
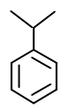
- (a) SO_2Cl_2 (b) SOCl_2 (c) Cl_2 (d) NaOCl (1998)

39. Toluene when treated with Br_2/Fe gives *p*-bromotoluene as the major product because CH_3 group

- (a) is para directing
(b) is meta directing
(c) activates the ring by hyperconjugation
(d) deactivates the ring (1999)



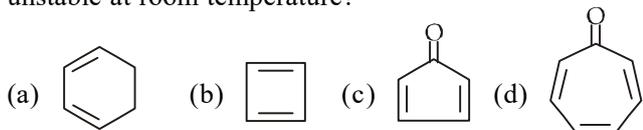
The major products P and Q are

- (a)  and $\text{CH}_3\text{CH}_2\text{CHO}$
(b)  and CH_3COCH_3
(c)  and CH_3COCH_3
(d)  and $\text{CH}_3\text{CH}_2\text{CHO}$ (2006)

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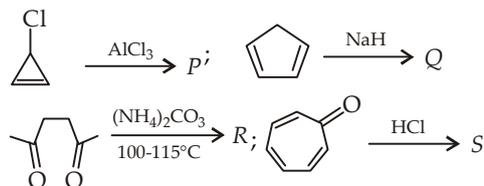
41. Which of the following molecules, in pure form, is(are) unstable at room temperature?



(2012)

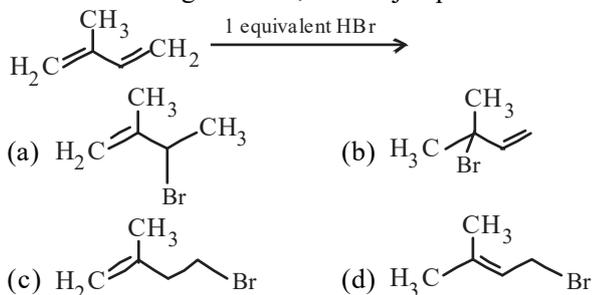
42. Among *P*, *Q*, *R* and *S*, the aromatic compound(s) is(are)

(a) *P* (b) *Q* (c) *R* (d) *S*



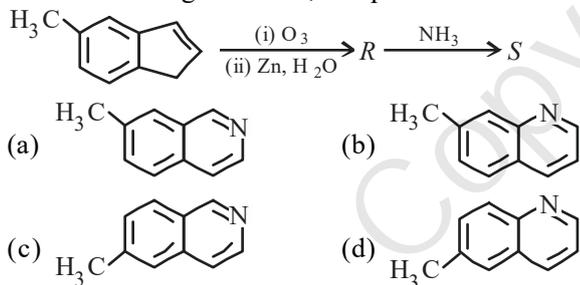
(2013)

43. In the following reaction, the major product is



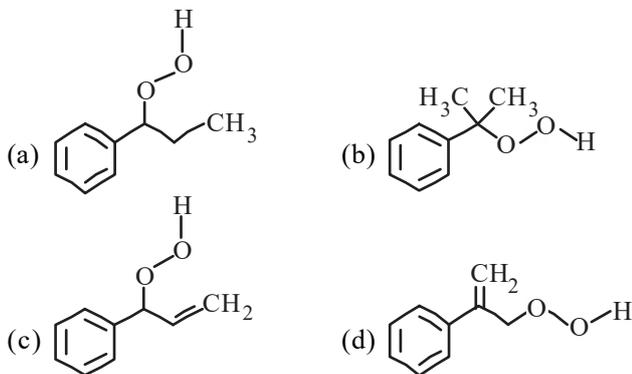
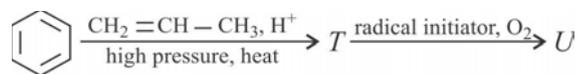
(2015)

44. In the following reactions, the product *S* is



(2015)

45. The major product *U* in the following reaction is



(2015)

Fill in the Blanks

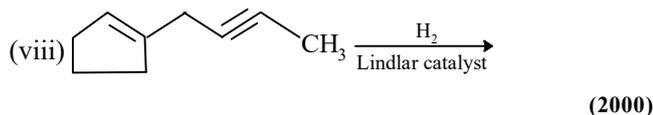
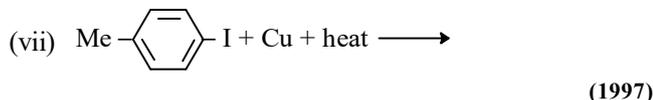
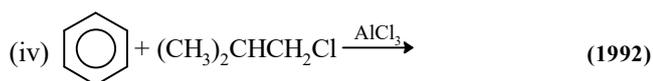
46. is most acidic. (Ethane, Ethene, Ethyne) (1981)
47. The compound prepared by the action of magnesium on ethyl bromide in dry ether is known as reagent. (1982)
48. Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess methyl iodide. The final product is (1983)
49. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with (1983)
50. The interaction of elemental sulphur with Grignard reagent followed by hydrolysis gives (1991)
51. Kolbe electrolysis of potassium succinate gives CO₂ and (1993)
52. Addition of water to acetylenic compounds is catalyzed by and (1993)
53. The bond dissociation energy needed to form the benzyl radical from toluene is than the formation of the methyl radical from methane. (1994)

True / False

54. Moist ethylene can be dried by passing it through concentrated sulphuric acid. (1982)

Subjective Problems

55. Give one characteristic test which would distinguish CH₄ from C₂H₂. (1979)
56. One mole of a hydrocarbon, (*A*) reacts with one mole of bromine giving a dibromo compound C₅H₁₀Br₂. Substance (*A*) on treatment with cold dilute alkaline potassium permanganate solution forms a compound C₅H₁₂O₂. On ozonolysis (*A*) gives equimolar quantities of propanone and ethanal. Deduce the structural formula of (*A*). (1981)
57. Write the structural formula of the major product in each of the following cases:
- the compound obtained by hydration of ethyne is treated with dilute alkali (1981)
 - bromoethane reacts with one-half of the molar quantity of silver carbonate. (1981)
 - ethene mixed with air is passed under pressure over a silver catalyst at 250°C. (1981)



58. Outline the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two). (1981)

59. State with balanced equations, what happens when:

(i) Propene is bubbled through a hot aqueous solution of potassium permanganate. (1982)

(ii) Chloral is heated with aqueous sodium hydroxide. (1984)

60. Give reasons for the following:

(i) Methane does not react with chlorine in the dark. (1983)

(ii) Propene reacts with HBr to give isopropyl bromide but does not give *n*-propyl bromide. (1983)

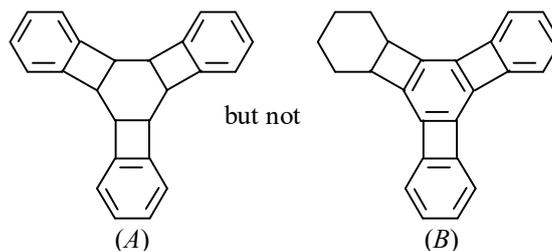
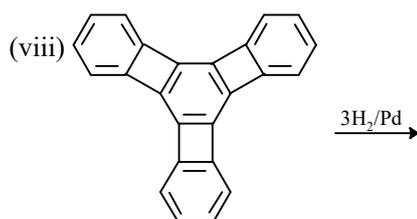
(iii) Although benzene is highly unsaturated, normally it does not undergo addition reaction. (1983)

(iv) Toluene reacts with bromine in the presence of light to give benzyl bromide while in presence of FeBr_3 it gives *p*-bromotoluene. Give explanation for the above observations. (1996)

(v) Explain very briefly why alkynes are generally less reactive than alkenes towards electrophilic reagents such as H^+ . (1997)

(vi) The carbon-carbon bond in 1, 3-butadiene is shorter than that of *n*-butane. (1998)

(vii) *tert*-Butylbenzene does not give benzoic acid on treatment with acidic KMnO_4 . (2000)



(2005)

61. State the conditions under which the following preparation is carried out. Give the necessary equations which need not be balanced:

Lead tetraethyl from sodium-lead alloy (1983)

62. (i) '2-Methyl propene can be converted into isobutyl bromide by hydrogen bromide', is true under what conditions?

(ii) 'Ethyne and its derivatives will give white precipitate with ammonical silver nitrate solution', is true under what conditions? (1984)

63. A certain hydrocarbon *A* was found to contain 85.7 percent carbon and 14.3 percent hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon *B*. 1.00 g of hydrocarbon *A* just decolourised 38.05 g of a 5 per cent solution (by weight) of Br_2 in CCl_4 . Compound *A*, on oxidation with concentrated KMnO_4 , gave compound *C* (molecular formula $\text{C}_4\text{H}_8\text{O}$) and acetic acid. Compound *C* could easily be prepared by the action of acidic aqueous mercuric sulphate on 2-butyne. Determine the molecular formula of *A* and deduce the structure of *A*, *B* and *C*. (1984)

64. How would you distinguish between

(i) 2-butyne and 1-butyne (1985)

(ii) cyclohexane and cyclohexene (1988)

65. How can you prepare benzene from lime? (1987)

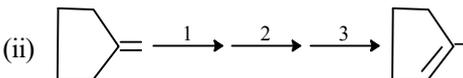
66. What happens when excess chlorine is passed through boiling toluene in the presence of sunlight? (1987)

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

Hydrocarbons

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68. *n*-Butane is produced by the monobromination of ethane followed by the Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g *n*-butane, if the bromination takes place with 90 percent yield and the Wurtz reaction with 85 percent yield. (1989)
69. Identify, $B(C_4H_8)$ which adds on HBr in the presence and in the absence of peroxide to give the same product, C_4H_9Br . (1993)
70. Identify, $D(C_6H_{12})$, an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound, C_6H_{14} . (1993)
71. 1, 4-Pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound *X* which upon reaction with excess of Mg in dry ether forms *Y*. Compound *Y* on treatment with ethyl acetate followed by dilute acid yields *Z*. Identify the structures of compounds *X*, *Y* and *Z*. (1995)
72. An organic compound $E(C_5H_8)$ on hydrogenation gives compound $F(C_5H_{12})$. Compound *E* on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound *E*. (1995)
73. A hydrocarbon *A*, of the formula C_8H_{10} , on ozonolysis gives compound $B(C_4H_6O_2)$ only. The compound *B* can also be obtained from the alkyl bromide, $C(C_3H_5Br)$ upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify *A*, *B* and *C* and also give equations for the reactions. (1996)
74. Give the structures of the major organic products from 3-ethyl-2-pentene under each of the following reaction conditions :
 (a) HBr in the presence of peroxide
 (b) Br_2/H_2O
 (c) $Hg(OAc)_2/H_2O; NaBH_4$ (1996)
75. Write down the structures of *A* and *B*.

$$PhC \equiv CH \xrightarrow{NaNH_2/MeI} A \xrightarrow{Na/NH_3(0)} B$$
 (1997)
76. One mole of the compound *A* (molecular formula C_8H_{12}), incapable of showing stereoisomerism, reacts with only one mole of H_2 on hydrogenation over Pd. *A* undergoes ozonolysis to give a symmetrical diketone $B(C_8H_{12}O_2)$. What are the structures of *A* and *B*? (1997)
77. The hydrocarbon *A*, adds one mole of hydrogen in the presence of a platinum catalyst to form *n*-hexane. When *A* is oxidised vigorously with $KMnO_4$, a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of *A* and explain. (1997)
78. Show the steps to carry out the following transformations.
 (i) Ethylbenzene \longrightarrow benzene (1998)
 (ii) Ethylbenzene \longrightarrow 2-phenylpropanoic acid. (1998)
79. Complete the following reactions with appropriate structures of product/reagents.
 (i) $C_6H_5CH=CH_2 \xrightarrow{Br_2} [A] \xrightarrow[\text{(ii) } CH_3I]{\text{(i) } NaNH_2(3.0 \text{ equiv.})} [B]$ (1998)
- (ii)  (1999)
80. An alkene (*A*) $C_{16}H_{16}$ on ozonolysis gives only one product (*B*) C_8H_8O . Compound (*B*) on reaction with $NaOH/I_2$ yields sodium benzoate. Compound (*B*) reacts with KOH/NH_2NH_2 yielding a hydrocarbon (*C*) C_8H_{10} . Write the structures of compounds (*B*) and (*C*). Based on this information, two isomeric structures can be proposed for alkene (*A*). Write their structures and identify the isomer which on catalytic hydrogenation ($H_2/Pd - C$) gives a racemic mixture. (2001)
81. Write down the heterogeneous catalyst involved in the polymerisation of ethylene. (2003)
82. $A(C_6H_{12}) \xrightarrow{HCl} B + C$
 $(C_6H_{13}Cl)$
 $B \xrightarrow{\text{alc. KOH}} D$ (isomer of *A*)
 $D \xrightarrow{\text{ozonolysis}} E$ (it gives negative test with Fehling solution but responds to iodoform test).
 $A \xrightarrow{\text{ozonolysis}} F + G$ (both gives positive Tollen's test but do not give iodoform test).
 $F + G \xrightarrow{\text{conc. NaOH}} HCOONa + A$ primary alcohol
 Identify from *A* to *G*. (2003)
83. Draw Newmann projection of relatively less stable staggered form of *n*-butane. What is the reason of low stability of this form van der Waals repulsion, torsional strain, or both? (2004)
84. Write the structures of $(CH_3)_3N$ and $(Me_3Si)_3N$. Are they isostructural? Justify your answer. (2005)

Reasoning Type

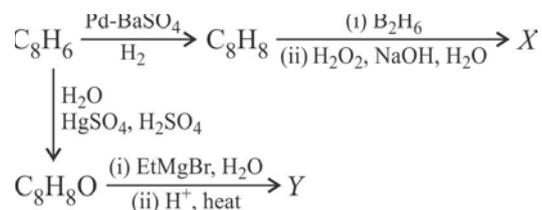
This section contains reasoning type questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Hydrocarbons

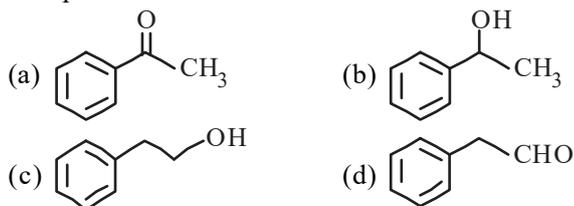
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Comprehension - 3

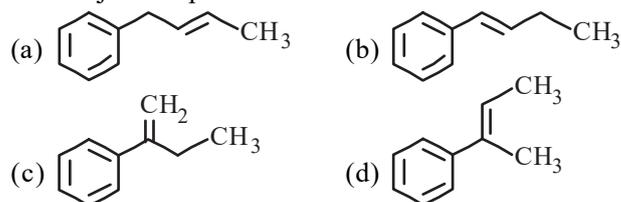
In the following reactions



92. Compound X is



93. The major compound Y is



(2015)

Integer Answer Type

94. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentyl-hexane using alcoholic KOH is

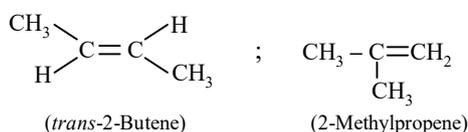
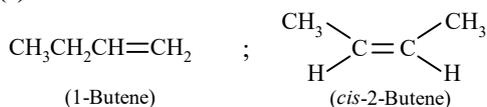
(2011)

ANSWER KEY

- | | | | | | |
|-----------------------------------|-----------------|--------------|--|--------------|------------------|
| 1. (b) | 2. (b) | 3. (a) | 4. (c) | 5. (c) | 6. (c) |
| 7. (a) | 8. (a) | 9. (c) | 10. (a) | 11. (b) | 12. (a) |
| 13. (b) | 14. (b) | 15. (b) | 16. (d) | 17. (b) | 18. (d) |
| 19. (a) | 20. (a) | 21. (d) | 22. (a) | 23. (c) | 24. (b) |
| 25. (b) | 26. (a) | 27. (b) | 28. (d) | 29. (a) | 30. (d) |
| 31. (b) | 32. (a) | 33. (a) | 34. (a) | 35. (d) | 36. (b) |
| 37. (b) | 38. (c) | 39. (a, c) | 40. (c) | 41. (b, c) | 42. (a, b, c, d) |
| 43. (d) | 44. (a) | 45. (b) | 46. Ethyne | 47. Grignard | 48. 2-Butyne |
| 49. C ₂ H ₂ | 50. Thioalcohol | 51. Ethylene | 52. H ₂ SO ₄ , HgSO ₄ | 53. Less | 54. False |
| 85. (a) | 86. (c) | 87. (b) | 88. (d) | 89. (b) | 90. (a) |
| 91. (c) | 92. (c) | 93. (d) | 94. (5) | | |

Explanations

- (b): Because it is an unsaturated hydrocarbon.
- (b): Methane is the principal product of organic decay in swamps and marshes, the gas being set free by the action of bacteria, this method of formation in nature has given rise to the name marsh gas for methane.
- (a): Higher the molecular weight higher is the b.p., *i.e.*, *n*-hexane.
- (c): Four isomers are

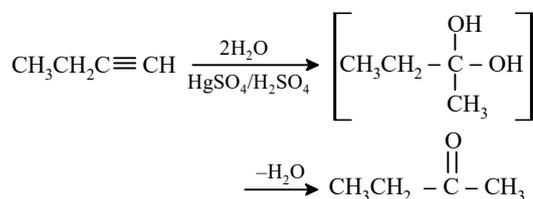


- (c): $\text{CH}_3\text{C}\equiv\text{CH} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4, \text{HgSO}_4} \text{CH}_3\text{CH}(\text{OH})=\text{CH}_2$
 CH_3COCH_3 (acetone)
- (c): $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CH}_3\text{CH}_2\text{OSO}_3\text{H}$
 $\text{C}_6\text{H}_6 + \text{H}_2\text{SO}_4 \longrightarrow \text{C}_6\text{H}_5\text{SO}_3\text{H} + \text{H}_2\text{O}$
 $\text{C}_6\text{H}_{14} + \text{H}_2\text{SO}_4 \longrightarrow$ No reaction
 $\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{C}_6\text{H}_5\text{NH}_3^+\text{HSO}_4^-$
 Thus only hexane (C_6H_{14}) does not dissolve in H_2SO_4 , even on warming.
- (a): Alkaline potassium permanganate is called Baeyer's reagent.
- (a): In alkynes acidic hydrogen is present and it is attached to triply bonded C atoms. The hydrogen can be easily removed by means of a strong base.
- (c): Anti-Markownikoff's addition of HBr is observed only with unsymmetrical alkenes *i.e.* propene, 1-butene, pent-2-ene. As 2-butene is symmetrical so in its case anti-Markownikoff's addition will not be observed.
- (a): Chlorination beyond monochlorination in the preparation of alkyl halides in presence of ultraviolet light is suppressed if excess alkane is used.
 $\text{C}_2\text{H}_6(\text{excess}) + \text{Cl}_2 \xrightarrow{\text{U.V. light}} \text{C}_2\text{H}_5\text{Cl}$
- (b): In *n*-octane we find the longest carbon chain of eight carbon atoms so its b.p. will be highest.
- (a): In ethylene there is restricted rotation where as in acetylene there is no rotation. Hexachloromethane has more rotation than ethylene but less than ethane because of larger

size of chlorine atoms present in it than those of hydrogen atoms in ethane.

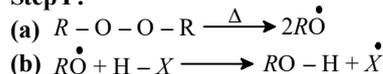
- (b): $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Br} \xrightarrow[\text{-HBr}]{\text{Alc. KOH}} \text{CH}_3\text{CH}=\text{CH}_2$ (Propene)
- (b): The chief product formed would be $\text{CH}_3\text{CH}_2\underset{\text{CH}_3}{\text{CH}}-\text{Br}$
 A 2° H-atom is extracted more easily than 1° H-atom.
- (b): $\text{CH}_3-\overset{\text{CH}_3}{\text{C}}\text{HCH}_2\text{MgBr} \xrightarrow[\text{dry ether}]{\text{C}_2\text{H}_5\text{OH}} \text{CH}_3-\overset{\text{CH}_3}{\text{C}}\text{HCH}_2\text{C}_2\text{H}_5 + \text{Mg} \begin{array}{l} \text{Br} \\ \diagup \end{array}$
- (d): It is a *trans*-elimination reaction. Thus *meso*-di-bromobutane on debromination yields *trans*-2-butene.
- (b): No peroxide effect is observed in addition of H-Cl.
- (d): Cyclohexane is less denser than water so it floats.

- (a): $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{MgCl} + \text{D}_2\text{O} \xrightarrow{\text{Peroxide}} \text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{D} + \text{Mg} \begin{array}{l} \text{OD} \\ \diagup \\ \text{Cl} \end{array}$
- (a): Hydration of alkynes *via* mercuration occurs according to Markownikoff's rule.

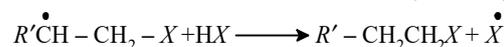
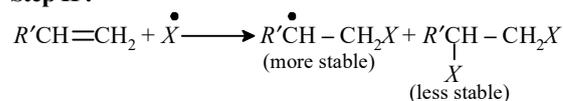


- (d): The terminal hydrogen is acidic in $\text{CH}_3\text{C}\equiv\text{CH}$ (propyne) and it reacts with ammonical AgNO_3 . In propene, $\text{CH}_3\text{CH}=\text{CH}_2$, there is no acidic hydrogen.
- (a): From amongst given olefins (a) and (b) are less stable (Saytzeff's rule). Moreover *syn*-isomer is more reactive than *anti*-because of sterical hindrance.
- (c): Because one of the steps is endothermic in both cases.

Step I:



Step II:

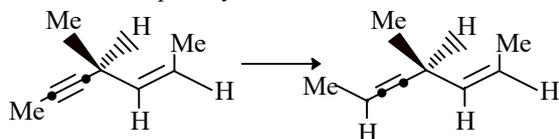


For HCl step I(b) is endothermic and step II is exothermic.
 For HI step I(b) is exothermic and step II is endothermic.

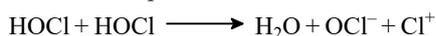
Hydrocarbons

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24. (b): Addition on a triple bond occurs by *syn*-addition of hydrogen. The configuration of double bond already present is *cis*. The compound formed will have a plane of symmetry and thus it will be optically inactive.



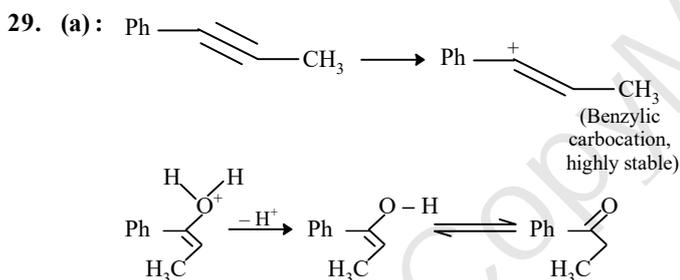
25. (b): Alkenes undergo electrophilic addition reactions. HOCl on self ionisation produces Cl^+ which attacks first.



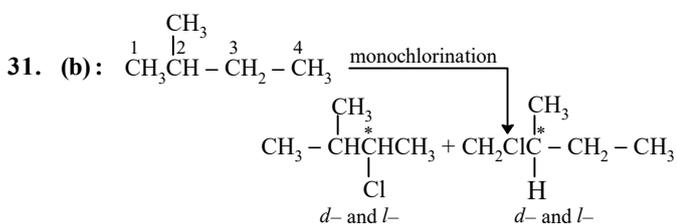
26. (a): Formation of a π -bond occurs by the sideways overlap of *p*-orbitals of two C-atoms. The molecular plane does not have any π -electron density since the *p*-orbitals are perpendicular to the plane containing the ethene molecule. The nodal plane in the π -bond of ethene is located in the molecular plane.

27. (b): Br^\bullet is less reactive and more selective and so the most stable free radical (3° free radical) will be the major product.

28. (d): There will be no reaction between but-2-yne and Cu_2Cl_2 because it has no acidic hydrogen. In but-1-yne the terminal hydrogen is acidic ($\text{CH}_3\text{CH}_2 - \text{C} \equiv \text{CH}$) so it will give a red ppt. with ammonical Cu_2Cl_2 .

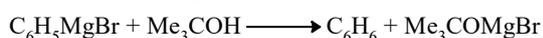


30. (d): When an alkyne is reduced with H_2 in presence of Pd/BaSO_4 , a *cis*-alkene is obtained. H_2/Pt will reduce it (alkyne) to an alkane. An alkyne will not be reduced by NaBH_4 . A *trans*-alkene will be formed by reduction of an alkyne by active metal in liquid NH_3 .

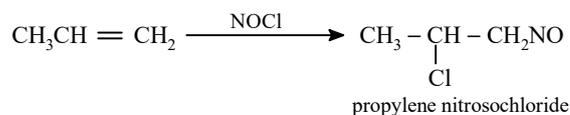


Chlorination at C - 2 and C - 4 produces no chiral compound.

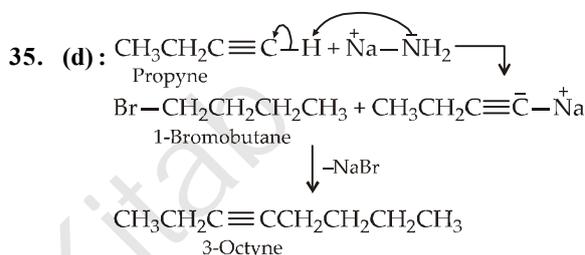
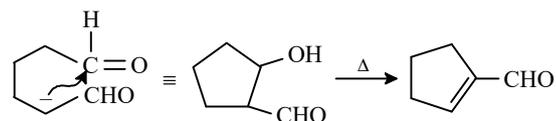
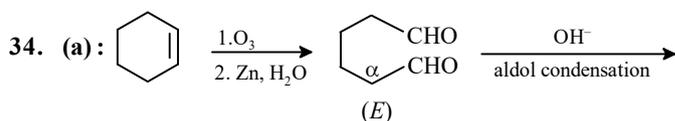
32. (a): Grignard reagent reacts with compounds containing active hydrogen to form hydrocarbons corresponding to alkyl (or aryl) part of the reagent.



33. (a): $\text{NOCl} \rightarrow \text{NO}^+ + \text{Cl}^-$



The reaction follows Markownikoff's rule.

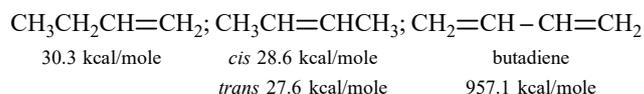


36. (b): More the branching, lesser will be the surface area and lesser will be the boiling point as van der Waals forces decrease.

Hence, the correct order of their boiling point is $\text{III} > \text{II} > \text{I}$.

37. (b): We know that higher the stability, lower is the heat of hydrogenation. But-2-ene is more stable than but-1-ene because the double bond present in but-2-ene is in the centre of the molecule ($\text{CH}_3\text{CH}=\text{CHCH}_3$). Moreover *trans*-2-butene is more stable than *cis*-2-butene and thus its *i.e.* *trans*-2-butene, heat of hydrogenation per mole will be less.

Values of heats of hydrogenation are listed here :

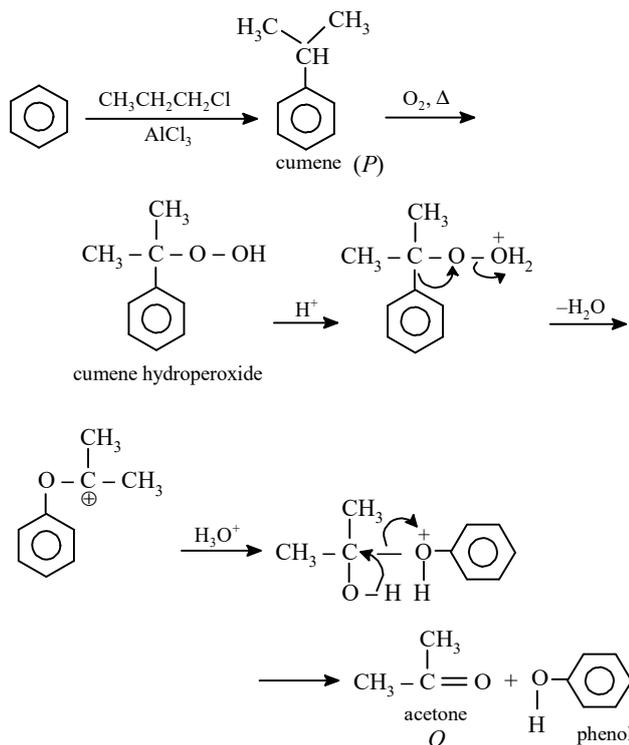


Trans-2-butene is more stable than *cis*-2-butene because in *trans*-2-butene the bulky groups are far apart whereas in *cis*-2-butene the bulky groups are crowded together. Due to this *cis*-isomer has more van der Waals strain than *trans*-isomer and thus *cis*-isomer is less stable.

38. (c): Chlorination of toluene to form benzyl chloride is a free radical substitution reaction. Only Cl_2 can give Cl^\bullet (chlorine free radical) in presence of light.

39. (a, c): Methyl group activates the benzene nucleus due to its electron releasing nature and also shows hyperconjugation. It is an *ortho* and *para*-directing group *i.e.*, on substitution it forms always a mixture of *ortho* and *para* derivatives.

40. (c) : It is cumene hydroperoxide rearrangement reaction.



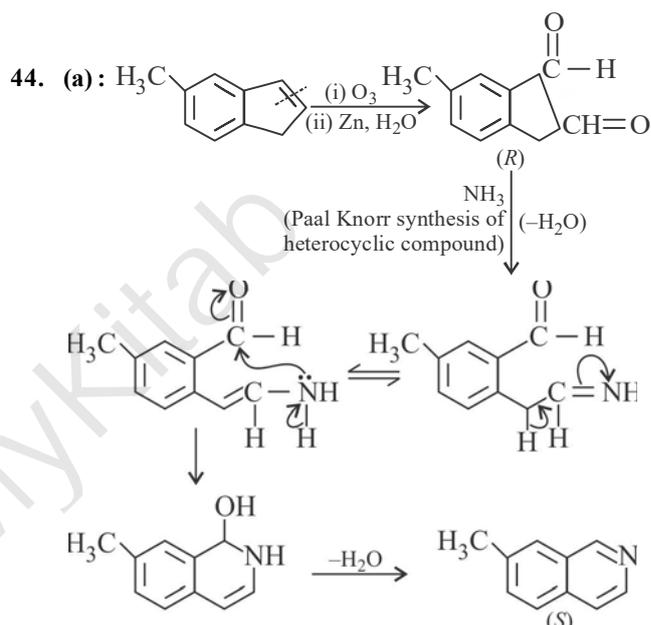
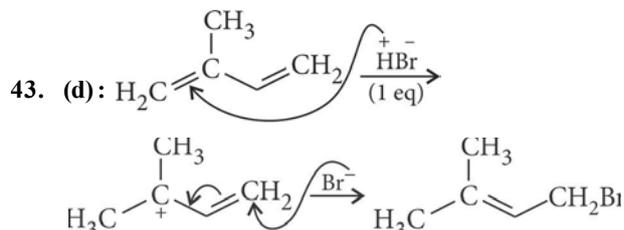
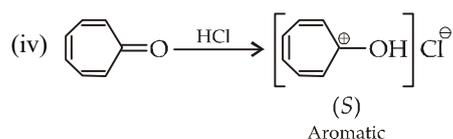
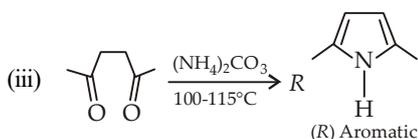
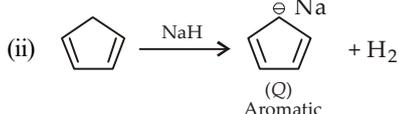
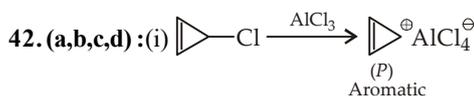
Mechanism:

Step I : In the formation of product P, the electrophile $\text{CH}_3\text{CH}_2\text{CH}_2^\oplus$ rearranges to $\text{CH}_3\text{CH}^\oplus\text{CH}_3$ for the electrophilic substitution.

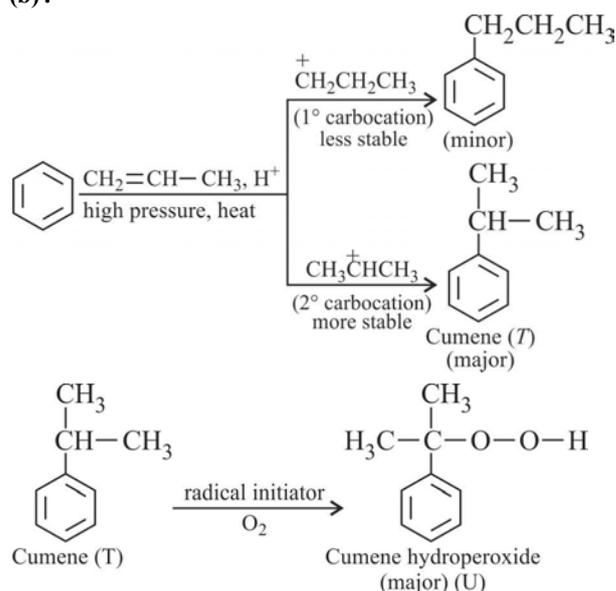
Step II : Cumene (iso-propyl benzene) is oxidised by exposure to air to temporarily produce cumene hydroperoxide.

Step III : Cumene hydroperoxide is then hydrolysed in an acidic medium to give phenol and acetone. Loss of water molecule from the hydroperoxide leaves an electron-deficient oxygen. Migration of the phenyl to the oxygen leads to a more stable resonance hybridised structure of tertiary benzylic radical, which in turn produce acetone and phenol after an attachment of a water molecule and rearrangement.

41. (b, c) : (b) and (c) are antiaromatic and unstable while (a) is non-aromatic and (d) is aromatic and stable at room temperature.



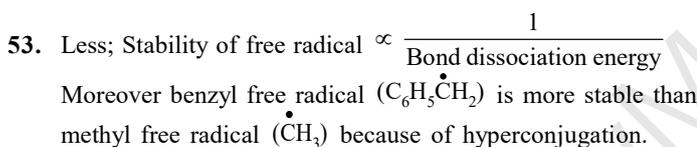
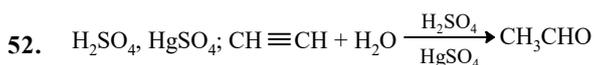
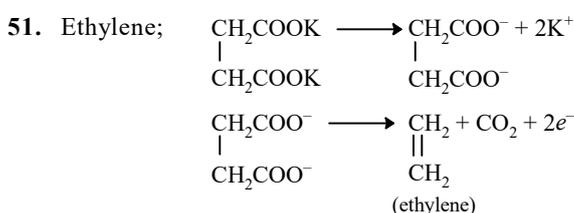
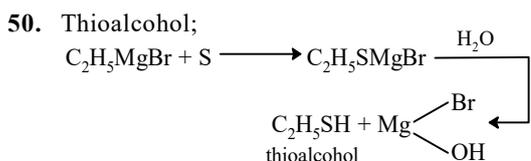
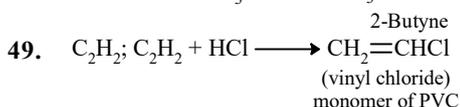
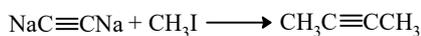
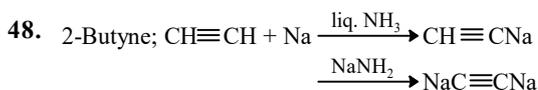
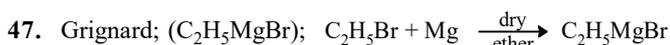
45. (b) :



46. Ethyne; Due to high *s*-character (*sp* hybrid) of $\text{C} \equiv \text{C}$ bond in ethyne.

Hydrocarbons

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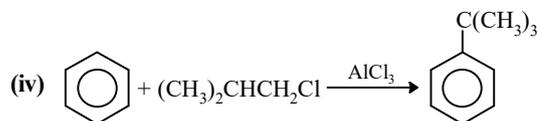
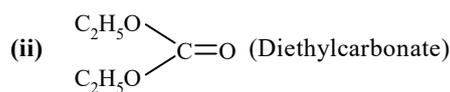
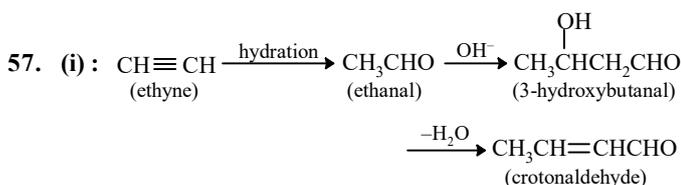
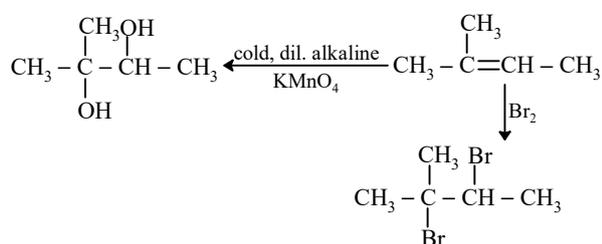
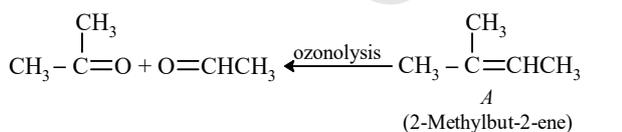


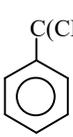
54. False

Ethylene reacts with sulphuric acid to form ethyl hydrogen sulphate. It can be dried by passing it through P_2O_5 .

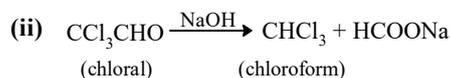
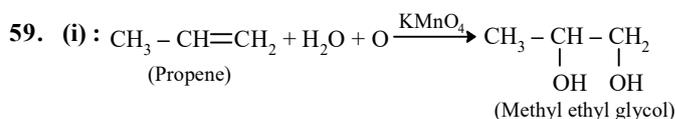
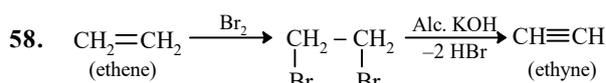
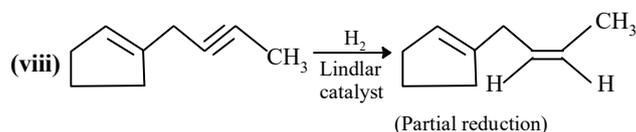
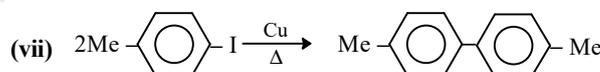
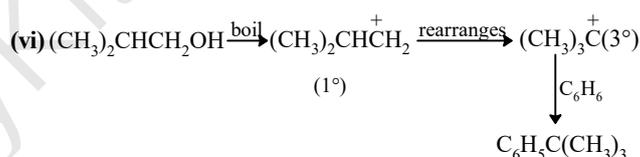
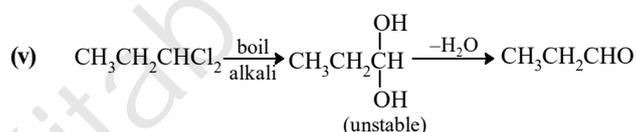
55. Bromine water test : C_2H_2 decolourises while CH_4 does not.

56. As the compound *A* on ozonolysis forms equimolar quantities of propanone and ethanal so *A* should be 2-methylbut-2-ene.



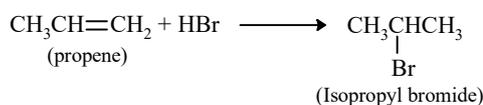
The above product (i.e. ) is formed because the

carbocation $(CH_3)CHCH_2^+$ (1°) formed during reaction arranges to more stable carbocation $(CH_3)_3C^+$ (3°).



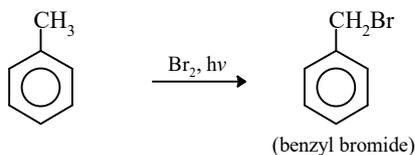
60. (i) : Chlorination of methane involves a free radical mechanism. In dark chlorine does not yield chlorine free radicals ($\cdot Cl$) and so the reaction does not occur.

(ii) Addition of HBr in this case will occur according to Markownikoff's rule since peroxide is not present.

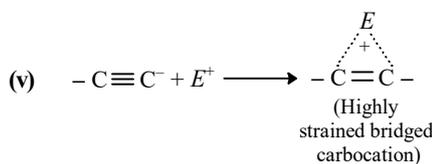
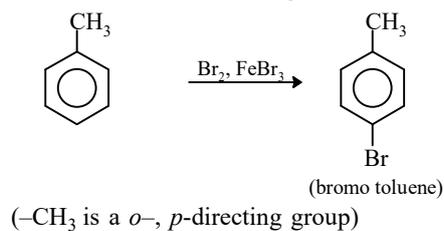


(iii) π -electrons of benzene are delocalised and so these are unreactive towards addition reactions.

(iv) In presence of sunlight, toluene undergoes side chain bromination through a free radical mechanism.

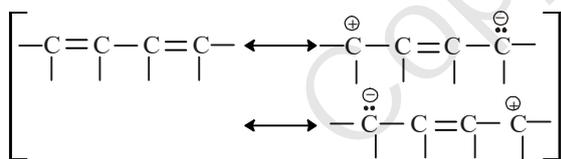


In presence of FeBr_3 , toluene undergoes electrophilic substitution in the benzene ring



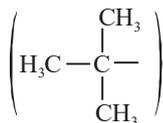
The bridged intermediate carbocation formed by the initial attack of the electrophile on the $-\text{C}\equiv\text{C}-$ triple bond is less stable since it is highly strained. Also in acetylenic carbon atoms, the π -electrons are held more tightly by carbon nuclei and so they are less readily available for reaction with electrophiles.

(vi) 1, 3-Butadiene, being a conjugated diene, is a resonance hybrid.

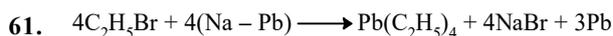


In it we find two structures as charged structures and they induce some double bond character in the central $\text{C}-\text{C}$ bond and so this bond gets shortened.

(vii) Benzoic acid is not obtained when *tert.*-butylbenzene is treated with acidic KMnO_4 , because *tert.*-butyl group does not contain any hydrogen on central C-atom.



(viii) Hydrogenation takes place on the surface of catalyst through adsorption-desorption steps. The three benzene rings attached to the central benzene ring are not in the same plane during adsorption. Only central benzene ring will directly be adsorbed on the surface of Pd where hydrogenation will occur.



62. (i) : Under ordinary conditions *tert.*-butyl bromide is formed. In presence of peroxide isobutyl bromide is formed.

(ii) Only ethyne and the derivatives having at least one acetylenic hydrogen atom ($-\text{C}\equiv\text{CH}$) will form a white ppt. with ammonical silver nitrate solution at room temperature.

63. Empirical Formula of A

Element	%age	Relative number of atoms	Simplest whole number ratio
Carbon (C)	85.7	$85.7/12 = 7.14$	$7.14/7.14 = 1$
Hydrogen (H)	14.3	$14.3/1 = 14.3$	$14.3/7.14 = 2$

\therefore Empirical formula of A is CH_2 .

Molecular formula of A

1 g of A needs $\text{Br}_2 = 38.05$ g of 5% Br_2

$$= \frac{38.05}{100} \times 5 \text{ g of } 100\% \text{ Br}_2 = 1.90 \text{ g of } 100\% \text{ Br}_2$$

\therefore 1.90 g of Br_2 is consumed by 1 g of compound A

\therefore 160 g (1 mole) of Br_2 will be consumed by

$$= \frac{1}{1.90} \times 160 \text{ g of } A = 84.2 \text{ g of } A$$

Hence molecular weight of A = 84

Empirical formula of A = CH_2

\therefore Empirical formula weight of A = $12 + 2 \times 1 = 14$

$$\text{Hence } n = \frac{\text{Molecular wt.}}{\text{Emp. formula wt.}} = \frac{84}{14} = 6$$

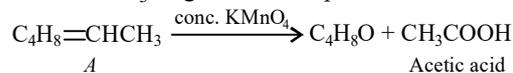
\therefore Molecular formula of A = $n \times$ Empirical formula

$$= 6 \times \text{CH}_2 \text{ or } (\text{CH}_2)_6 = \text{C}_6\text{H}_{12}$$

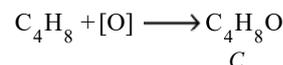
Structural formula

Since A (a hydrocarbon) consumes 1 molar equivalent of hydrogen so it contains one $\text{C}-\text{C}$ double bond.

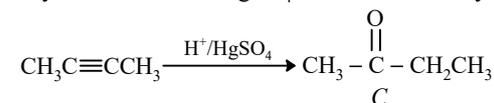
The formation of compound C ($\text{C}_4\text{H}_8\text{O}$) and acetic acid when the compound A is oxidised by KMnO_4 indicates the presence of $=\text{CHCH}_3$ fragment in compound A i.e., A is



The fragment C_4H_8 of A on oxidation forms the compound C ($\text{C}_4\text{H}_8\text{O}$).



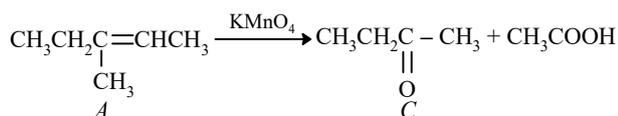
Since the compound C ($\text{C}_4\text{H}_8\text{O}$) can be easily obtained from butyne-2 and acidic HgSO_4 so C must be ethylmethyl ketone.



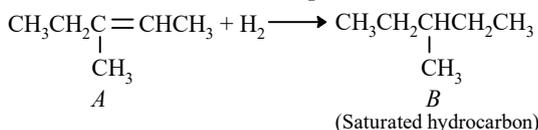
The formation of ketone C from C_4H_8 fragment of A can be explained by the following structure of A

Hydrocarbons

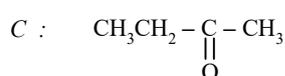
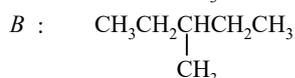
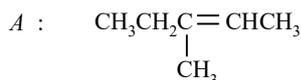
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The formation of *B* can be represented as under:

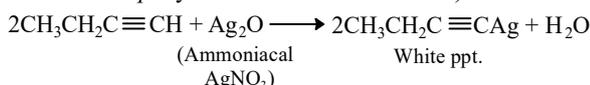


Thus



64. (i) : Ammoniacal AgNO_3 solution will give a white ppt. with terminal alkynes.

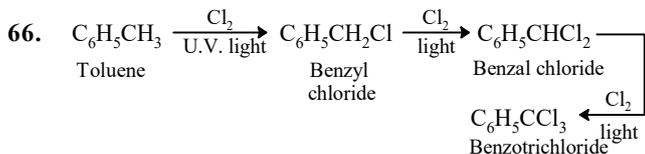
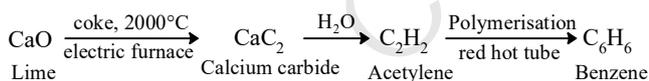
Ammonical Cu_2Cl_2 will give a red ppt. with terminal alkynes. (Terminal alkynes contain acidic hydrogen atom. H atom attached to *sp* hybridised carbon is acidic.)



(In $\text{CH}_3\text{C}\equiv\text{CCH}_3$, no acidic hydrogen is present)

(ii) Cyclohexane does not respond to bromine water test or Baeyer's test but cyclohexene gives positive response to bromine water test (*i.e.* decolourises bromine water) and Baeyer's reagent test.

65.



This follows free radical mechanism.

67. The two isomers of *X* are *Y* and *Z*.
The compound *X* contains C, H and Cl.

$$\% \text{ age of Cl in compound } X = \frac{35.5 \times 2.9}{143.5} \times 100 = 71.74\%$$

Empirical formula of *X*

Element	% age	Relative number of atoms	Simplest whole number ratio
C	24.24	24.24/12 = 2.02	2.02/2.02 = 1
H	4.04	4.04/1 = 4.04	4.04/2.02 = 2
Cl	71.74	71.74/35.5 = 2.02	2.02/2.02 = 1

Hence empirical formula of *X* is CH_2Cl .

Since both the isomers of *X* (*i.e.* *Y* and *Z*) react with aqueous KOH.

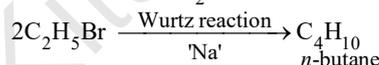
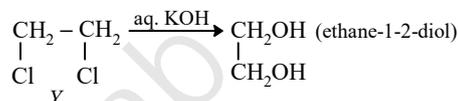
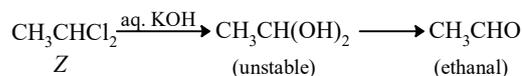
$\therefore Y \xrightarrow{\text{aq. KOH}}$ dihydroxy compound *i.e.*, *Y* has two Cl atoms on adjacent C-atoms.

$Z \xrightarrow{\text{aq. KOH}}$ CH_3CHO *i.e.*, *Z* has two Cl atoms on the same C atom.

Thus *Y* should be $\text{CH}_2(\text{Cl})-\text{CH}_2(\text{Cl})$ (1, 2 -dichloroethane)

and *Z* should be CH_3CHCl_2 (1, 1 -dichloroethane)

Reactions



Amount of *n*-butane to be produced = 55/58 mol

$$\left[\text{mol. wt. of } n\text{-butane} = 58 \right]$$

$$= 0.948 \text{ mol.}$$

Amount of $\text{C}_2\text{H}_5\text{Br}$ required to obtain 0.948 mol of

$$\text{C}_4\text{H}_{10} = 2 \times 0.948 \text{ mol}$$

\therefore Amount of 85% $\text{C}_2\text{H}_5\text{Br}$ required is $\frac{2 \times 0.948 \times 100}{85}$ mol

$$[\because \text{yield} = 85\%]$$

Since one mol of C_2H_6 gives one mole of $\text{C}_2\text{H}_5\text{Br}$ and % yield of monobromination is 90%, hence amount of C_2H_6 required is

$$\frac{2 \times 0.948 \times 100}{85 \times 90} \times 100 = 2.48 \text{ mol}$$

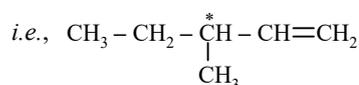
Volume of 2.23 mol of ethane at NTP = 2.48 \times 22400 ml
= 55552 ml
= 55.552 Litres

Hence, required volume of ethane = 55.552 Litres.

69. *B* must be a symmetric alkene (butene-2, $\text{CH}_3\text{CH}=\text{CHCH}_3$) because it will form the same product in presence as also in absence of peroxide. In both cases the product will be $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$.

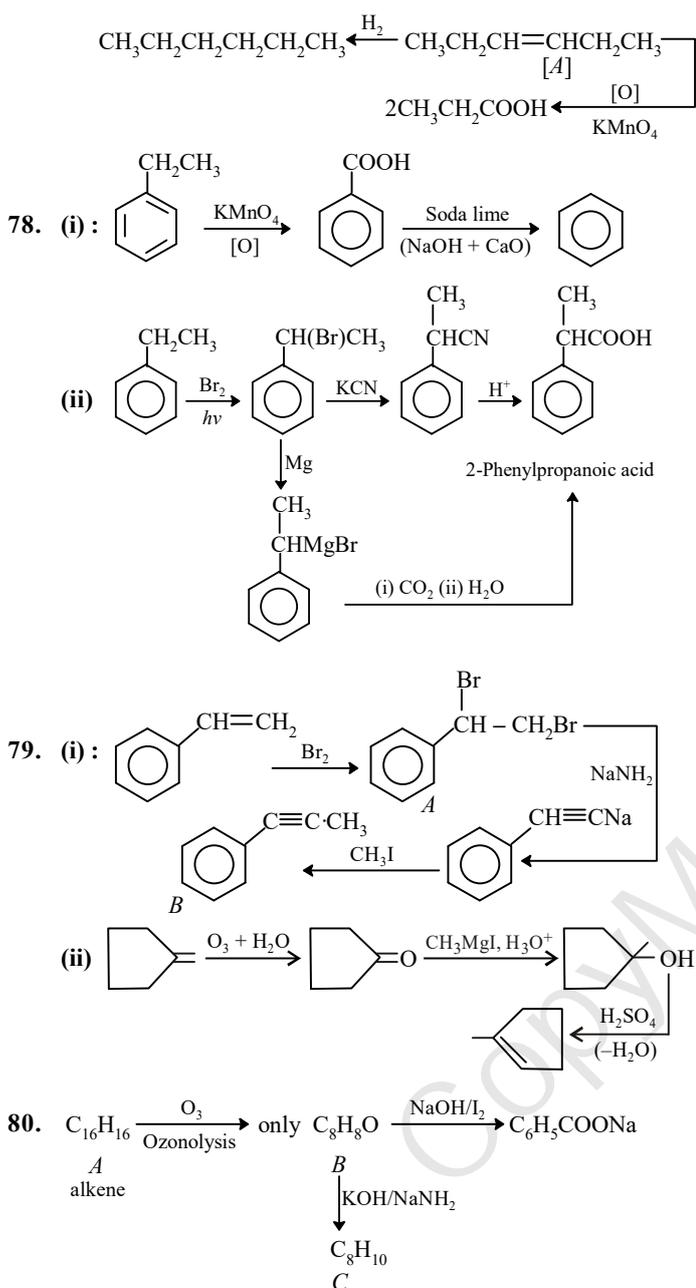
70. Since the hydrocarbon (*D*) is optically active so it must have an asymmetric carbon atom. The product C_6H_{14} obtained on hydrogenation of *D* (*i.e.* C_6H_{12}) is not optically active so it has no asymmetric carbon atom.

On the basis of above information we can assume that *D* (C_6H_{12}) is 3-methylpent-1-ene.



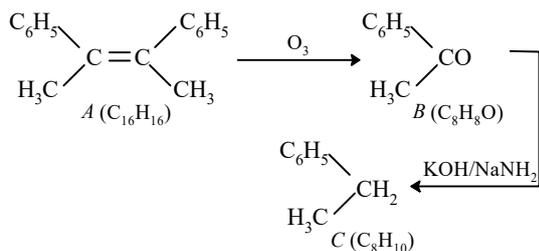
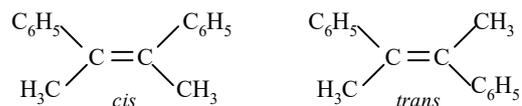
Hydrocarbons

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(i) Conversion of *B* to *C* indicates the presence of $-\text{COCH}_3$ group in *B* so structural formula of *B* is $\text{C}_6\text{H}_5\text{COCH}_3$.

(ii) Since only compound *B* is obtained from alkene *A*, the alkene must be

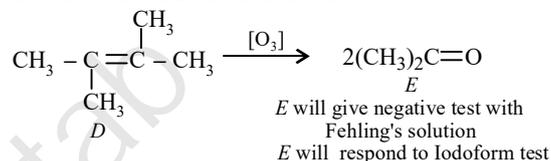
Isomeric structures of *A*

Catalytic hydrogenation of alkenes takes place in *cis*-(*syn*) manner, hence racemic mixture will be formed by the *trans*-isomer.

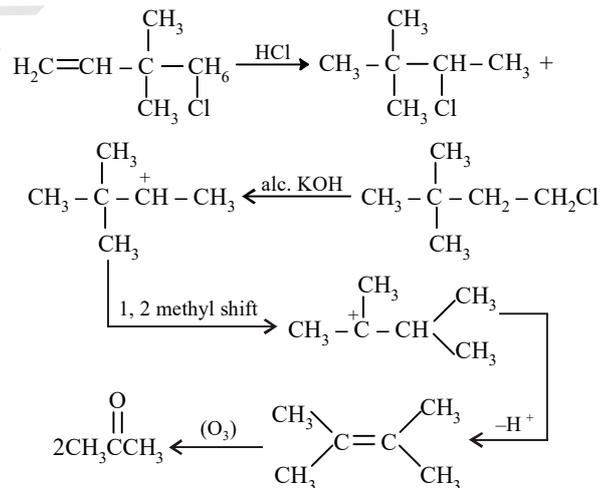
81. Ziegler Natta catalyst ($\text{R}_3\text{Al} + \text{TiCl}_4$).

82. (i) Formation of HCOONa and a primary alcohol due to Cannizzaro's reaction of *F* and *G* indicates that either *F* and *G* should be HCHO . Thus the alkene *A* should have $\text{CH}_2 =$ grouping. The remaining 5 carbons of *A* should have grouping $=\text{HC}-\text{C}_4\text{H}_9$.

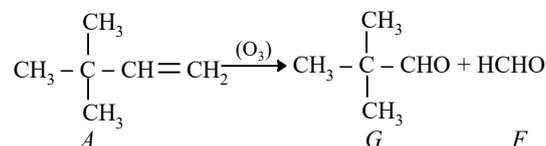
(ii) Formation of only *E* by the ozonolysis of *D* indicates that the structure of *D* is as follows



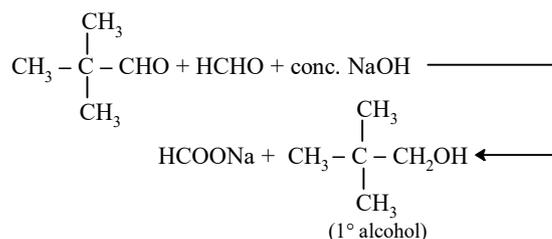
(iii) Since *A* is an isomer of *D* so should have following structure.



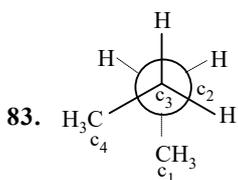
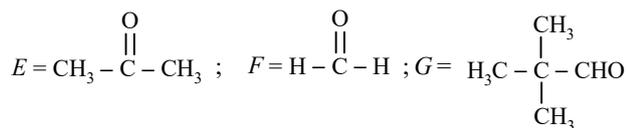
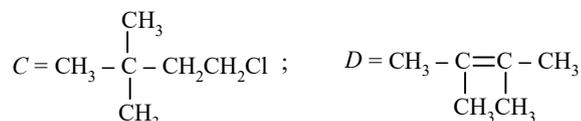
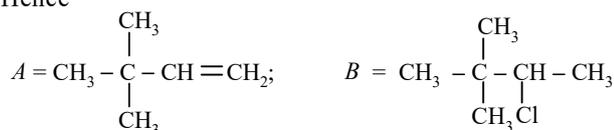
Compound *A* on ozonolysis gives compound *F* and *G* as follows:



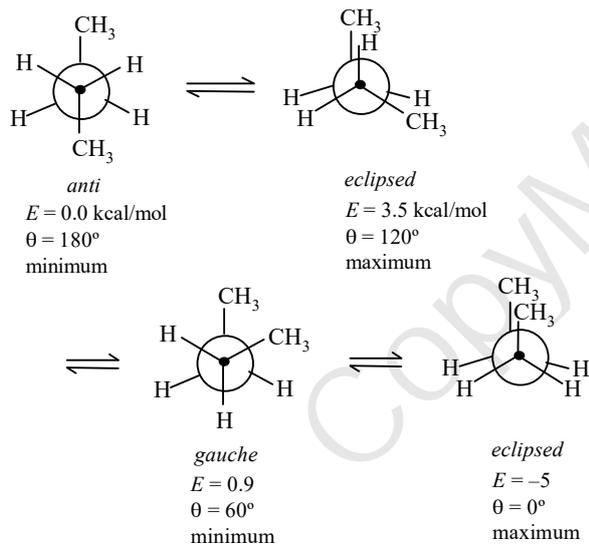
Compounds *G* and *F* give Crossed Cannizzaro's reaction with concentrated NaOH solution.



Hence

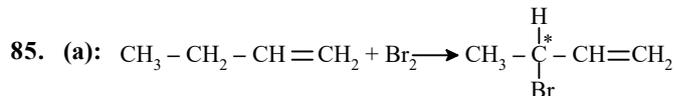
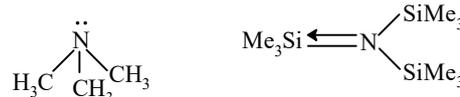


There are two energy minima, the *gauche* and *anti* forms, which are both staggered and thus have no torsional strain.



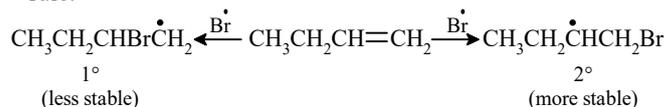
The *anti* form is the absolute energy minimum, since the *gauche* form has a small steric interaction between the two methyl groups. At a dihedral angle of 60 degrees, one hydrogen of each of the methyl groups is relatively close to a hydrogen of the other methyl group (van der Waals repulsion). The reason of instability is van der Waals strain. The electrostatic force of repulsion acting between the two methyl groups present in close proximity is responsible for making it the least stable.

84. $(\text{CH}_3)_3\text{N}$ and $(\text{Me}_3\text{Si})_3\text{N}$ are not isostructural. $(\text{CH}_3)_3\text{N}$ is pyramidal and $(\text{Me}_3\text{Si})_3\text{N}$ is trigonal planar. In silicon vacant *d*-orbitals are available which can accommodate lone pair of electrons from N ($p\pi - d\pi$ back bonding) and it leads to planar structure.



C* is an asymmetric carbon atom

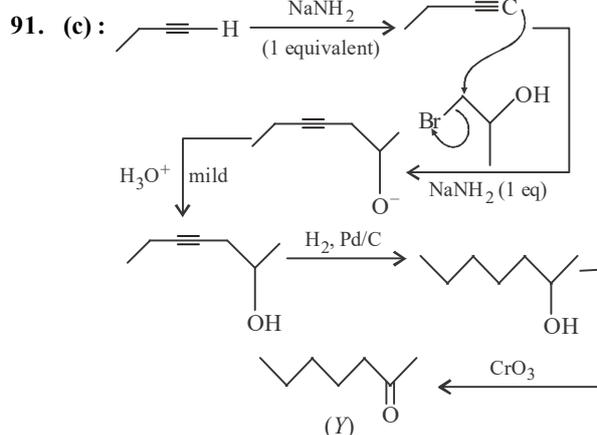
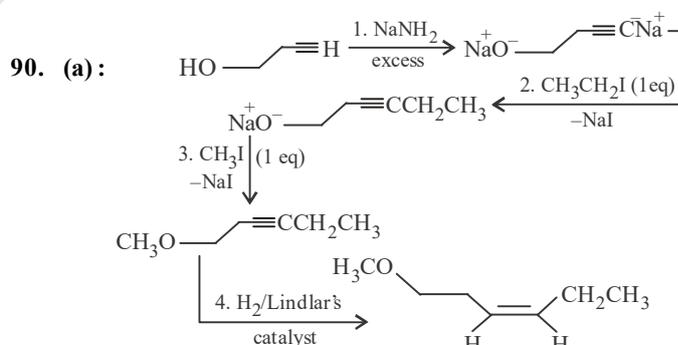
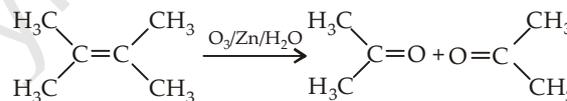
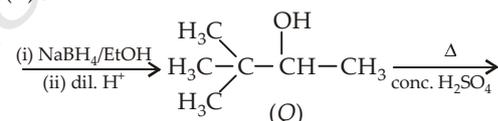
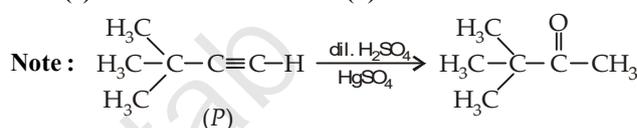
86. (c): In presence of peroxide, HBr adds on to an alkene via free radical mechanism. 2° free radical is more stable than 1° free radical. The product obtained is *anti*-Markownikoff's rule.



87. (b): It is an example of *anti*-addition.

88. (d)

89. (b)



Hydrocarbons

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X and Y are functional isomers of each other and Y gives iodoform test.

92. (c)

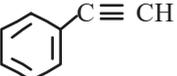
93. (d): Double bond equivalent = $(a + 1) - \frac{b}{2}$

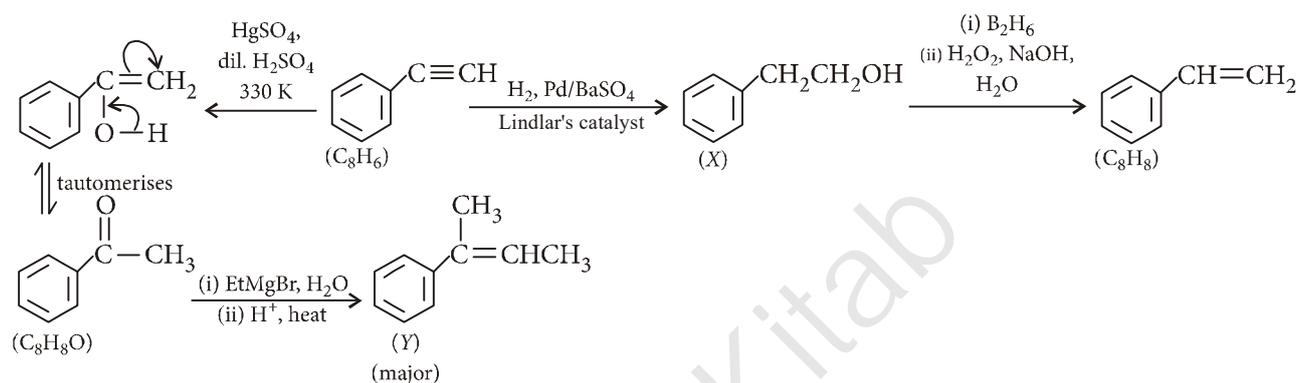
where a = No. of C-atoms

b = No. of H-atoms

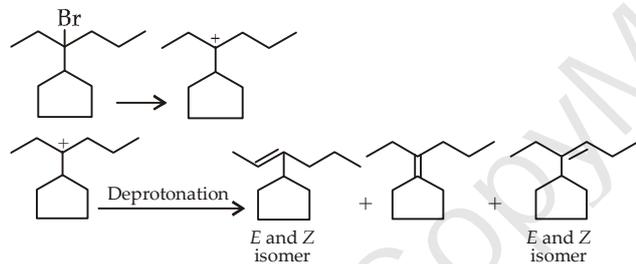
D.B.E. for $C_8H_6 = (8 + 1) - \frac{6}{2} = 6$

\therefore The compound has 1 ring + 5 double bonds.

Hence, C_8H_6 is 



94. (5): Total no. of alkenes will be = 5



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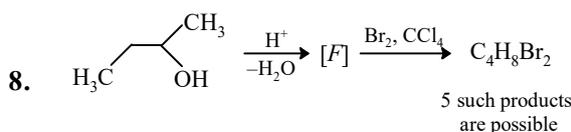
Halogen Derivatives

Multiple Choice Questions with ONE Correct Answer

- Chlorobenzene can be prepared by reacting aniline with
 - hydrochloric acid
 - cuprous chloride
 - chlorine in presence of anhydrous aluminium chloride
 - nitrous acid followed by heating with cuprous chloride
 (1984)
- The reaction of toluene with chlorine in presence of ferric chloride gives predominantly
 - benzoyl chloride
 - m*-chlorotoluene
 - benzyl chloride
 - o*- and *p*-chlorotoluene
 (1986)
- The number of structural and configurational isomers of a bromo compound, C_5H_9Br , formed by the addition of HBr to 2-pentyne respectively are
 - 1 and 2
 - 2 and 4
 - 4 and 2
 - 2 and 1
 (1988)
- 1-chlorobutane on reaction with alcoholic potash gives
 - 1-butene
 - 1-butanol
 - 2-butene
 - 2-butanol
 (1991)
- The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is
 - 2
 - 3
 - 4
 - 1
 (1997)
- A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of
 - carbanion
 - carbene
 - free-radical
 - carbocation
 (1999)
- Identify the set of reagent/reaction conditions *X* and *Y* in the following set of transformations.

$$CH_3 - CH_2 - CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3 - \underset{\substack{| \\ Br}}{CH} - CH_3$$
 - X* = dilute aqueous NaOH, 20°C; *Y* = HBr/acetic acid, 20°C
 - X* = concentrated alcoholic NaOH, 80°C; *Y* = HBr/acetic acid, 20°C
 - X* = dilute aqueous NaOH, 20°C; *Y* = $Br_2/CHCl_3$, 0°C

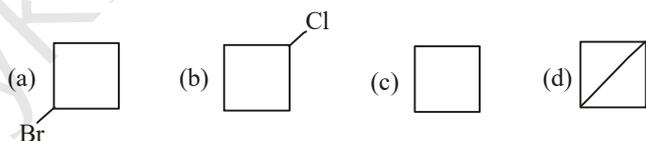
- (d) *X* = concentrated alcoholic NaOH, 80°C; *Y* = $Br_2/CHCl_3$, 0°C (2002)



How many structures of *F* are possible?

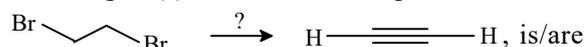
- (a) 2 (b) 5 (c) 6 (d) 3 (2003)

9. What would be the product formed when 1-bromo-3-chlorocyclobutane reacts with two equivalents of metallic sodium in ether?



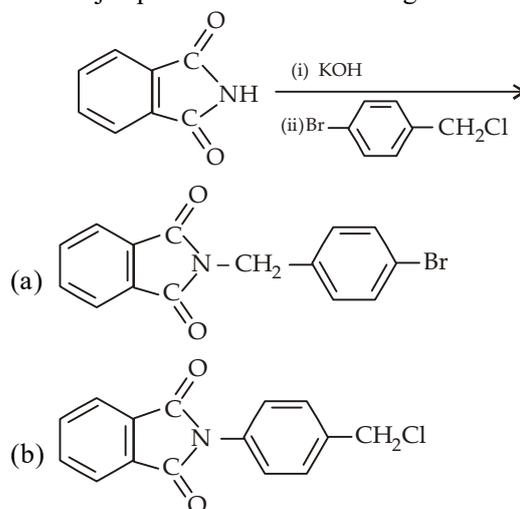
(2005)

10. The reagent(s) for the following conversion,



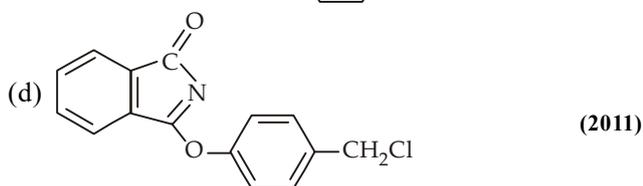
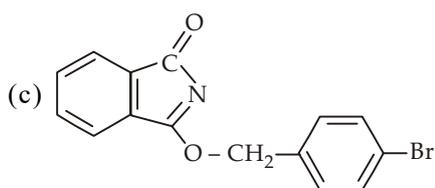
- (a) alcoholic KOH
 (b) alcoholic KOH followed by $NaNH_2$
 (c) aqueous KOH followed by $NaNH_2$
 (d) Zn/CH_3OH . (2007)

11. The major product of the following reaction is

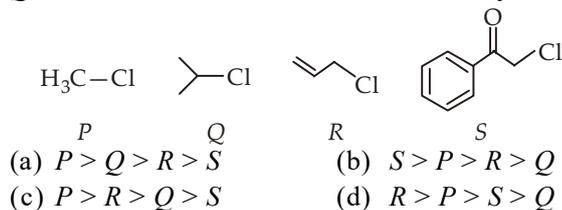


Halogen Derivatives

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12. KI in acetone, undergoes S_N2 reaction with each of *P*, *Q*, *R* and *S*. The rates of the reaction vary as

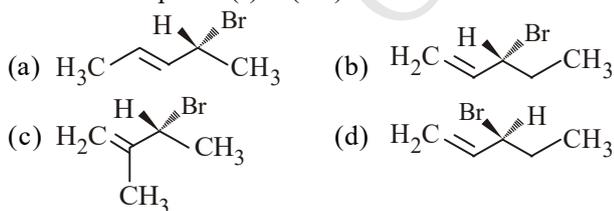


(2013)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

13. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to
 (a) the formation of less stable carbonium ion
 (b) resonance stabilisation
 (c) longer carbon-halogen bond
 (d) double bond between C and halogen (1990)

14. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is(are)



(2015)

Fill in the Blanks

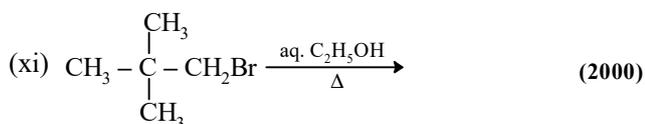
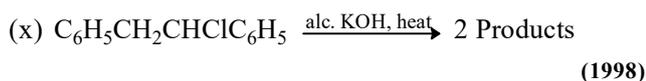
15. The halogen which is most reactive in the halogenation of alkanes under sunlight is (1981)
16. 1,3-Butadiene with bromine in molar ratio generates predominantly (1997)
17. Vinyl chloride on reaction with dimethyl copper gives (1997)

True / False

18. Carbon tetrachloride burns in air when lighted to give phosgene. (1983)
19. *m*-Chlorobromobenzene is an isomer of *m*-bromochlorobenzene. (1985)
20. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markownikoff's rule. (1989)
21. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methyl propane and 2-bromo-2-methyl propane in the ratio 9 : 1. (1993)

Subjective Problems

22. Show by chemical equations only, how you would prepare the following from the indicated starting materials. Specify the reagents in each step of the synthesis.
 (i) Hexachloroethane, C_2Cl_6 from calcium carbide.
 (ii) Chloroform from carbon disulphide. (1979)
23. Chloroform is stored in dark coloured bottles. Explain in not more than two sentences. (1980)
24. Write the structural formula of the major product in each of the following cases:
 (i) Chloroform reacts with aniline in the presence of excess alkali. (1981)
 (ii) $(CH_3)_2C(Cl) - CH_2CH_3 \xrightarrow{\text{alc. KOH}}$ (1992)
 (iii) $C_6H_5 - CH_2 - \underset{\text{Br}}{\underset{|}{CH}} - CH_3 \xrightarrow[\text{KOH, } \Delta]{\text{alcoholic}} ? \xrightarrow{\text{HBr}} ?$ (1993)
 (iv) $C_6H_5C_2H_5 \xrightarrow[2. \text{ NaCN}]{1. \text{ Br}_2, \text{ Heat, Light}}$ (1994)
 (v) (1997)
 (vi) $CH_3CH_2Br \xrightarrow{\text{AgCN}}$ (1997)
 (vii) (1997)
 (viii) (1997)
 (ix) (1997)

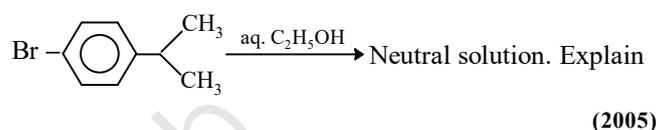
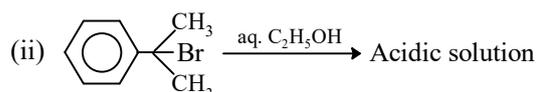


25. State the conditions under which the following preparation is carried out. Give the necessary equations which need not be balanced: Methyl chloride from aluminium carbide. (1983)
26. Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis. Ethyl benzene from benzene [C_2H_5OH , PCl_5 , anhydrous $AlCl_3$]. (1984)
27. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment? (1985)
28. What effect should the following resonance of vinyl chloride have on its dipole moment?
 $CH_2=CH-Cl \longleftrightarrow CH_2^- - CH_2=Cl^+$ (1987)
29. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. (1995)
30. An alkyl halide, X, of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of X, Y and Z. (1996)
31. How will you prepare *m*-bromiodobenzene from benzene (in not more than 5-7 steps)? (1996)
32. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic

reacts with ethanal to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (C). Write the structures of (A) and (B) and explain how (C) is obtained from (B). (2001)

33. Give reasons for the following:

(i) 7-Bromo-1, 3, 5-cycloheptatriene exists as ionic compound, while 5-bromo-1, 3-cyclopentadiene does not ionise even in presence of Ag^+ ion. Explain. (2004)



Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement - 2 is true; statement - 2 is a correct explanation for statement - 1.
 (b) Statement-1 is true; statement - 2 is true; statement - 2 is NOT a correct explanation for statement - 1.
 (c) Statement - 1 is true, statement - 2 is false.
 (d) Statement - 1 is false, statement - 2 is true.

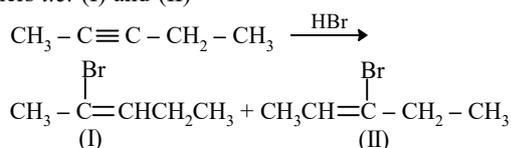
34. **Statement-1** : Bromobenzene upon reaction with Br_2/Fe gives 1, 4-dibromobenzene as the major product.
Statement-2 : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. (2008)

ANSWER KEY

- | | | | | | |
|------------------------|------------|--------------|--|-----------|-----------|
| 1. (d) | 2. (d) | 3. (b) | 4. (a) | 5. (a) | 6. (d) |
| 7. (b) | 8. (d) | 9. (d) | 10. (b) | 11. (a) | 12. (b) |
| 13. (b, d) | 14. (b, d) | 15. Chlorine | 16. 3,4-dibromo-1-butene (at low temp.)
or 1,4-dibromo-2-butene (at high temp.) | 19. False | 20. False |
| 17. Polyvinyl chloride | 18. False | 21. False | | | |
| 34. (c) | | | | | |

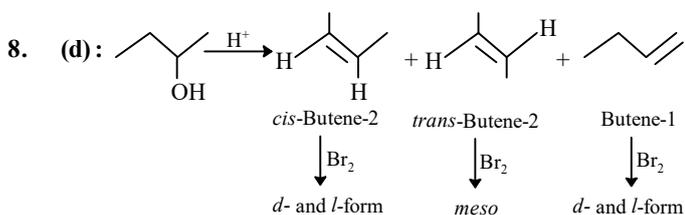
Explanations

1. (d): $C_6H_5NH_2 \xrightarrow[HCl]{HONO} C_6H_5N_2Cl \xrightarrow{CuCl} C_6H_5Cl$
2. (d): $-CH_3$ group is *o*-, *p*-directing group, so *o*- and *p*-chloro toluenes are obtained.
3. (b): When HBr adds on to 2-pentyne it gives two structural isomers *i.e.* (I) and (II)



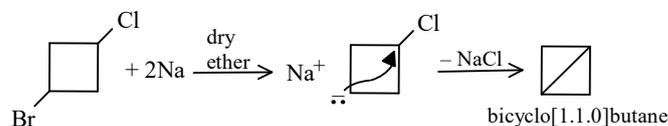
Each one of these (*i.e.* I and II) exists as a pair of geometrical isomers (*cis*- and *trans*-). Thus we have two structural and four configurational isomers.

4. (a): $H_3C - CH_2 - CH_2 - CH_2Cl \xrightarrow{alc. KOH} CH_3CH_2CH=CH_2$
(1-butene)
(Elimination reaction)
5. (a): $CH_3 - \underset{\text{CH}_3}{\overset{|}{CH}} - CH_2 - CH_3 \xrightarrow{Cl_2}$
- $$CH_2Cl - \overset{*}{\underset{\text{CH}_3}{\overset{|}{CH}}} - CH_2CH_3 + CH_3 - \underset{\text{CH}_3}{\overset{|}{CH}} - \overset{*}{\underset{\text{Cl}}{\overset{|}{CH}}} - CH_3$$
6. (d): $SbCl_5$ extracts chloride to form $SbCl_6^-$, leaving behind a carbocation.
7. (b): $CH_3 - CH_2 - CH_2Br \xrightarrow[NaOH (-HBr)]{conc. alcoholic} CH_3 - CH=CH_2$
- $$CH_3 - \underset{\text{Br}}{\overset{|}{CH}} - CH_3 \xleftarrow{\text{Markownikoff addition}} CH_3 - CH=CH_2$$

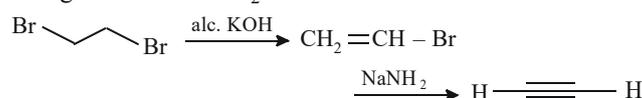


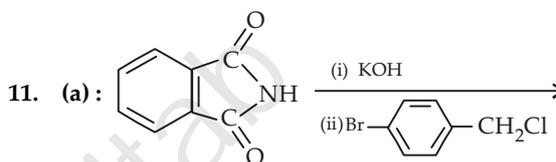
Thus we find 3 possible structures of F.

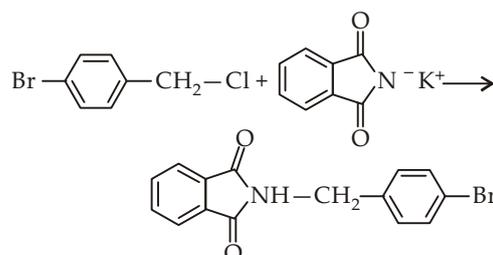
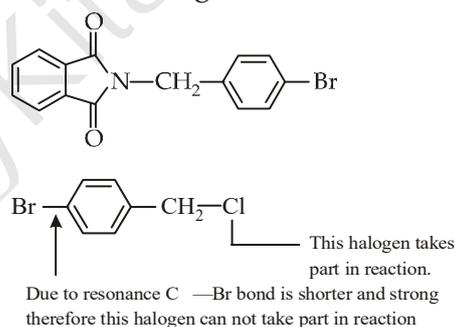
9. (d): In Wurtz reaction, an ether solution of an alkyl halide gives an alkane when heated with metallic sodium. For different halogens it is in the order : iodide > bromide > chloride. Since bromides are more reactive than chlorides in Wurtz reaction, therefore Wurtz reaction occurs on the side of Br atom.



10. (b): Simple alkyl halides are dehydrohalogenated by using strong base such as alc. KOH. Whereas vinyl halides require strongest base like NH_2^- for elimination.



11. (a): 



Hence, (a) is correct option.

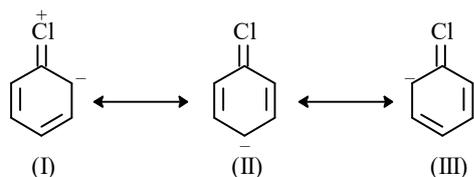
12. (b): The bulky groups cause steric hindrance in the formation of transition state. Therefore, higher homologues (Q) are less reactive than lower homologues (P).

In compound (S), the transition state is highly stabilized by

$Ph - \overset{O}{\parallel} C -$ group, so it has highest rate of reaction towards S_N2 .

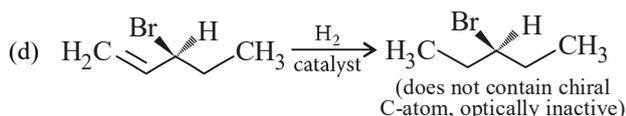
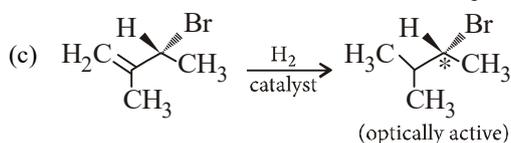
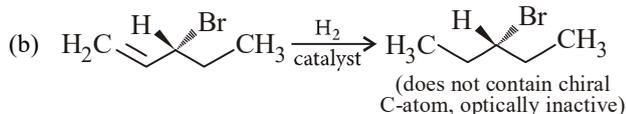
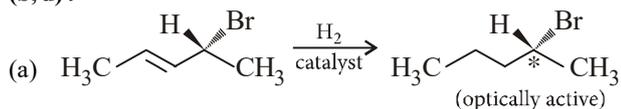
Hence, the order of rate of reaction is $S > P > R > Q$.

13. (b,d): The resonating structures I, II and III stabilise the aryl halides.



These structures include a double bond between C and Cl. The sp^2 hybridised carbon makes the C - Cl bond shorter and stronger.

14. (b, d):

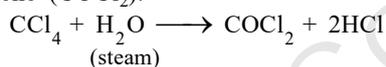


15. Chlorine

16. 3,4-dibromo-1-butene (at low temp.) or 1,4-dibromo-2-butene (at high temp.)

17. Polyvinyl chloride (PVC)

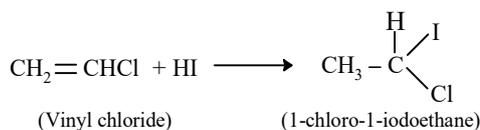
18. **False** : On reaction with super heated steam CCl_4 forms phosgene (COCl_2).



19. **False**

The given names represent the same compound.

20. **False**



This addition is in accordance with Markownikoff's rule because I^- (negative part of addendum) is added to the carbon atom with lesser number of hydrogen atoms.

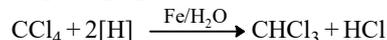
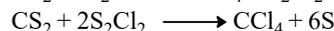
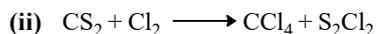
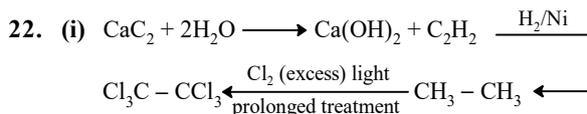
21. **False**

The ratio of the two products formed can be found by using the following relationship.

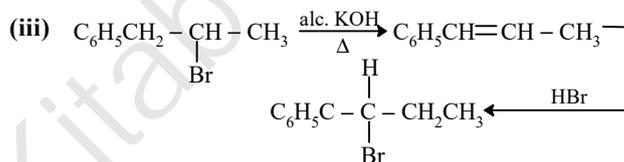
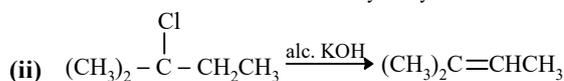
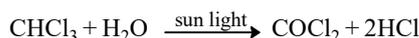
$$\frac{\text{1-Bromo-2-methylpropane}}{\text{2-Bromo-2-methylpropane}} = \frac{\text{Number of } 1^\circ\text{H}}{\text{Number of } 2^\circ\text{H}} \times \frac{\text{Reactivity of } 1^\circ\text{H}}{\text{Reactivity of } 2^\circ\text{H}} = \frac{9}{1} \times \frac{1}{3.8}$$

or 9 : 3.8.

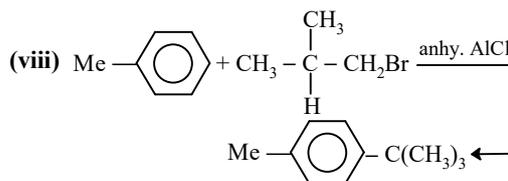
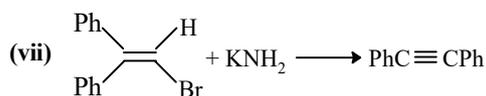
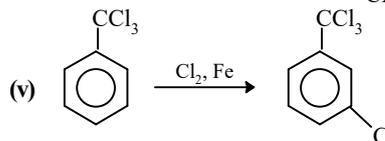
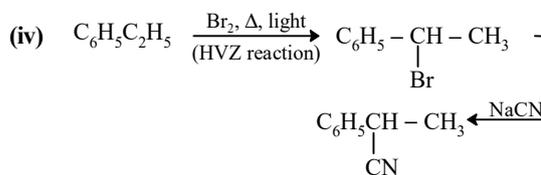
[\therefore Relative ratio of abstraction per H-atom is 5 : 3.8 : 1 for 3° , 2° and 1° H respectively].



23. Chloroform in contact with moisture present in the air and in presence of sunlight forms a highly poisonous gas - phosgene. To avoid the formation of phosgene, chloroform is stored in dark-coloured bottle to cut off sunlight.

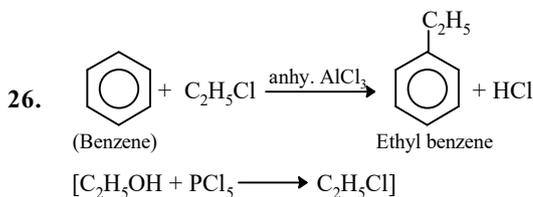
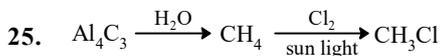
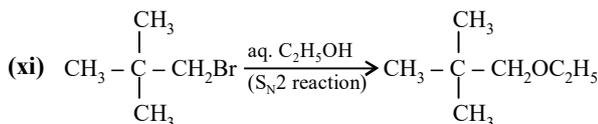
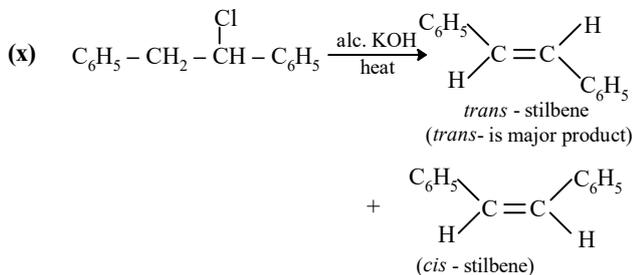
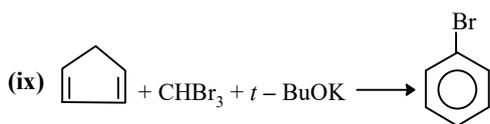


The carbocation formed on the addition of HBr are $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3^+$ and $\text{C}_6\text{H}_5\text{CH}^+\text{CH}_2\text{CH}_3$ of these $\text{C}_6\text{H}_5\text{CH}^+\text{CH}_2\text{CH}_3$ is stabilized due to resonance and so HBr adds on to it forming $\text{C}_6\text{H}_5-\underset{\text{Br}}{\text{CH}}-\text{CH}_2\text{CH}_3$ as the final product.

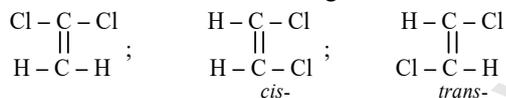


Halogen Derivatives

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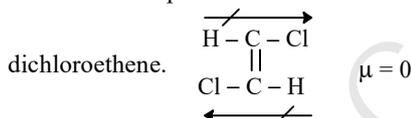


27. Dichloroethene exists in following three isomeric forms



1, 1-dichloroethene 1, 2-dichloroethene 1, 2-dichloroethene

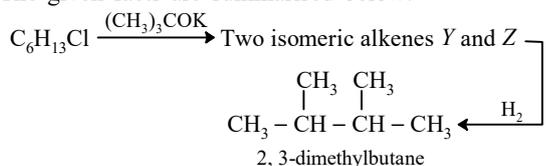
The resultant dipole moment will be zero in case of *trans*-1, 2-



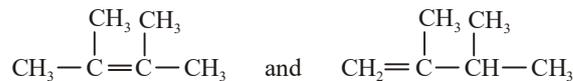
28. Due to resonance the dipole moment of vinyl chloride decreases. The positive charge on Cl and a negative charge on carbon (developed by resonance) oppose each other and so decrease the electronegativity of chlorine and thus the polarity of bond is decreased. Hence dipole moment decreases.

29. Reaction of optically active 2-iodobutane with NaI in acetone (S_N1) leads to the formation of equal amounts of the two enantiomers. Thus product, being a racemic mixture, will be optically inactive.

30. The given facts are summarised below:

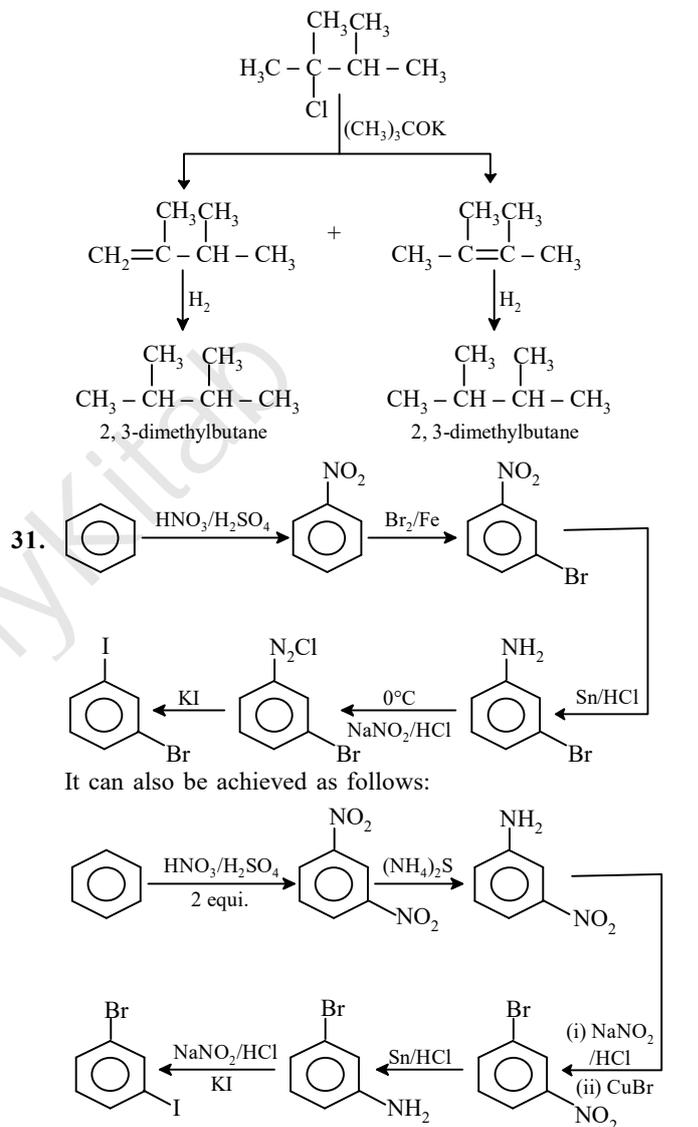


The two isomeric alkenes which on hydrogenation yield 2, 3-dimethylbutane are

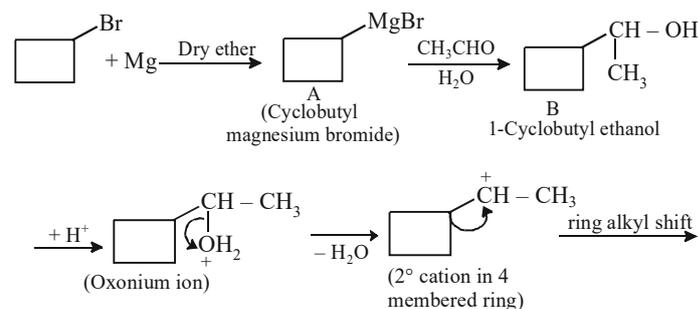


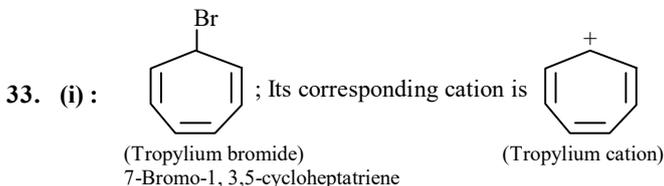
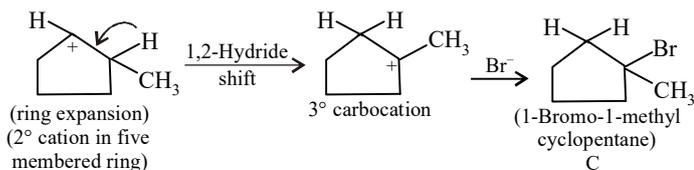
One of these is *Y* and the other is *Z*.

These structures explain the given facts as follows:

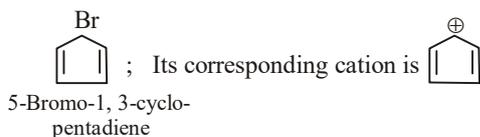


32.



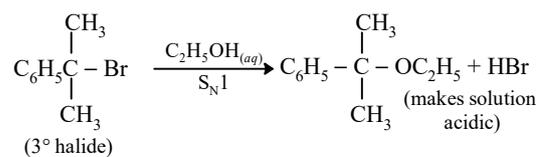


In this carbocation we find 6π ($4n + 2$) electrons, hence aromatic and can be easily formed.



This cation has 4π -electron so it is not aromatic hence not easily formed.

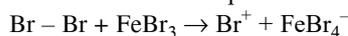
(ii) It is a 3° halide so it undergoes S_N1 reaction forming HBr as one of the products. Due to HBr the solution becomes acidic.



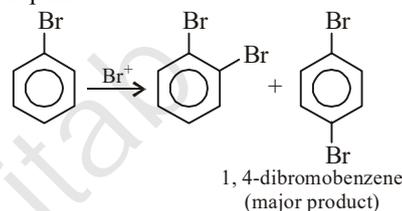
is an aryl halide so it does not undergo nucleophilic substitution reactions. Hence its solution will remain neutral.

34. (c) : Bromobenzene shows both $-I$ effect as well as $+M$ effect; but mesomeric effect dominates the $-I$ character and becomes the directing factor for incoming electrophile.

Formation of electrophile takes place.



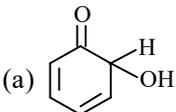
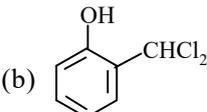
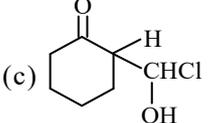
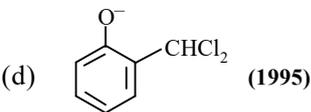
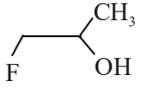
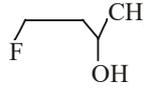
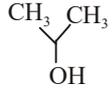
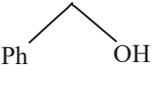
Bromobenzene acts as an *ortho-para* directors for upcoming electrophiles.



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Alcohols, Phenols and Ethers

Multiple Choice Questions with ONE Correct Answer

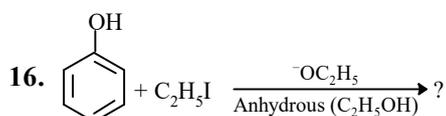
1. Ethyl alcohol is heated with conc. H_2SO_4 . The product formed is
 (a) $\text{H}_3\text{C} - \overset{\text{O}}{\parallel}{\text{C}} - \text{OC}_2\text{H}_5$ (b) C_2H_6
 (c) C_2H_4 (d) C_2H_2 (1980)
2. Which of the following is soluble in water?
 (a) CS_2 (b) $\text{C}_2\text{H}_5\text{OH}$
 (c) CCl_4 (d) CHCl_3 (1980)
3. 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 (1981)
4. Diethyl ether on heating with concentrated HI gives two moles of
 (a) ethanol (b) iodoform
 (c) ethyl iodide (d) methyl iodide (1983)
5. An industrial method of preparation of methanol is
 (a) catalytic reduction of carbon monoxide in presence of $\text{ZnO} - \text{Cr}_2\text{O}_3$
 (b) by reacting methane with steam at 900°C with a nickel catalyst
 (c) by reducing formaldehyde with lithium aluminium hydride
 (d) by reacting formaldehyde with aqueous sodium hydroxide solution (1984)
6. When phenol is treated with excess bromine water, it gives
 (a) *m*-bromophenol (b) *o*- and *p*-bromophenol
 (c) 2, 4-dibromophenol (d) 2, 4, 6-tribromophenol (1984)
7. HBr reacts fastest with
 (a) 2-methylpropan-2-ol (b) propan-1-ol
 (c) propan-2-ol (d) 2-methylpropan-1-ol (1986)
8. Which of the following compounds is oxidised to prepare ethyl methyl ketone?
 (a) 2-propanol (b) 1-butanol
 (c) 2-butanol (d) *t*-butyl alcohol (1987)
9. Phenol reacts with bromine in carbon disulphide at low temperature to give
 (a) *m*-bromophenol (b) *o*- and *p*-bromophenol
 (c) *p*-bromophenol (d) 2, 4, 6-tribromophenol (1988)
10. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives
 (a) *o*-cresol (b) *p*-cresol
 (c) 2, 4-dihydroxytoluene (d) benzoic acid (1990)
11. The reaction products of $\text{C}_6\text{H}_5\text{OCH}_3 + \text{HI} \xrightarrow{\Delta}$ is
 (a) $\text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{I}$ (b) $\text{C}_6\text{H}_5\text{I} + \text{CH}_3\text{OH}$
 (c) $\text{C}_6\text{H}_5\text{CH}_3 + \text{HOI}$ (d) $\text{C}_6\text{H}_6 + \text{CH}_3\text{OH}$ (1995)
12. When phenol is reacted with CHCl_3 and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates?
 (a)  (b) 
 (c)  (d)  (1995)
13. The order of reactivity of the following alcohols towards concentrated HCl is
 I  II  III  IV 
 (a) $\text{I} > \text{II} > \text{III} > \text{IV}$ (b) $\text{I} > \text{III} > \text{II} > \text{IV}$
 (c) $\text{IV} > \text{III} > \text{II} > \text{I}$ (d) $\text{IV} > \text{III} > \text{I} > \text{II}$ (1997)

14. The compound that will react most readily with NaOH to form methanol is

- (a) $(\text{CH}_3)_4\text{N}^+\text{I}^-$ (b) CH_3OCH_3
(c) $(\text{CH}_3)_3\text{S}^+\text{I}^-$ (d) $(\text{CH}_3)_3\text{CCl}$ (2001)

15. 1-Propanol and 2-propanol can be best distinguished by

- (a) oxidation with alkaline KMnO_4 followed by reaction with Fehling's solution
(b) oxidation with acidic dichromate followed by reaction with Fehling's solution
(c) oxidation by heating copper with acidic dichromate followed by reaction with Fehling's solution
(d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling's solution (2001)



- (a) $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ (b) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
(c) $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$ (d) $\text{C}_6\text{H}_5\text{I}$ (2003)

17. The product of acid catalysed hydration of 2-phenylpropene is

- (a) 3-phenyl-2-propanol (b) 1-phenyl-2-propanol
(c) 2-phenyl-2-propanol (d) 2-phenyl-1-propanol (2004)

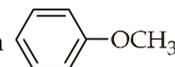
18. The best method to prepare cyclohexene from cyclohexanol is by using

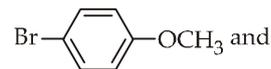
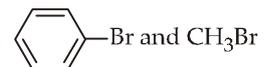
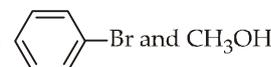
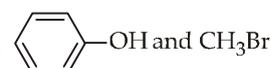
- (a) conc. $\text{HCl} + \text{ZnCl}_2$ (b) conc. H_3PO_4
(c) HBr (d) conc. HCl (2005)

19. The increasing order of boiling points of the below mentioned alcohols is

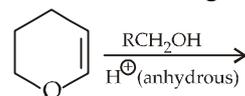
- (I) 1, 2-dihydroxy benzene (II) 1,3-dihydroxy benzene
(III) 1, 4-dihydroxy benzene (IV) hydroxy benzene

- (a) $\text{I} < \text{II} < \text{IV} < \text{III}$ (b) $\text{I} < \text{II} < \text{III} < \text{IV}$
(c) $\text{IV} < \text{II} < \text{I} < \text{III}$ (d) $\text{IV} < \text{I} < \text{II} < \text{III}$ (2006)

20. In the reaction  $\text{C}_6\text{H}_5\text{OCH}_3 \xrightarrow{\text{HBr}}$ the products are

- (a)  and H_2
(b)  and CH_3Br
(c)  and CH_3OH
(d)  and CH_3Br (2010)

21. The major product of the following reaction is

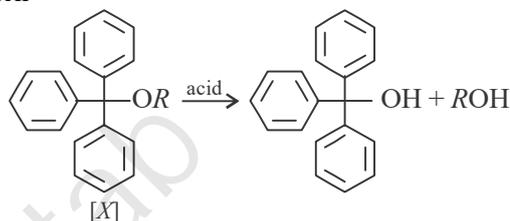


- (a) a hemiacetal (b) an acetal
(c) an ether (d) an ester (2011)

22. The compound that does not liberate CO_2 , on treatment with aqueous sodium bicarbonate solution, is

- (a) benzoic acid (b) benzenesulphonic acid
(c) salicylic acid (d) carboic acid (phenol). (2013)

23. The acidic hydrolysis of ether (X) shown below is fastest when

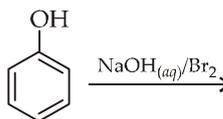


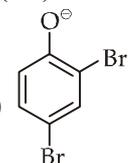
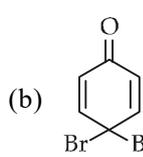
- (a) one phenyl group is replaced by a methyl group
(b) one phenyl group is replaced by a *para*-methoxyphenyl group
(c) two phenyl groups are replaced by two *para*-methoxyphenyl groups
(d) no structural change is made to X. (2014)

Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

24. The reaction of $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$ with HBr gives

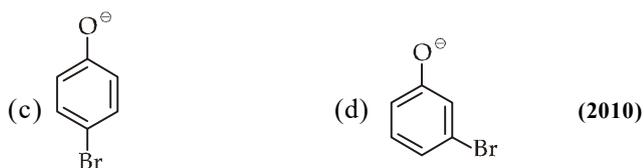
- (a) $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_4-\text{OH}$
(b) $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_4-\text{OH}$
(c) $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_3(\text{Br})-\text{OH}$
(d) $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_3(\text{Br})-\text{OH}$ (1998)

25. In the reaction  $\xrightarrow{\text{NaOH(aq)}/\text{Br}_2}$ the intermediate(s) is (are)

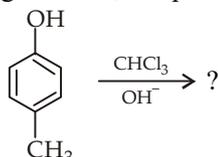
- (a)  (b) 

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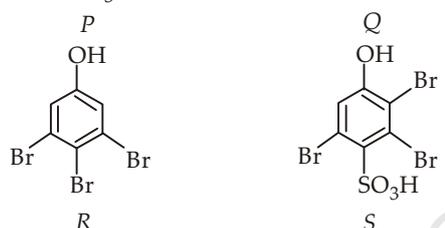
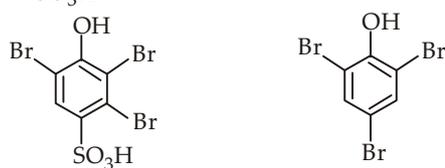
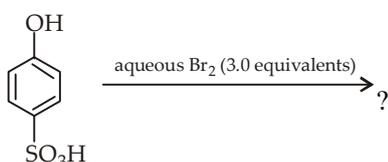


26. In the following reaction, the product(s) formed is (are)



- (a) *P* (major) (b) *Q* (minor)
(c) *R* (minor) (d) *S* (major) (2013)

27. The major product(s) of the following reaction is (are)

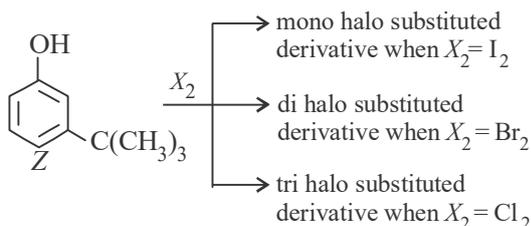


- (a) *P* (b) *Q*
(c) *R* (d) *S* (2013)

28. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are

- (a) *tert*-butanol and 2-methylpropan-2-ol
(b) *tert*-butanol and 1, 1-dimethylethan-1-ol
(c) *n*-butanol and butan-1-ol
(d) *iso*-butyl alcohol and 2-methylpropan-1-ol (2014)

29. The reactivity of compound *Z* with different halogens under appropriate conditions is given below :



The observed pattern of electrophilic substitution can be explained by

- (a) the steric effect of the halogen
(b) the steric effect of the *tert*-butyl group
(c) the electronic effect of the phenolic group
(d) the electronic effect of the *tert*-butyl group (2014)

Fill in the Blanks

30. Ethanol vapour is passed over heated copper and the product is treated with aqueous NaOH. The final product is (1983)
31. The acidity of phenol is due to the of its anion. (1984)
32. Formation of phenol from chlorobenzene is an example of aromatic substitution. (1989)
33. Phenol is acidic because of resonance stabilisation of its conjugate base, namely (1990)
34. Aliphatic ethers are purified by shaking with a solution of ferrous salt to remove which are formed on prolonged standing in contact with air. (1992)
35. Glycerine contains one hydroxyl group. (1997)

True / False

36. Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. (1986)

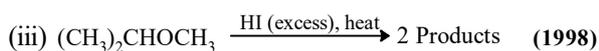
Subjective Problems

37. Give one characteristic test which would distinguish C_2H_5OH from $CHCl_3$. (1979)
38. An organic liquid (*A*), containing C, H and O with boiling point $78^\circ C$ and possessing a rather pleasant odour, on heating with concentrated sulphuric acid gives a gaseous product (*B*) with the empirical formula, CH_2 . *B* decolourises bromine water as well as alkaline $KMnO_4$ solution and takes up one mole of H_2 (per mole of *B*) in the presence of finely divided nickel at high temperature. Identify the substances *A* and *B*. (1979)
39. A compound (*X*) containing C, H and O is unreactive towards sodium. It does not add bromine. It also does not react with Schiff's reagent. On refluxing with an excess of hydriodic acid, (*X*) yields only one organic product (*Y*). On hydrolysis, (*Y*) yields a new compound (*Z*) which can be converted into (*Y*) by reaction with red phosphorus and iodine. The compound (*Z*) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60. What are the compounds (*X*), (*Y*) and (*Z*)? Write chemical equations leading to the conversion of (*X*) to (*Y*). (1981)

40. Write the structural formula of the main organic product formed when:

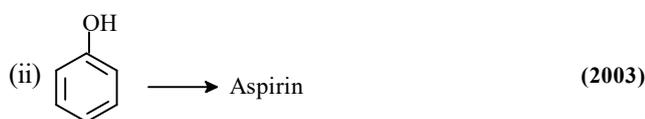


(ii) Predict the structure of the product in the following reaction.



41. How will you obtain?

(i) 1-propanol from 2-propanol (in three steps). (1982)



42. State with balanced equations what happens when: Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate. (1991)

43. Give reasons for the following:

(i) Sodium metal can be used for drying diethyl ether but not ethanol. (1982)

(ii) Suggest a reason for the large difference between the boiling points of butanol and butanal, although they have almost the same solubility in water. (1985)

(iii) Phenol is an acid but it does not react with sodium bicarbonate. (1987)

(iv) Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why? (1997)

(v) Acid catalysed dehydration of *t*-butanol is faster than that of *n*-butanol. (1998)

44. State the conditions under which the following preparation is carried out. Give the necessary equations which need not be balanced.

Ethanol from acetylene (1983)

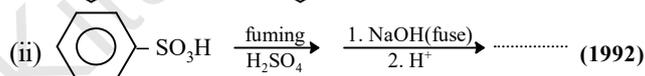
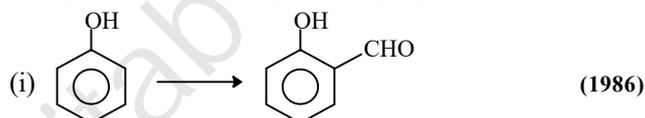
45. An alcohol *A*, when heated with concentrated H_2SO_4 gives an alkene *B*. When *B* is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound *C* is obtained. The compound *C* gives *D* when treated with warm dilute H_2SO_4 in presence of HgSO_4 . *D* can also be obtained either by oxidising *A* with KMnO_4 or from acetic acid through its calcium salt. Identify *A*, *B*, *C* and *D*. (1983)

46. What happens when *p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH? (1984)

47. A compound of molecular formula $\text{C}_7\text{H}_8\text{O}$ is insoluble in water and dilute sodium bicarbonate but dissolves in dilute aqueous sodium hydroxide and gives a characteristic colour with aqueous FeCl_3 . On treatment with bromine water, it readily gives a precipitate of $\text{C}_7\text{H}_5\text{OBr}_3$. Write down the structure of the compound. (1985)

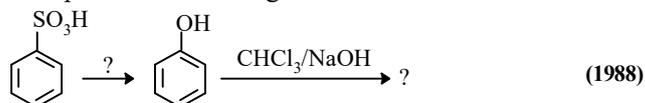
48. Give a chemical test/suggest a reagent to distinguish between the following pair of compounds: methanol and ethanol. (1985)

49. Complete the following with appropriate structures:



50. An organic compound (*A*) on treatment with acetic acid in the presence of sulphuric acid produces an ester (*B*), (*A*) on mild oxidation gives (*C*), (*C*) with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates (*A*) and (*D*), (*D*) with phosphorus pentachloride followed by reaction with ammonia gives (*E*), (*E*) on dehydration produces hydrocyanic acid. Identify the compounds *A*, *B*, *C*, *D* and *E*. (1987)

51. Complete the following reaction:



52. An organic compound containing C, H and O exists in two isomeric forms *A* and *B*. An amount of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 and 0.072 g of H_2O . *A* is insoluble in NaOH and NaHCO_3 while *B* is soluble in NaOH. *A* reacts with concentrated HI to give compounds *C* and *D*. *C* can be separated from *D* by the ethanolic AgNO_3 solution and *D* is soluble in NaOH. *B* reacts readily with bromine water to give compound *E* of molecular formula, $\text{C}_7\text{H}_5\text{OBr}_3$. Identify *A*, *B*, *C*, *D* and *E* with justification and give their structures. (1991)

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53. Compound X (molecular formula, C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate. With excess of $MeMgBr$, 0.42 g of X gives 224 ml of CH_4 at STP. Treatment of X with H_2 in presence of Pt catalyst followed by boiling with excess HI, gives n -pentane. Suggest structure for X and write the equation involved.

(1992)

54. Identify $C(C_4H_8)$ which when treated with H_2O/H_2SO_4 gives $C_4H_{10}O$ which cannot be resolved into optical isomers.

(1993)

55. When t -butanol and n -butanol are separately treated with a few drops of dilute $KMnO_4$, in one case only the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate?

(1994)

56. 3, 3-Dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism.

(1996)

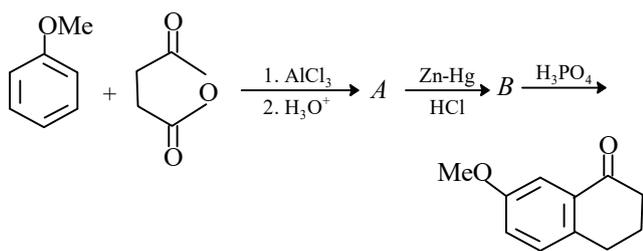
57. A compound $D(C_8H_{10}O)$ upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid $E(C_7H_6O_2)$. Write the structures of D , E and explain the formation of E .

(1996)

58. An optically active alcohol $A(C_6H_{10}O)$ absorbs two moles of hydrogen per mole of A upon catalytic hydrogenation and gives a product B . The compound B is resistant to oxidation by CrO_3 and does not show any optical activity. Deduce the structures of A and B .

(1996)

59. Predict the structures of the intermediates/products in the following reaction sequence :



(1996)

60. 2, 2-Dimethyloxirane can be cleaved by acid (H^+). Write mechanism.

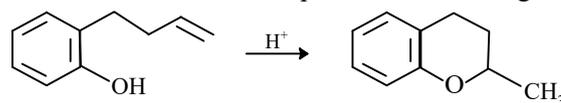
(1997)

61. Which of the following is the correct method for synthesising methyl- t -butyl ether and why?



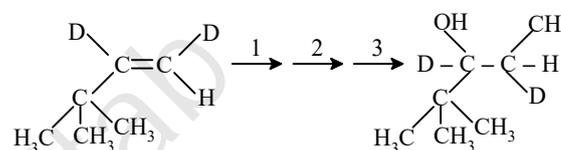
(1997)

62. Write the intermediate steps for the following reaction.



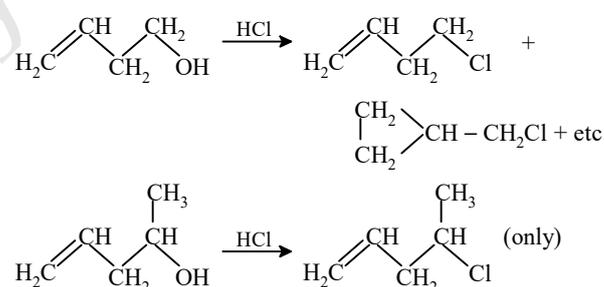
(1998)

63. Complete the following reaction with appropriate reagents:



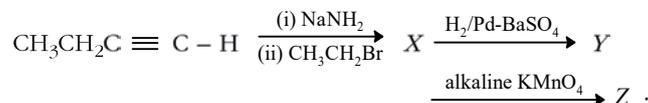
(1999)

64. Explain briefly the formation of the products giving the structures of the intermediates.



(1999)

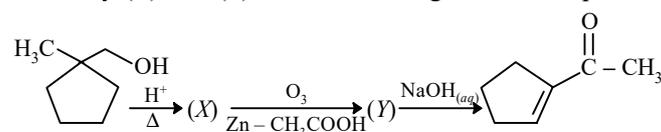
65. Identify X , Y and Z in the following synthetic scheme and write their structures.



Is the compound Z optically active? Justify your answer.

(2002)

66. Identify (X) and (Y) in the following reaction sequence.



(2005)

Matrix Match Type

67. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists:

- | List I | List II |
|--------|--|
| P. | 1. (i) Hg(OAc) ₂ ;
(ii) NaBH ₄ |
| Q. | 2. NaOEt |
| R. | 3. Et-Br |
| S. | 4. (i) BH ₃ ;
(ii) H ₂ O ₂ /NaOH |

- | P | Q | R | S |
|-------|---|---|---|
| (a) 2 | 3 | 1 | 4 |
| (b) 3 | 2 | 1 | 4 |
| (c) 2 | 3 | 4 | 1 |
| (d) 3 | 2 | 4 | 1 |

(2013)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

68. **Statement-1** : Solubility of *n*-alcohols in water decreases with increase in molecular weight.

Statement-2 : The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permits enhanced hydrogen bonding with water.

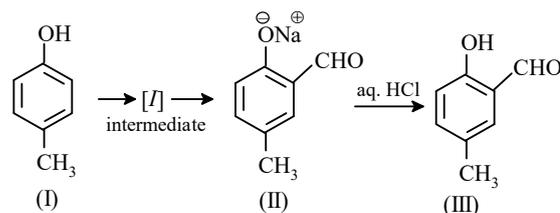
(1988)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension-1

Reimer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, *ortho* to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.



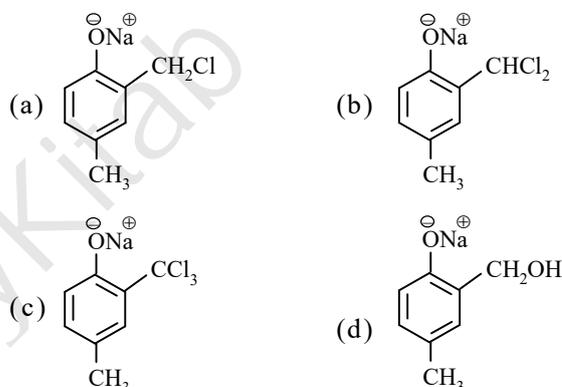
69. Which of the following reagents is used in the above reaction?

- (a) aq. NaOH + CH₃Cl (b) aq. NaOH + CH₂Cl₂
 (c) aq. NaOH + CHCl₃ (d) aq. NaOH + CCl₄.

70. The electrophile in this reaction is

- (a) :CHCl (b) ⁺CHCl₂
 (c) :CCl₂ (d) ·CCl₃.

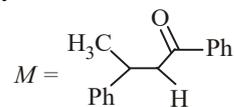
71. The structure of the intermediate *I* is



(2007)

Comprehension-2

A tertiary alcohol *H* upon acid catalysed dehydration gives a product *I*. Ozonolysis of *I* leads to compounds *J* and *K*. Compound *J* upon reaction with KOH gives benzyl alcohol and a compound *L*, whereas *K* on reaction with KOH gives only *M*.

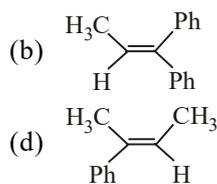
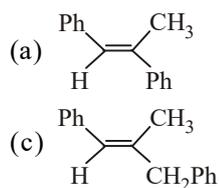


72. Compound *H* is formed by the reaction of

- (a) + PhMgBr
 (b) + PhCH₂MgBr
 (c) + PhCH₂MgBr
 (d) +

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73. The structure of compound *I* is74. The structures of compound *J*, *K* and *L*, respectively, are

- (a) PhCOCH_3 , $\text{PhCH}_2\text{COCH}_3$ and $\text{PhCH}_2\text{COO}^- \text{K}^+$
 (b) PhCHO , PhCH_2CHO and $\text{PhCOO}^- \text{K}^+$
 (c) PhCOCH_3 , PhCH_2CHO and $\text{CH}_3\text{COO}^- \text{K}^+$
 (d) PhCHO , PhCOCH_3 and $\text{PhCOO}^- \text{K}^+$ (2008)

ANSWER KEY

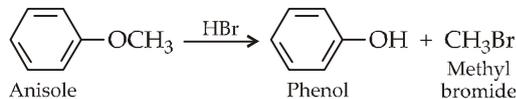
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|-----------------------------|------------------|-------------------|---------------|---------------|-----------|
| 1. (c) | 2. (b) | 3. (d) | 4. (c) | 5. (a) | 6. (d) |
| 7. (a) | 8. (c) | 9. (b) | 10. (d) | 11. (a) | 12. (d) |
| 13. (c) | 14. (a) | 15. (c) | 16. (b) | 17. (c) | 18. (b) |
| 19. (c) | 20. (d) | 21. (b) | 22. (d) | 23. (c) | 24. (b) |
| 25. (a, c) | 26. (b, d) | 27. (b) | 28. (a, c, d) | 29. (a, b, c) | 30. Aldol |
| 31. Resonance stabilisation | 32. Nucleophilic | 33. Phenoxide ion | 34. Peroxides | 35. Secondary | |
| 36. False | 67. (a) | 68. (c) | 69. (c) | 70. (c) | 71. (b) |
| 72. (b) | 73. (a) | 74. (d) | | | |

Alcohols, Phenols and Ethers

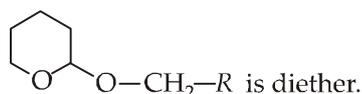
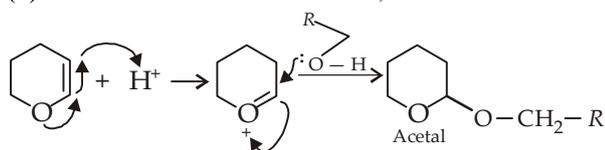
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19. (c) : 1,4-dihydroxy benzene shows highest boiling point among given compounds due to intermolecular H-bonding.

20. (d) : Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to stronger aryl-oxygen bond. The reaction yields phenol and alkyl halide. Thus,



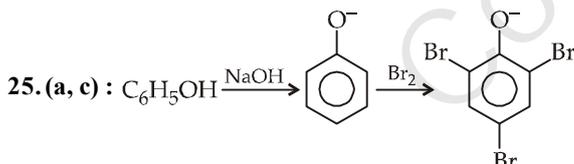
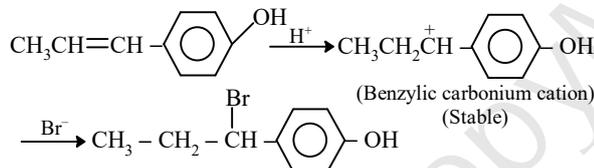
21. (b) : Diether is known as acetal. So,



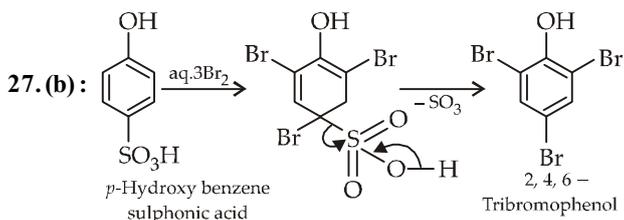
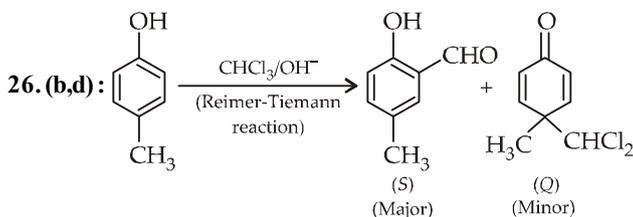
22. (d) : Phenol is weaker acid than carbonic acid (H_2CO_3) and does not liberate CO_2 on treatment with aqueous sodium bicarbonate solution.

23. (c) : Rate of $\text{S}_{\text{N}}1$ reaction is proportional to the stability of carbocation. When two phenyl groups are replaced by two $\text{MeO-C}_6\text{H}_4$ groups, the carbocation formed will be more stable. Hence, the reaction is fastest.

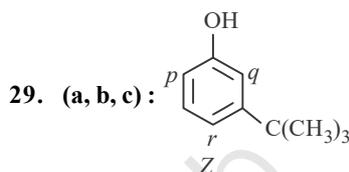
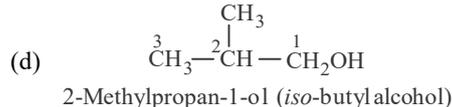
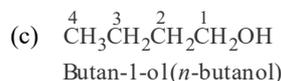
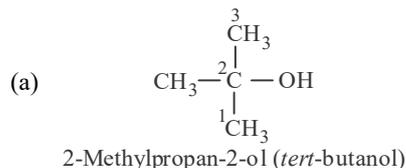
24. (b) : We can represent the mechanism as follows:



Due to presence of $-ve$ charge on the oxygen atom of phenoxide ion there is strong activation of benzene ring as a result we get trisubstituted product (a) and (c) can be intermediates.

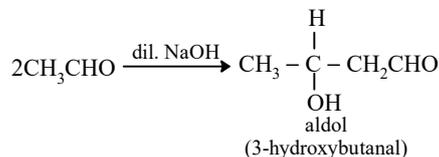
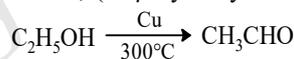


28. (a, c, d) : $\text{C}_4\text{H}_{10}\text{O}$ is a monohydric alcohol, i.e., $\text{C}_4\text{H}_9\text{OH}$. Its isomeric alcohols are

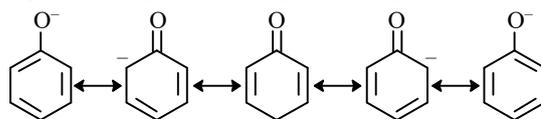


p , q and r are suitable positions as per electronic effect of $-\text{OH}$ group. Due to steric effect of the *tert*-butyl group, the bulky electrophiles are less likely to attack positions q and r . Hence, position p is suitable for I_2 , positions p and r are suitable for Br_2 and Cl_2 being smaller can attack all p , q and r positions.

30. Aldol ; (or β -hydroxybutanal)



31. Resonance stabilisation;

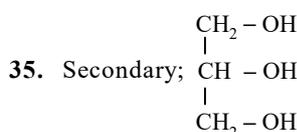


32. Nucleophilic

33. Phenoxide ion

34. Peroxides; When allowed to stand in contact with air ethers get converted to unstable peroxides ($\text{R}_2\text{O} \longrightarrow \text{O}$) which are highly explosive even in low concentration. Ether is always purified before distillation.

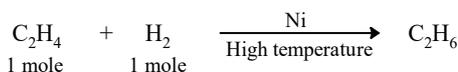
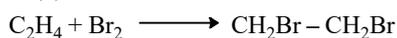
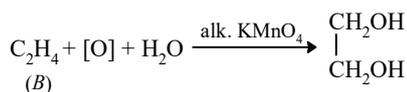
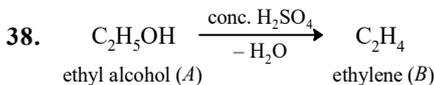
The peroxides formed can be removed by washing ether with ferrous salt solution. Ferrous reduces peroxide to alcohols. Peroxides can also be removed by distillation with concentrated H_2SO_4 which oxidises peroxides.



36. False

C_2H_5ONa is obtained by action of Na on C_2H_5OH .

37. Chloroform can be distinguished from ethyl alcohol by carbylamine test. Chloroform on heating with aq. KOH and aniline gives an offensive smell while C_2H_5OH does not.

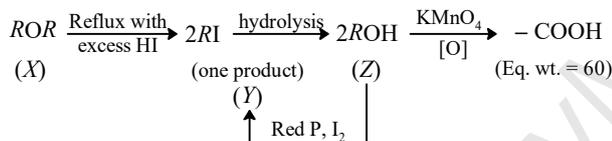


A is ethyl alcohol and B is ethylene.

39. Since the compound X is unreactive towards sodium so it is neither an acid nor an alcohol.

Since the compound X is unreactive towards Schiff's base so it is not an aldehyde.

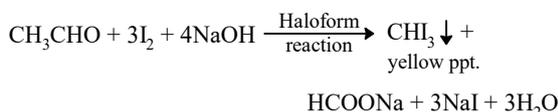
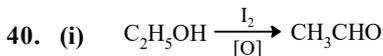
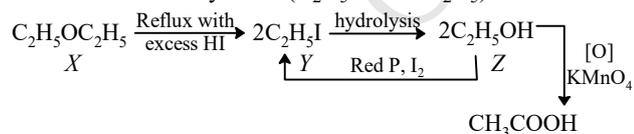
The compound X forms only one product on reaction with excess HI, indicates that the compound X may be ether. The reactions can be written as:



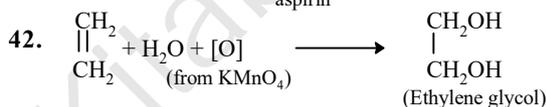
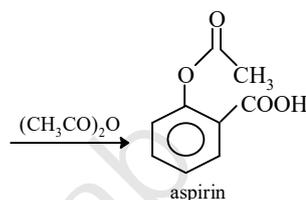
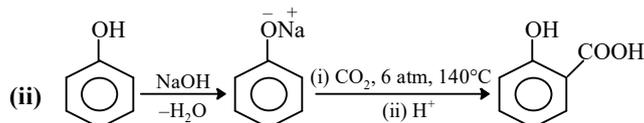
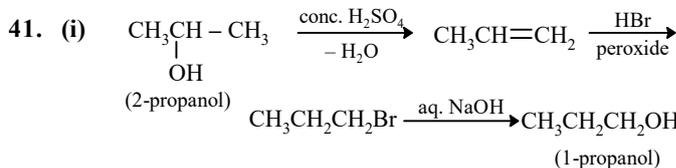
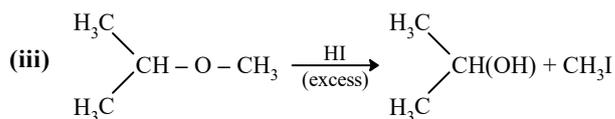
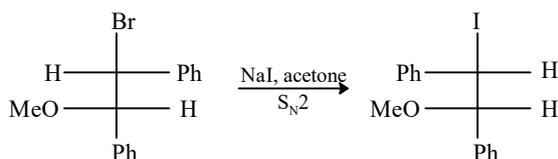
Since the equivalent weight of carboxylic acid is 60 so it must be CH_3COOH .

The alcohol Z in that case should be C_2H_5OH and the compound Y should be ethyl iodide.

X is therefore diethylether ($C_2H_5 - O - C_2H_5$)

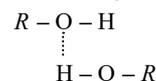


(ii) Br is replaced by I (S_N2 mechanism) which involves Walden inversion at the place of replacement.

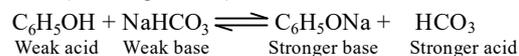


43. (i): Since there is an active hydrogen atom in ethanol ($CH_3CH_2O - H$) so it reacts with sodium metal (Na). In ether ($CH_3 - O - CH_3$) and benzene () there is no replaceable hydrogen atom so they do not react with sodium. Hence they can be dried by metallic sodium.

(ii) The b.p. of carbonyl compounds are lower than corresponding alcohols as there is no intermolecular hydrogen bonding in carbonyl compounds whereas in alcohols there is intermolecular hydrogen bonding.

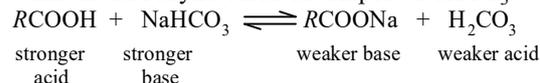


(iii) Phenol (a weaker acid) reacts with $NaHCO_3$ (a weaker base) to form phenoxide ion (a stronger base) and carbonic acid (a stronger acid).

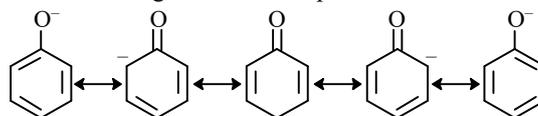


Since acid-base equilibria lies towards the weaker acid and weaker base, phenol does not decompose $NaHCO_3$.

Whereas carboxylic acids decompose $NaHCO_3$.



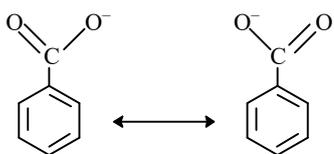
(iv) The resonating structures of phenoxide ion are:



The resonating structures of benzoate ion are:

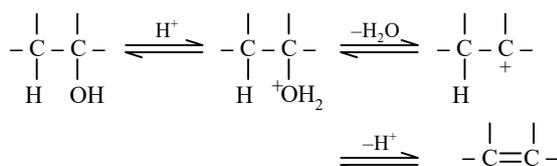
Alcohols, Phenols and Ethers

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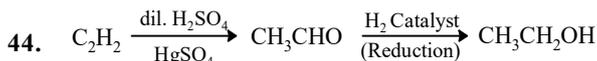


The benzoate ion is more stabilized because in it the negative charge is on more electronegative oxygen atom. In phenoxide ion the negative charge is on less electronegative carbon atom. Because of this benzoic acid is a stronger acid than phenol.

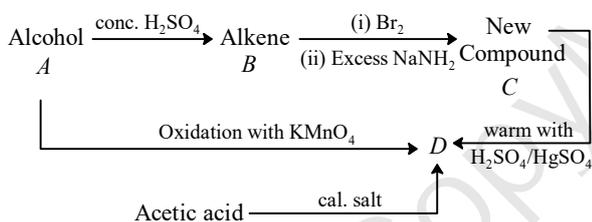
(v) The acid catalysed dehydration of an alcohol proceeds via the formation of a carbocation.



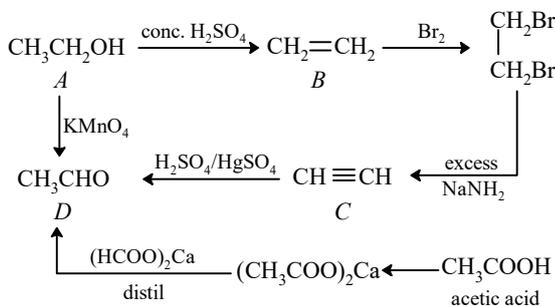
Since 3° carbocation (formed in case of *tert*-butanol is more stable than 1° carbocation (formed in case of *n*-butanol) the dehydration in *tert*-butanol proceeds faster than in *n*-butanol.



45. The facts given in the problem can be summarised as follows:

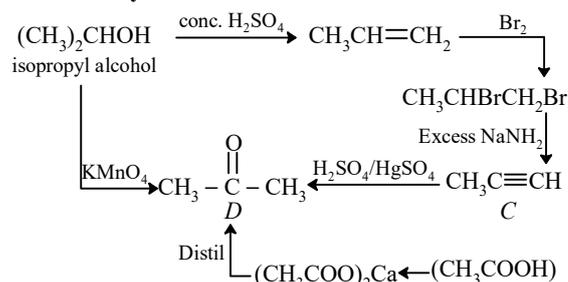


From the above it appears that *C* is an alkyne and *D* is an aldehyde or ketone. Since *D* can be obtained from acetic acid through its calcium salt it must be either acetaldehyde or acetone. Hence proceeding backwards *A* may be either ethyl alcohol or isopropyl alcohol. Both of these can explain various reactions.

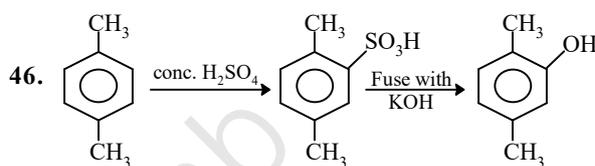


Hence *A* = Ethyl alcohol (C_2H_5OH)
B = Ethylene ($CH_2 = CH_2$)
C = Acetylene ($CH \equiv CH$)
D = Acetaldehyde (CH_3CHO)

Alternatively

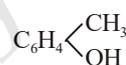


Hence *A* = Isopropyl alcohol, $CH_3CH(OH)CH_3$
B = Propene ($CH_3CH = CH_2$)
C = Propyne ($CH_3C \equiv CH$)
D = Acetone (CH_3COCH_3)

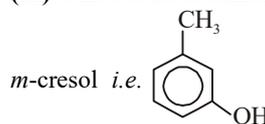


2, 5-Dimethyl phenol

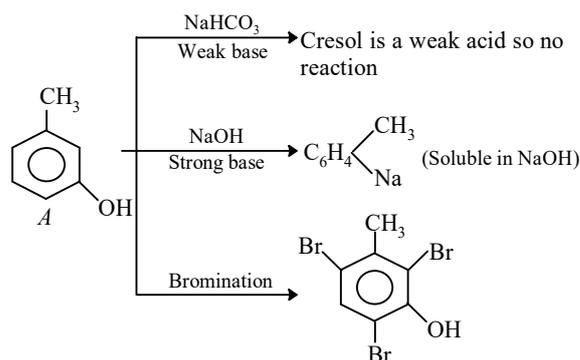
47. (i) Since *A* gives characteristic colour with aqueous $FeCl_3$ so it contains a phenolic group.
(ii) Since *A* when treated with Br_2 forms $C_7H_5OBr_3$ (ppt.) and considering the molecular formula of *A*, it is most likely to be cresol.



(iii) Since *A* on bromination forms tribromoderivative so it is

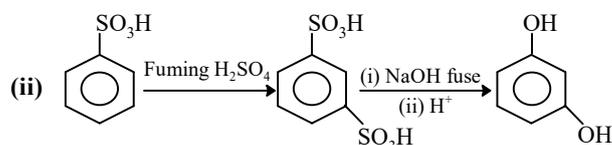


The reactions are:



48. Ethanol gives iodoform test but methanol does not give iodoform test.
 $C_2H_5OH + 6NaOH + 4I_2 \rightarrow CHI_3 \downarrow + 5NaI + HCOONa + 5H_2O$

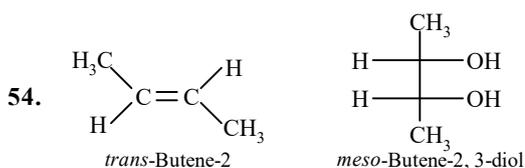
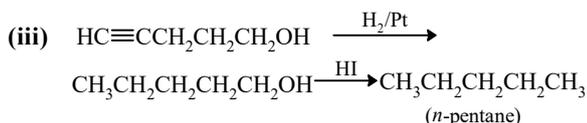
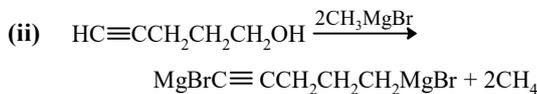
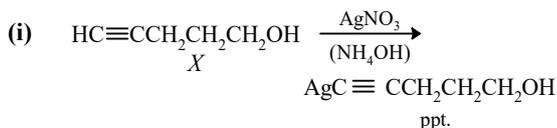
49. (i) $CHCl_3 + NaOH, 60^\circ C, 3-5 \text{ atm.}$



Alcohols, Phenols and Ethers

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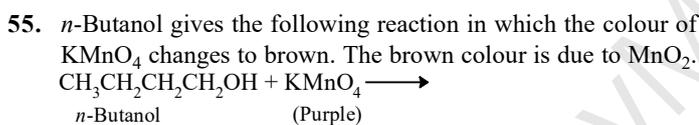
Reactions of compound X



It should be a *trans*-isomer because on hydration ($\text{H}_2\text{O}/\text{H}_2\text{SO}_4$) it gives non-resolvable compounds (*i.e.* *meso*-isomer).

We know that electrophilic addition on alkene occurs in *trans* manner.

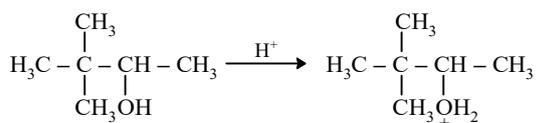
Thus *cis*-2-butene on hydration gives *dl*-butan-2,3-diol (resolvable in *d*- and *l*-isomers) while *trans*-butene-2 produces *meso*-butan-2,3-diol (non-resolvable).



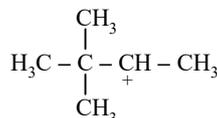
tert. alcohols are not oxidised easily and so there is no change in purple colour of KMnO_4 .

56. Various steps involved in the suggested mechanism are:

(a) Protonation of hydroxyl group

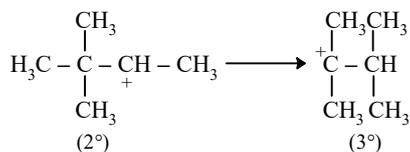


(b) Removal of H_2O to form a secondary (2°) carbonium ion.

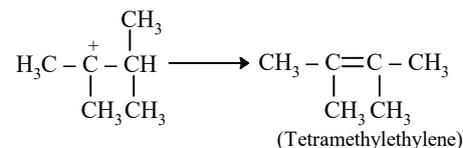


(2°) secondary carbonium ion.

(c) The conversion of secondary (2°) carbonium ion to stable tertiary (3°) carbonium ion by shift of $-\text{CH}_3$ group.

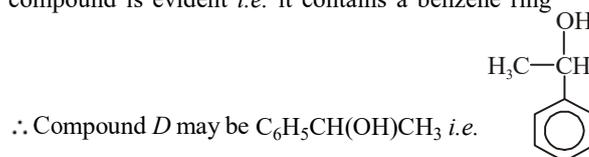


(d) The removal of H^+ to form a double bond.

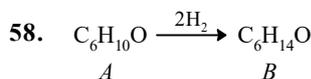
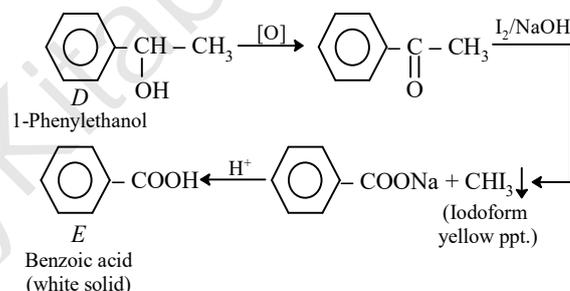


57. Since the compound *D* ($\text{C}_8\text{H}_{10}\text{O}$) gives haloform reaction (*i.e.* forms iodoform an reaction with $\text{I}_2(\text{NaOH})$) so it must contain either $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ or $-\overset{\text{OH}}{\text{C}}\text{HCH}_3$ group.

From the molecular formula of *D* aromatic content of the compound is evident *i.e.* it contains a benzene ring



The given reactions are:

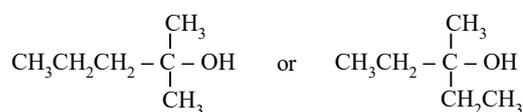


(i) Since *B* is resistant to oxidation, it must be *tert.* alcohol.

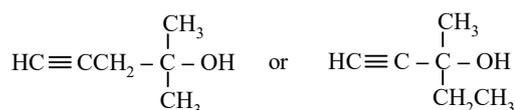
(ii) Since *B* is optically inactive, it must have at least two similar alkyl groups.

Thus the five carbon atoms can be adjusted into three alkyl groups (of which two are similar) either as

$-\text{CH}_3$, $-\text{CH}_3$ and $-\text{C}_3\text{H}_7$ or as $-\text{C}_2\text{H}_5$, $-\text{C}_2\text{H}_5$ and $-\text{CH}_3$. Thus the possible structure of alcohol *B* is either



Hence the corresponding compound *A* is either

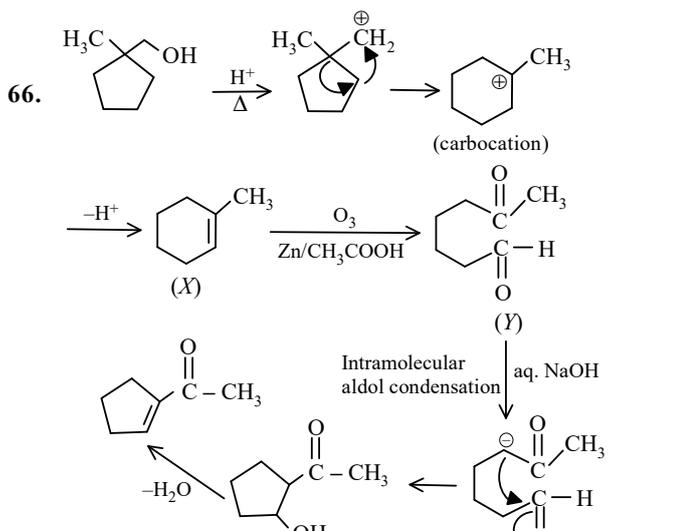
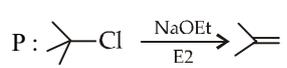
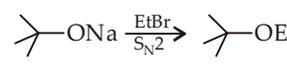
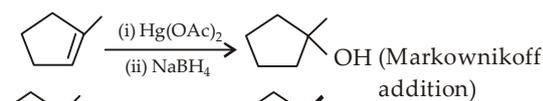
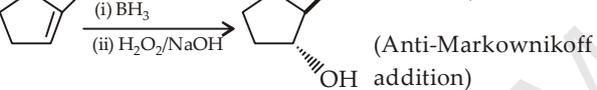


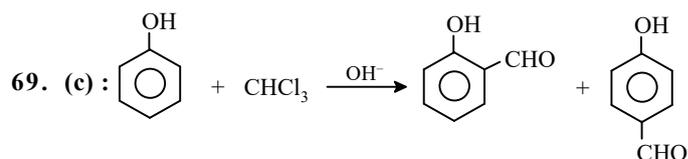
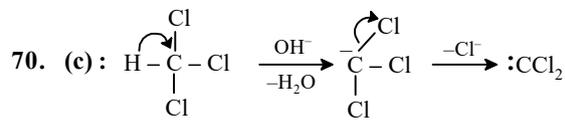
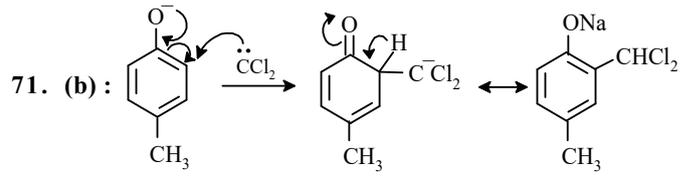
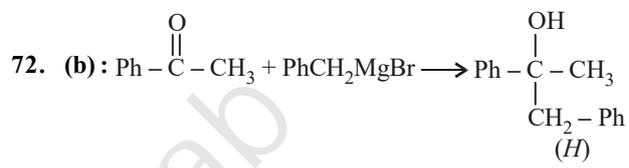
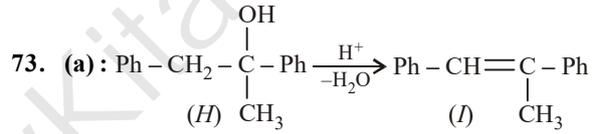
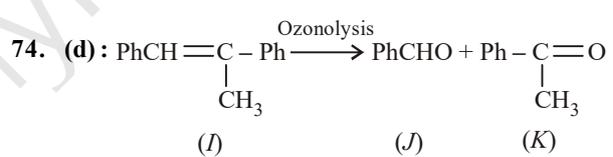
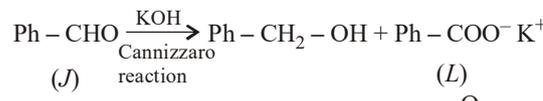
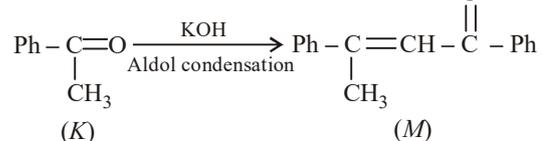
However compound *A* is optically active so its structure should

be $\text{HC}\equiv\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_2\text{CH}_3}{\text{C}}}-\text{OH}$ which contains a chiral C-atom.

Alcohols, Phenols and Ethers

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66. 
67. (a) P:  Q: 
- R:  OH (Markovnikoff addition)
- Q:  OH addition)
68. (c) : The first three members of alcohols are highly soluble in water. The solubility in water is due to hydrogen bonding as -OH groups present both in alcohol and water are highly polarised. The solubility in water decreases with rise of molecular mass. The solubility of higher members decreases in water. The alcohols possess both hydrophilic and hydrophobic moieties. With increase in molecular mass, the hydrophobic part of the alcohols increases. This reduces their water solubility. Thus we find that statement-1 is correct but statement-2 is not correct so the correct answer is (c).

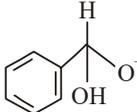
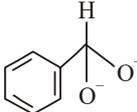
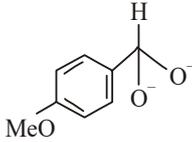
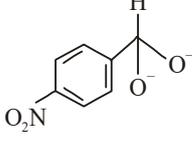
69. (c) : 
70. (c) : 
71. (b) : 
72. (b) : 
73. (a) : 
74. (d) : 
- 
- 



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Aldehydes and Ketones

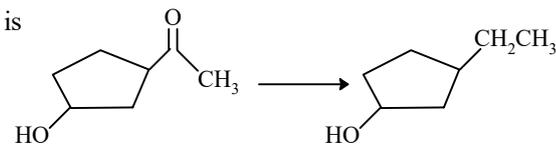
Multiple Choice Questions with ONE Correct Answer

1. The reagent with which both acetaldehyde and acetone react easily is
 (a) Fehling's reagent (b) Grignard reagent
 (c) Schiff's reagent (d) Tollen's reagent
 (1981)
2. A compound that gives a positive iodoform test is
 (a) 1-pentanol (b) 2-pentanone
 (c) 3-pentanone (d) pentanal (1982)
3. When acetaldehyde is heated with Fehling's solution it gives a precipitate of
 (a) Cu (b) CuO
 (c) Cu₂O (d) Cu + Cu₂O + CuO
 (1983)
4. The Cannizzaro reaction is not given by
 (a) trimethylacetaldehyde (b) acetaldehyde
 (c) benzaldehyde (d) formaldehyde (1983)
5. The compound that will not give iodoform on treatment with alkali and iodine is
 (a) acetone (b) ethanol
 (c) diethyl ketone (d) isopropyl alcohol
 (1985)
6. Polarisation of electrons in acrolein may be written as
 (a) $\overset{\delta^-}{\text{CH}_2}=\text{CH}-\overset{\delta^+}{\text{C}}=\text{O}$ (b) $\overset{\delta^-}{\text{CH}_2}=\text{CH}-\text{CH}=\overset{\delta^+}{\text{O}}$
 (c) $\overset{\delta^-}{\text{CH}_2}=\overset{\delta^+}{\text{C}}-\text{CH}=\text{O}$ (d) $\overset{\delta^+}{\text{CH}_2}=\text{CH}-\text{CH}=\overset{\delta^-}{\text{O}}$
 (1988)
7. The enolic form of acetone contains
 (a) 9 sigma bonds, 1 pi-bond and 2 lone pairs
 (b) 8 sigma bonds, 2 pi-bonds and 2 lone pairs
 (c) 10 sigma bonds, 1 pi-bond and 1 lone pair
 (d) 9 sigma bonds, 2 pi bonds and 1 lone pair
 (1990)
8. *m*-Chlorobenzaldehyde on reaction with concentrated KOH at room temperature gives
 (a) potassium *m*-chlorobenzoate and *m*-hydroxy benzaldehyde
 (b) *m*-hydroxy benzaldehyde and *m*-chlorobenzyl alcohol
 (c) *m*-chlorobenzyl alcohol and *m*-hydroxybenzyl alcohol
 (d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol.
 (1991)
9. In the Cannizzaro reaction given below,
 $2\text{PhCHO} \longrightarrow \text{PhCH}_2\text{OH} + \text{PhCO}_2^-$, the slowest step is
 (a) the attack of OH^- at the carbonyl group
 (b) the transfer of hydride to the carbonyl group
 (c) the abstraction of proton from the carboxylic acid
 (d) the deprotonation of PhCH₂OH.
 (1997)
10. In a Cannizzaro reaction, the intermediate that will be the best hydride donor is
 (a)  (b) 
 (c)  (d) 
 (1997)
11. The enol form of acetone, after treatment with D₂O, gives
 (a) $\text{CH}_3-\overset{\text{OD}}{\text{C}}=\text{CH}_2$ (b) $\text{CD}_3-\overset{\text{O}}{\text{C}}-\text{CD}_3$
 (c) $\text{CH}_2=\overset{\text{OH}}{\text{C}}-\text{CH}_2\text{D}$ (d) $\text{CD}_2=\overset{\text{OD}}{\text{C}}-\text{CD}_2$
 (1999)

Aldehydes and Ketones

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12. The appropriate reagent for the following transformation is

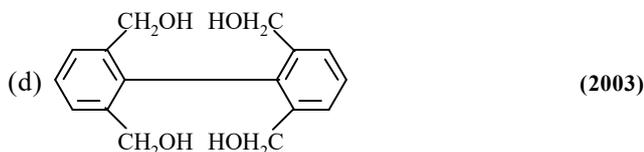
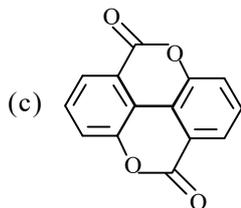
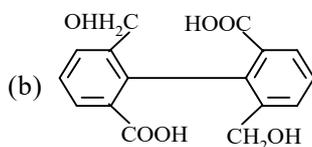
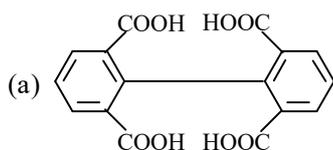


- (a) Zn(Hg), HCl
(b) $\text{NH}_2\text{NH}_2, \text{OH}^-$
(c) H_2/Ni
(d) NaBH_4 (2000)

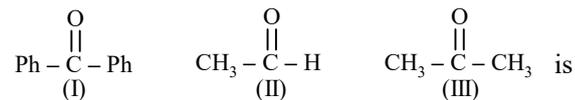
13. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives

- (a) benzyl alcohol and sodium formate
(b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate
(d) benzyl alcohol and methyl alcohol (2001)

14. Major product is



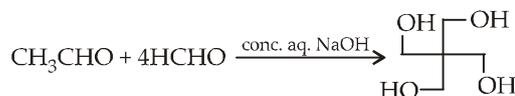
15. The correct order of reactivity of PhMgBr with



- (a) (I) > (II) > (III) (b) (III) > (II) > (I)
(c) (II) > (III) > (I) (d) (I) > (III) > (II)

(2004)

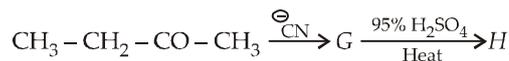
16. The number of aldol reaction(s) that occurs in the given transformation is



- (a) 1 (b) 2 (c) 3 (d) 4

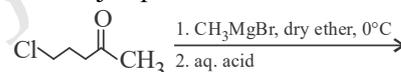
(2012)

17. The major product H of the given reaction sequence is



- (a) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{COOH}$
(b) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CN}$
(c) $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}(\text{OH})-\text{COOH}$
(d) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CO}-\text{NH}_2$ (2012)

18. The major product in the following reaction is



- (a) $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ (b) $\text{H}_2\text{C}=\text{CH}-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{CH}_3$
(c) (d) (2014)

**Multiple Choice Questions with
ONE or MORE THAN ONE Correct Answer**

19. Base catalysed aldol condensation occurs with

- (a) propionaldehyde
(b) benzaldehyde
(c) 2-methyl propionaldehyde
(d) 2, 2-dimethylpropionaldehyde (1984)

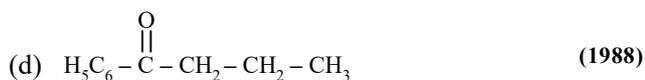
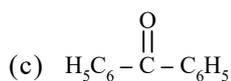
20. Which of the following compounds will react with ethanolic KCN?

- (a) Ethyl chloride (b) Acetyl chloride
(c) Chlorobenzene (d) Benzaldehyde

(1984)

21. Keto-enol tautomerism is observed in

- (a) $\text{H}_5\text{C}_6-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ (b) $\text{H}_5\text{C}_6-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$



22. Which of the following are the examples of aldol condensation?

- (a) $2\text{CH}_3\text{CHO} \xrightarrow{\text{dil. NaOH}} \text{CH}_3\text{CHOHCH}_2\text{CHO}$
 (b) $2\text{CH}_3\text{COCH}_3 \xrightarrow{\text{dil. NaOH}} \text{CH}_3\text{COCH}_3\text{CH}_2\text{COCH}_3$
 (c) $2\text{HCHO} \xrightarrow{\text{dil. NaOH}} \text{CH}_3\text{OH}$
 (d) $\text{C}_6\text{H}_5\text{CHO} + \text{HCHO} \xrightarrow{\text{dil. NaOH}} \text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (1989)

23. Which of the following will give yellow precipitate with I_2/NaOH ?

- (a) $\text{ICH}_2\text{COCH}_2\text{CH}_3$ (b) $\text{CH}_3\text{COOCOCH}_3$
 (c) CH_3CONH_2 (d) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ (1997)

24. A new carbon-carbon bond formation is possible in

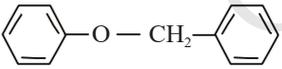
- (a) Cannizzaro reaction
 (b) Friedel-Crafts alkylation
 (c) Clemmensen reaction
 (d) Reimer-Tiemann reaction (1998)

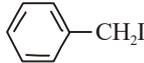
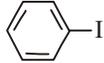
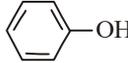
25. Which of the following will react with water?

- (a) CHCl_3 (b) Cl_3CCHO
 (c) CCl_4 (d) $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1998)

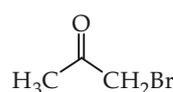
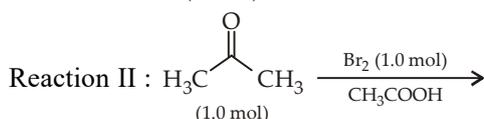
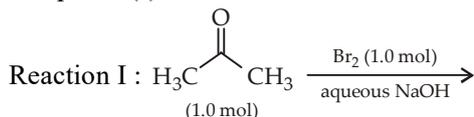
26. Which of the following will undergo aldol condensation?

- (a) Acetaldehyde (b) Propanaldehyde
 (c) Benzaldehyde (d) Trideuteroacetaldehyde (1998)

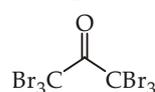
27. The ether  when treated with HI produces

- (a)  (b) 
 (c)  (d)  (1993)

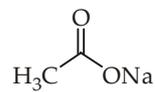
28. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)



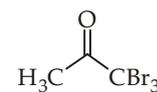
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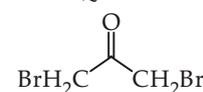
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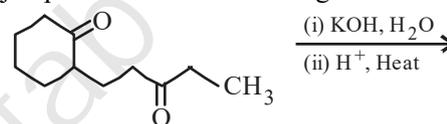
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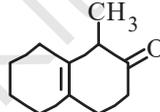
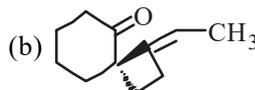
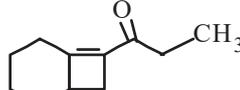
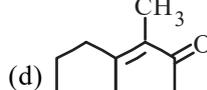


U

- (a) Reaction I : P and Reaction II : P
 (b) Reaction I : U, acetone and Reaction II : Q, acetone
 (c) Reaction I : T, U, acetone and Reaction II : P
 (d) Reaction I : R, acetone and Reaction II : S, acetone (JEE 2013)

29. The major product of the following reaction is



- (a)  (b) 
 (c)  (d)  (2015)

Fill in the Blanks

30. Fehling's solution A consists of an aqueous solution of copper sulphate, while Fehling's solution B consists of an alkaline solution of (1990)

31. The structure of the intermediate product, formed by the oxidation of toluene with CrO_3 and acetic anhydride, whose hydrolysis gives benzaldehyde is (1992)

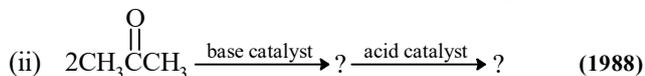
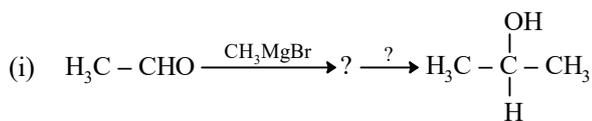
32. The structure of the enol form of $\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CO} - \text{CH}_3$ with intramolecular hydrogen bonding is (1993)

True / False

33. Benzaldehyde undergoes aldol condensation in an alkaline medium. (1982)

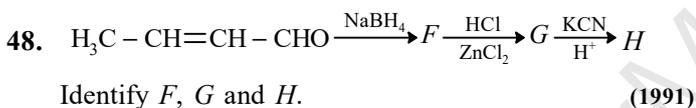
34. The yield of ketone when a secondary alcohol is oxidised is more than the yield of aldehyde when a primary alcohol is oxidised. (1983)

45. Complete the following reactions :



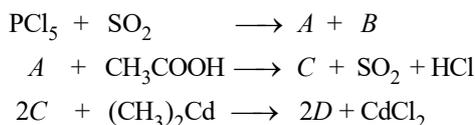
46. A hydrocarbon *A* (molecular formula C_5H_{10}) yields 2-methylbutane on catalytic hydrogenation. *A* adds HBr (in accordance with Markownikoff's rule) to form a compound *B* which on reaction with silver hydroxide forms an alcohol *C*, $\text{C}_5\text{H}_{12}\text{O}$. Alcohol *C* on oxidation gives a ketone *D*. Deduce the structures of *A*, *B*, *C* and *D* and show the reactions involved. (1988)

47. A ketone *A* which undergoes haloform reaction gives compound *B* on reduction. *B* on heating with sulphuric acid gives compound *C*, which forms monoozonide *D*. *D* on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify *A*, *B* and *C*. Write down the reactions involved. (1989)



49. Arrange the following in increasing order of expected enol content
 $\text{CH}_3\text{COCH}_2\text{CHO}$, CH_3COCH_3 , CH_3CHO , $\text{CH}_3\text{COCH}_2\text{COCH}_3$
 (1992)

50. In the following reactions identify the compounds *A*, *B*, *C* and *D*.



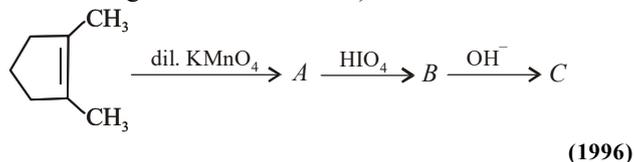
(1994)

51. When gas *A* is passed through dry KOH at low temperature, a deep red coloured compound *B* and a gas *C* are obtained. The gas *A*, on reaction with but-2-ene, followed by treatment with $\text{Zn}/\text{H}_2\text{O}$ yields acetaldehyde. Identify *A*, *B* and *C*. (1994)

52. An organic compound *A*, C_8H_6 , on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound *B*, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound *B*, when

treated with iodine in aqueous KOH, yields *C* and a yellow compound *D*. Identify *A*, *B*, *C* and *D* with justification. Show how *B* is formed from *A*. (1994)

53. Suggest appropriate structures for the missing compounds. (The number of carbon atoms remains the same throughout the reactions.)

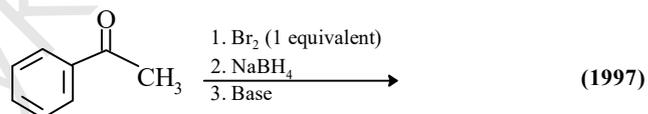


(1996)

54. A hydrocarbon *A* of the formula C_7H_{12} on ozonolysis gives a compound *B* which undergoes aldol condensation giving 1-acetylcyclopentene. Identify *A* and *B*. (1997)

55. How many asymmetric carbon atoms are created during the complete reduction of benzil ($\text{PhCO}-\text{COPh}$) with LiAlH_4 ? Also write the number of possible stereoisomers in the product. (1997)

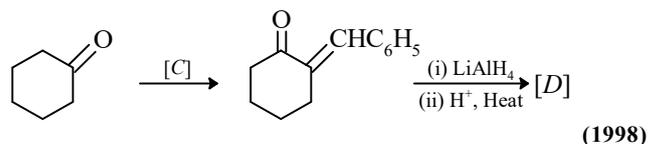
56. Predict the major product in the following reaction:



(1997)

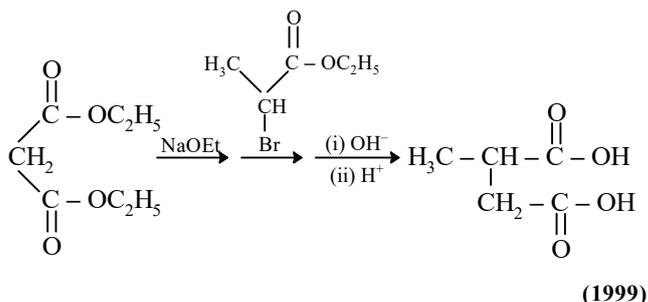
57. An aldehyde *A* ($\text{C}_{11}\text{H}_{18}\text{O}$), which does not undergo self aldol condensation, gives benzaldehyde and two moles of *B* on ozonolysis. Compound *B*, on oxidation with silver ion gives oxalic acid. Identify the compounds *A* and *B*. (1998)

58. Complete the following reaction with appropriate structures of products/reagents



(1998)

59. Explain briefly the formation of the products giving the structures of the intermediates.



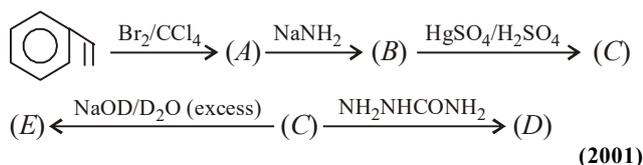
(1999)

Aldehydes and Ketones

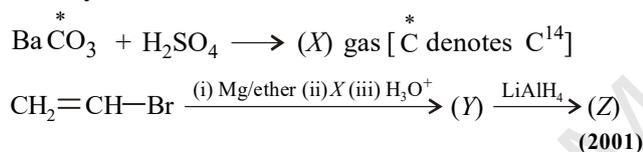
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60. An organic compound A , $C_6H_{10}O$ on reaction with CH_3MgBr followed by acid treatment gives compound B . The compound B on ozonolysis gives compound C , which in presence of a base gives 1-acetylcyclopentene D . The compound B on reaction with HBr gives compound E . Write the structures of A , B , C and E . Show how D is formed from C . (2000)

61. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures



62. Identify (X), (Y) and (Z) in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H_2C^*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C^* carbon in the entire scheme.



63. Five isomeric *para*-disubstituted aromatic compounds A to E with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations, give structures of the compounds.

- Both A and B form a silver mirror with Tollen's reagent; also B gives a positive test with $FeCl_3$ solution.
- C gives positive iodoform test.
- D is readily extracted in aqueous $NaHCO_3$ solution.
- E on acid hydrolysis gives 1, 4-dihydroxybenzene.

(2002)

64. An organic compound (P) of molecular formula $C_5H_{10}O$ is treated with dilute H_2SO_4 to give two compounds (Q) and (R) both of which responds iodoform test. The rate of reaction of (P) with dilute H_2SO_4 is 10^{10} faster than the reaction of ethylene with dilute H_2SO_4 . Identify the organic compounds, (P), (Q) and (R) and explain the extra reactivity of (P). (2004)

65. A monomer of a polymer on ozonolysis gives two moles of CH_2O and one mole of CH_3COCHO . Write the structure of monomer and write all - 'cis' configuration of polymer chain. (2005)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
- Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
- Statement-1 is true, statement-2 is false.
- Statement-1 is false, statement-2 is true.

66. **Statement-1** : Dimethylsulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds.

Statement-2 : It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates.

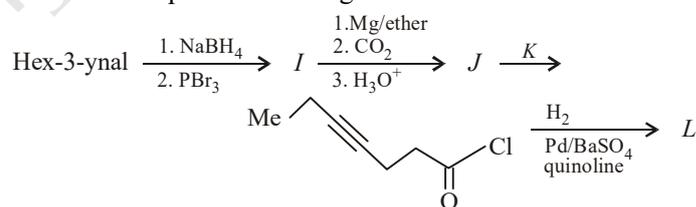
(2001)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension-1

In the following reaction sequence products I , J and L are formed. K represents a reagent.



67. The structure of the product I is

-
-
-
-

68. The structures of compounds J and K , respectively, are

- and $SOCl_2$
- and SO_2Cl_2
- and $SOCl_2$
- and CH_3SO_2Cl

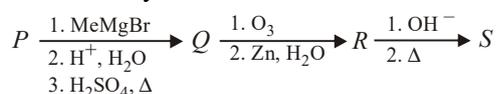
69. The structure of product *L* is

- (a)
- (b)
- (c)
- (d)

(2008)

Comprehension-2

A carbonyl compound *P*, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin *Q*. Ozonolysis of *Q* leads to a dicarbonyl compound *R*, which undergoes intramolecular aldol reaction to give predominantly *S*.



70. The structure of the carbonyl compound *P* is

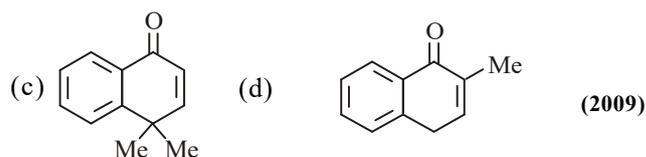
- (a)
- (b)
- (c)
- (d)

71. The structure of the products *Q* and *R*, respectively are

- (a)
- (b)
- (c)
- (d)

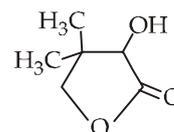
72. The structure of product *S* is

- (a)
- (b)



Comprehension-3

Two aliphatic aldehydes *P* and *Q* react in the presence of aqueous K_2CO_3 to give compound *R*, which upon treatment with HCN provides compound *S*. On acidification and heating, *S* gives the product shown below :



73. The compounds *P* and *Q* respectively are

- (a)
- (b)
- (c)
- (d)

74. The compound *R* is

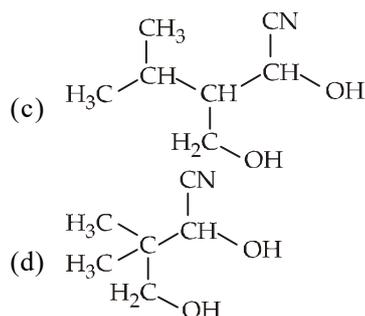
- (a)
- (b)
- (c)
- (d)

75. The compound *S* is

- (a)
- (b)

Aldehydes and Ketones

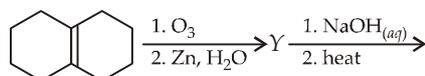
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(2010)

Integer Answer Type

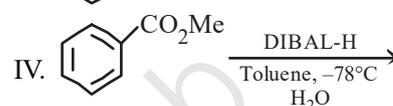
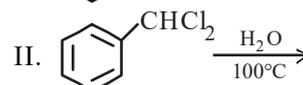
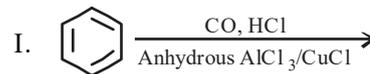
76. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is



(2010)

77. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with NaBH_4 (NOTE : stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are (2014)

78. Among the following, the number of reaction(s) that produce(s) benzaldehyde is



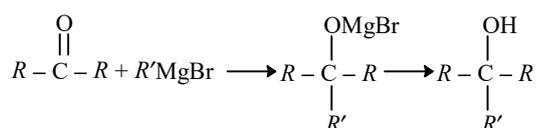
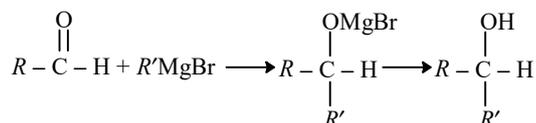
(2015)

ANSWER KEY

- | | | | | | |
|--------------------------------|---------------|---|------------|---------|------------|
| 1. (b) | 2. (b) | 3. (c) | 4. (b) | 5. (c) | 6. (d) |
| 7. (a) | 8. (d) | 9. (b) | 10. (d) | 11. (b) | 12. (b) |
| 13. (a) | 14. (b) | 15. (c) | 16. (c) | 17. (b) | 18. (d) |
| 19. (a, c) | 20. (a, b, d) | 21. (b, d) | 22. (a, b) | 23. (d) | 24. (b, d) |
| 25. (b) | 26. (a, b, d) | 27. (a, d) | 28. (c) | 29. (a) | |
| 30. Sodium potassium tartarate | | 31. $\text{C}_6\text{H}_5\text{CH}(\text{OCOCH}_3)_2$ | | 32. | |
| 33. False | 34. True | 35. False | 66. (a) | 67. (d) | 68. (a) |
| 69. (c) | 70. (b) | 71. (a) | 72. (b) | 73. (b) | 74. (a) |
| 75. (d) | 76. (3) | 77. (5) | 78. (4) | | |

Explanations

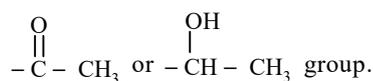
1. (b): Fehling's solution, Schiff's reagent and Tollen's reagent react only with aldehydes, but Grignard reagent reacts with both aldehydes and ketones.



2. (b): Iodoform test is given by only those compounds that contain a $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ or $-\overset{\text{OH}}{\text{C}}-\text{CH}_3$ group *i.e.* pentanone-2 will respond to this test as it contains $-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ group.

The structure of pentanone-2 is $\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$

3. (c): $\text{CH}_3\text{CHO} + 2\text{Cu}^{2+} + \text{OH}^- \longrightarrow \text{CH}_3\text{COOH} + \text{Cu}_2\text{O} \downarrow$
(Fehling's solution) red ppt.
4. (b): Acetaldehyde (CH_3CHO) does not undergo Cannizzaro's reaction since it contains α -H atoms. All other given aldehydes undergo Cannizzaro's reaction as they do not contain α -hydrogen atoms.
5. (c): Iodoform test is given by compounds having

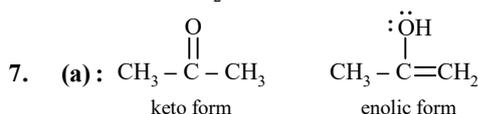


Acetone ($\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$) contains this group whereas

ethanol and isopropyl alcohol get oxidised to acetaldehyde (CH_3CHO) and acetone ($\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$) respectively in

presence of I_2 and they therefore give iodoform test. Hence only diethyl ketone ($\text{C}_2\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_2\text{H}_5$) does not give iodoform test.

6. (d): Because of $-R$ effect of $-\text{CHO}$ group, oxygen atom carries δ^- (negative) charge and carbon carries δ^+ (positive) charge *i.e.* $\overset{\delta^+}{\text{C}}=\overset{\delta^-}{\text{O}}-\text{CH}=\overset{\delta^-}{\text{O}}$.

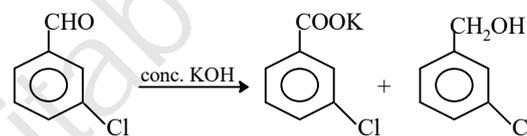


Number of σ -bonds in enolic form = 9

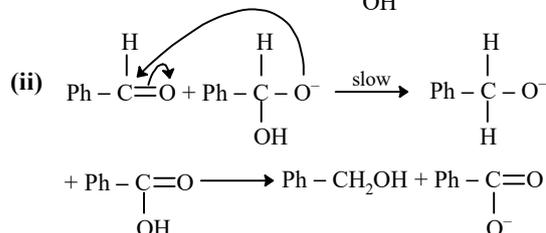
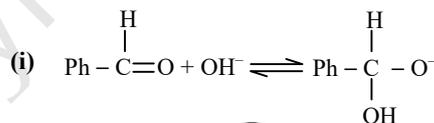
Number of π -bonds in enolic form = 1.

Number of lone pair of electrons in enolic form = 2 (on O atom).

8. (d): It is an example of Cannizzaro's reaction.

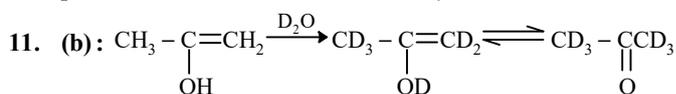


9. (b): The possible mechanism is



The slowest step is hydride transfer step (*i.e.* transfer of hydride to carbonyl group) shown in step (ii).

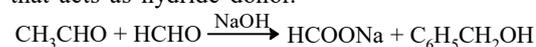
10. (d): $-\text{NO}_2$ group is an electron withdrawing group and its presence facilitates the release of hydride ion.



12. (b): $\text{Zn}-\text{Hg}/\text{HCl}$ can reduce $-\text{OH}$ group also. However, the action of hydrazine is carbonyl group specific.

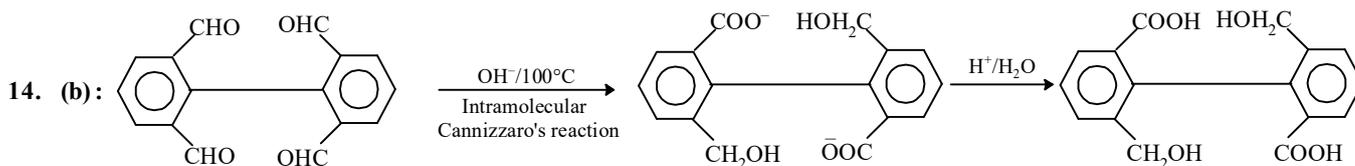
13. (a): Initially OH^- attacks at carbonyl carbon atom of HCHO than that of PhCHO because of the following reason:

- (i) the more electrophilic carbonyl carbon
 (ii) the less steric hindrance in formation of hydroxyalkoxide that acts as hydride donor.

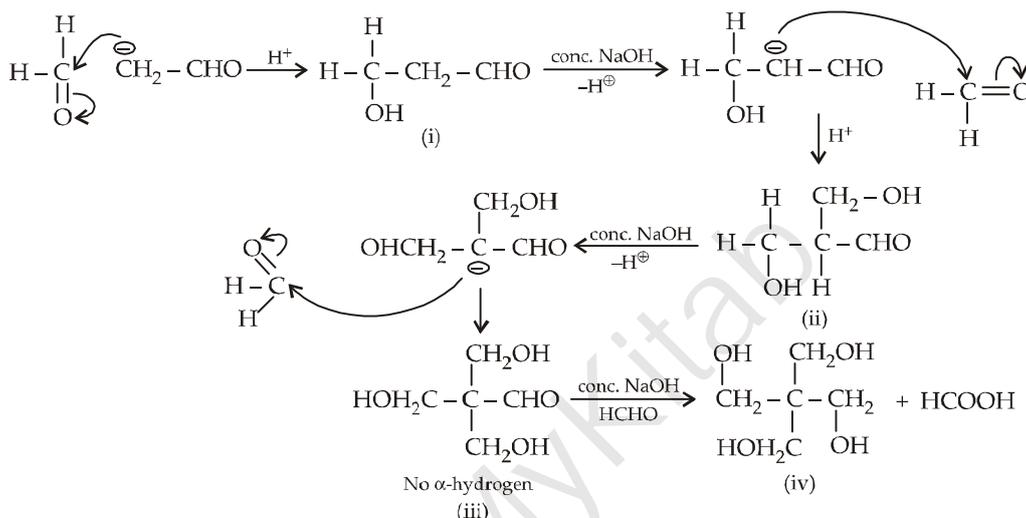


Aldehydes and Ketones

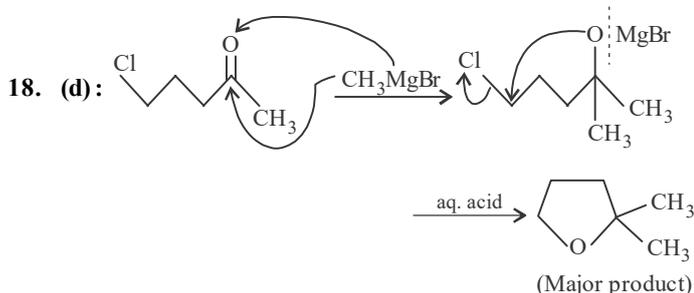
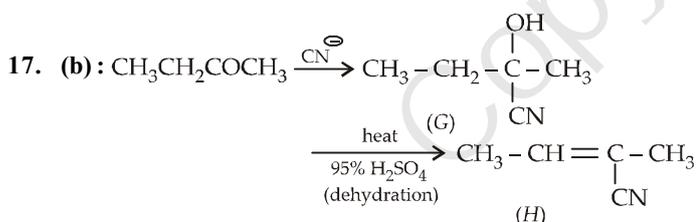
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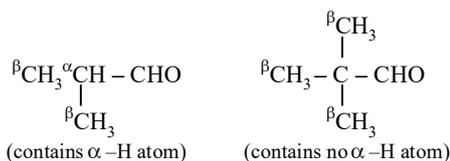
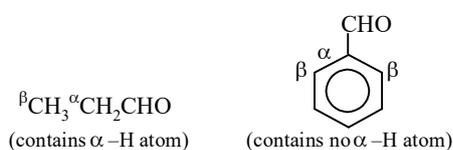
15. (c): PhMgBr reacts with a carbonyl compound and the reaction is nucleophilic addition reaction which depends upon electrophilicity and steric crowding around carbonyl group. Thus CH₃CHO is most reactive and C₆H₅COC₆H₅ is least reactive.



(i), (ii) and (iii) are aldol products but when two aldehydes without α -hydrogen reacts in presence of conc. NaOH they undergo cross Cannizzaro reaction not aldol reaction. Thus the final product is obtained by three cross aldol condensation processes and one cross-Cannizzaro reaction.



19. (a, c): Aldehydes having at least one α -H-atom undergo aldol condensation.



\therefore (a) and (c) will undergo aldol condensation.

20. (a, b, d): Ethyl chloride (C₂H₅Cl) and acetyl chloride (CH₃COCl) react with alc. KCN by nucleophilic substitution reaction.

Benzaldehyde (C₆H₅CHO) undergoes benzoin condensation

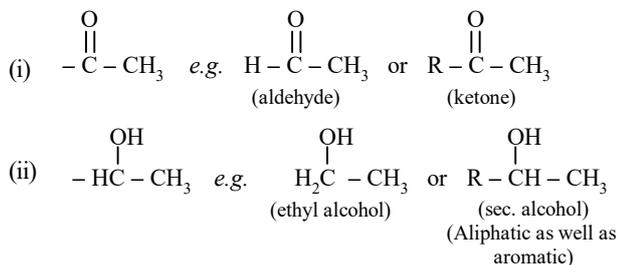


Thus only chlorobenzene does not react.

21. (b, d): Those compounds which have an α -H-atom (on the C adjacent to the CO group) can exhibit keto-enol tautomerism.

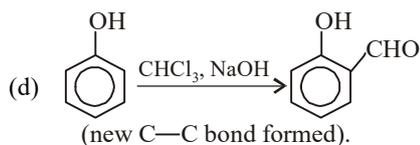
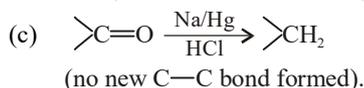
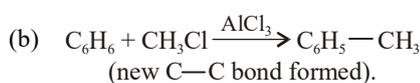
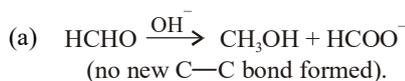
22. (a, b): In aldol condensation, two molecules of aldehydes or ketones condense together and there is no change in number of carbon atoms.

23. (d): Haloform reaction is given by those compounds that contain either of the following grouping



In the given options only (d) contains such a grouping.

24. (b, d):

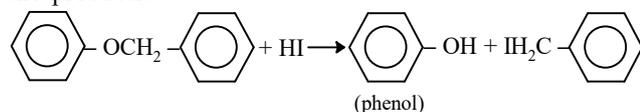


25. (b): Chloral (CCl_3CHO) on reaction with water forms chloral hydrate [$\text{CCl}_3\text{CH}(\text{OH})_2$] which is quite stable because of intramolecular hydrogen bonding.

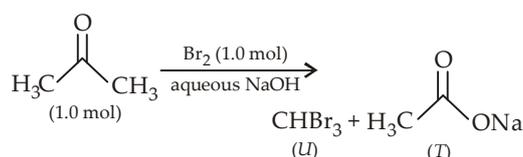
26. (a, b, d): Carbonyl compounds containing α -H (or α -D) atom undergoes aldol condensation.

Except option (c) i.e. $\text{C}_6\text{H}_5\cdot\text{CHO}$, all others have α -H atom so they undergo aldol condensation.

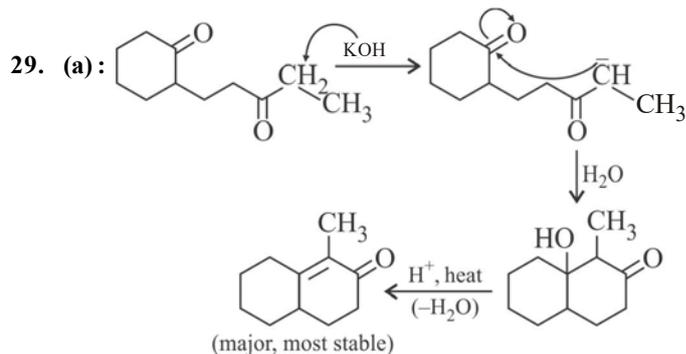
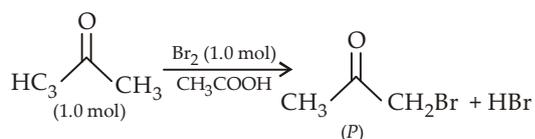
27. (a, d): Aromatic ethers when cleaved form phenol as one of the products.



28. (c): Reaction I :

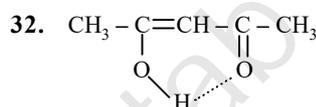
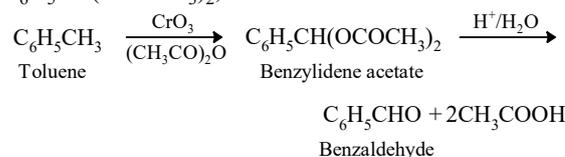


Reaction II :



30. Sodium potassium tartarate

31. $\text{C}_6\text{H}_5\text{CH}(\text{OCOCH}_3)_2$;



33. False

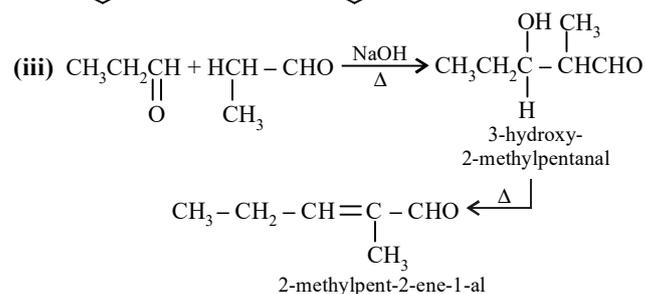
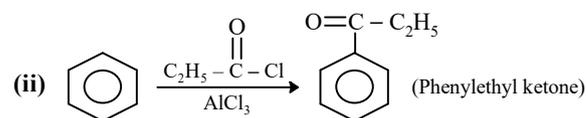
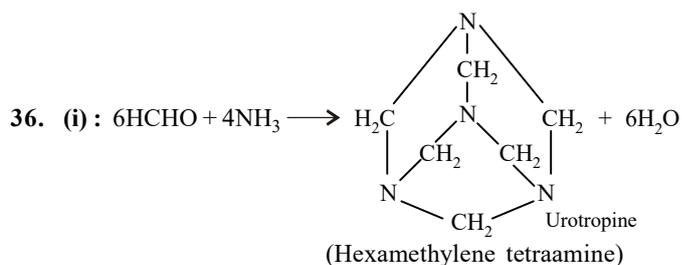
In benzaldehyde α -hydrogen atom is not present so it does not undergo aldol condensation but it undergoes Cannizzaro's reaction.

34. True

Since aldehydes are very susceptible to further oxidation to yield acids, however ketones are not easily oxidised further and can be obtained in high yields.

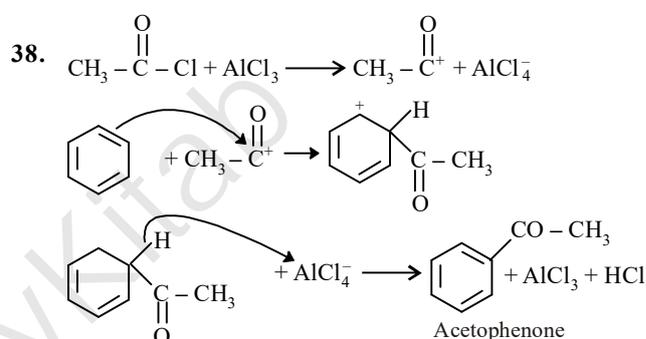
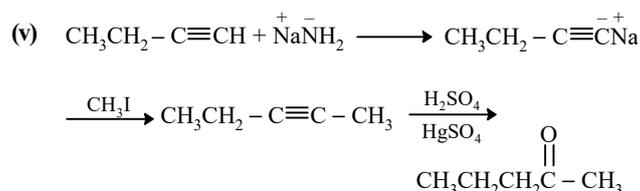
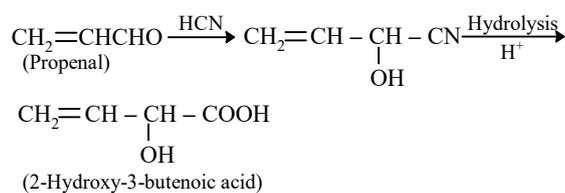
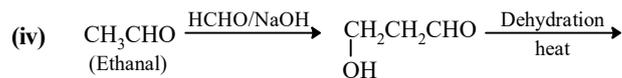
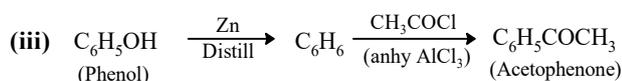
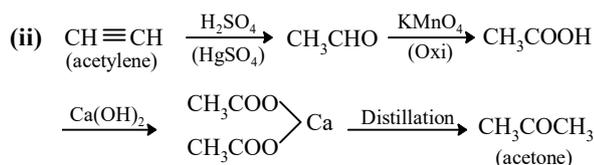
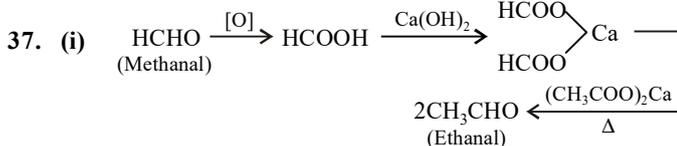
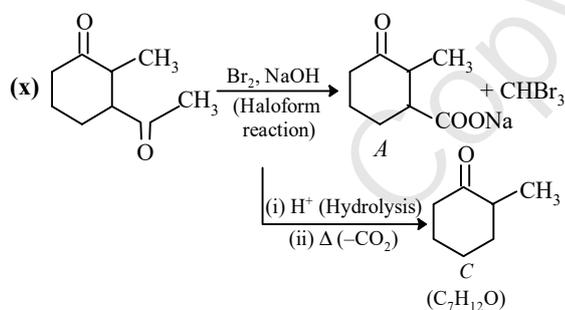
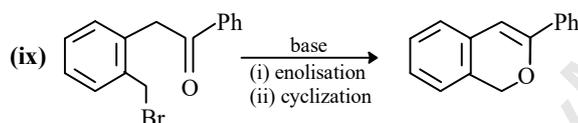
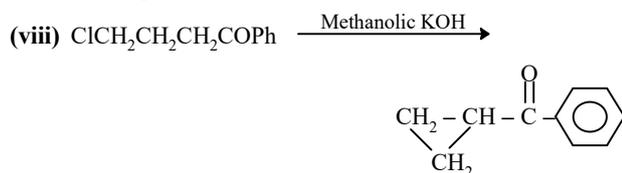
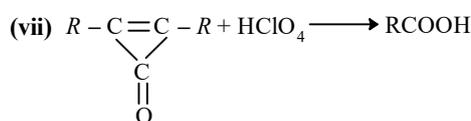
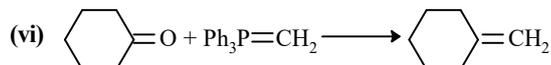
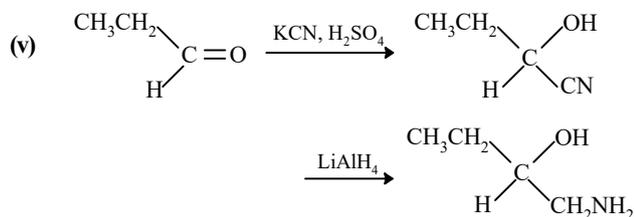
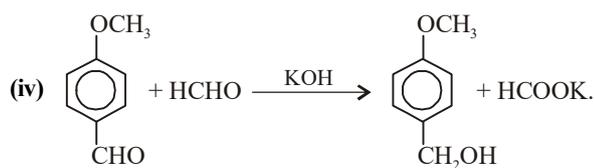
35. False

Grignard reagent on reaction with ketones yield *tert* alcohols. In present case *tert* butanol will be formed.

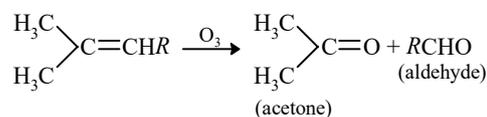


Aldehydes and Ketones

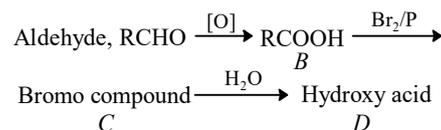
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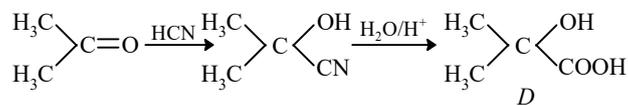
39. Ozonolysis of *A* to acetone and aldehyde indicates the presence of following structure in the molecule of *A* (alkene)



As given in the problem, we have



Structure of *D* (hydroxy acid) is determined by the reaction



The compound *D* is obtained by the hydrolysis of *C* with aqueous alkali, since *C* is a bromo compound, therefore it has a bromo group where the compound *D* has a hydroxy group. Therefore structure of *C* is



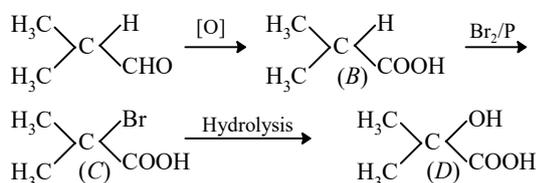
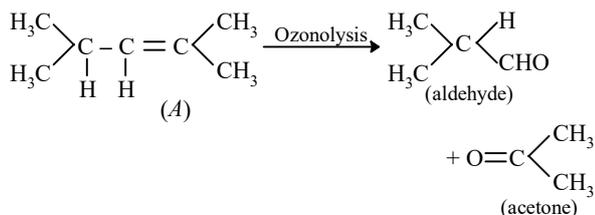
The compound *C* is formed by bromination of compound *B*, therefore the compound *B* is



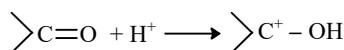
The compound *B* is formed by oxidation of an aldehyde therefore the structure of the aldehyde is



The aldehyde and acetone are formed by the ozonolysis of alkene *A*. Therefore the double bond in the alkene is at a position where there is oxygen atom in the aldehyde and acetone. Thus the compounds and reactions are:

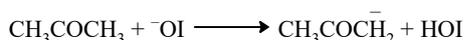


40. (i) In weakly acidic medium carbonyl compound is protonated to form conjugate acid.

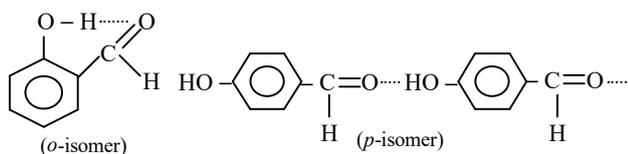


In strongly acidic medium ($\text{pH} < 3.5$), the unshared pair of electrons on N of the reagent is protonated to give an electrophile which cannot react. In basic media there is no protonation of carbonyl group.

(ii) Haloform reaction is a base promoted reaction (in this reaction the first step is removal of acidic hydrogen). Hypoiodite ion being stronger base than iodide ion, can easily remove acidic hydrogen atom.

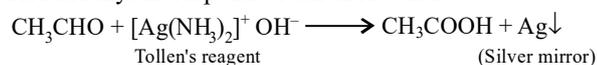


(iii) *ortho*-Hydroxybenzaldehyde has intramolecular hydrogen bonding whereas in case of *para*-hydroxybenzaldehyde we have intermolecular hydrogen bonding.

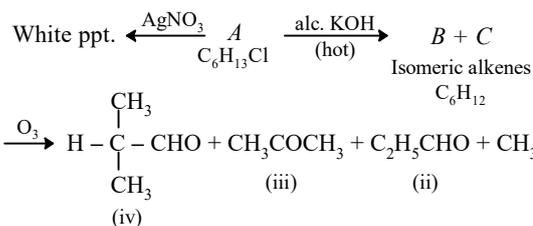


41. By use of Tollen's reagent or Fehling's solution or Schiff's reagent test.

Acetaldehydes respond to all these tests.

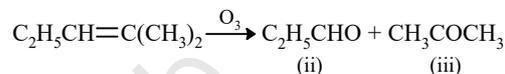
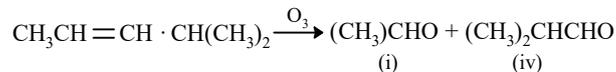


42. The given facts can be summarized as follows:

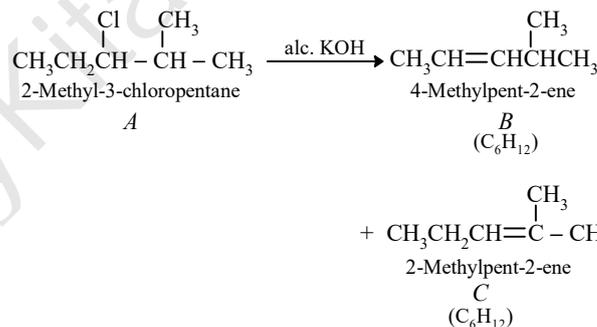


Taking into consideration the structures of four isomeric compound [*i.e.* (i) to (iv)], the structures of isomeric alkenes *A* and *B* with molecular formula (C_6H_{12}) may be written as $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}(\text{CH}_3)_2$ and $\text{C}_2\text{H}_5\text{CH}=\text{C}(\text{CH}_3)_2$

These olefins on ozonolysis yield the products (i) to (iv).



Thus the compound *A* should be a chloride that can eliminate a molecule of HCl to give *B* and also *C*.



43. -CHO + CH₃CHO

44. Calculation of Empirical Formula

Element	% age	Relative number of atoms	Simplest ratio
C	69.77	5.81	5
H	11.63	11.63	10
O	18.60	1.16	1

Empirical formula = $\text{C}_5\text{H}_{10}\text{O}$

Molecular weight = 86

Empirical formula weight = $5 \times 12 + 10 \times 1 + 1 \times 16$
= $60 + 10 + 16 = 86$

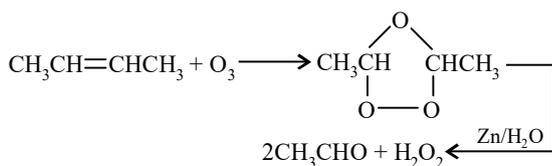
$$\therefore n = \frac{86}{86} = 1$$

Hence molecular formula = $\text{C}_5\text{H}_{10}\text{O}$

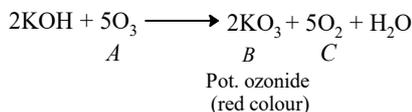
Since the compound forms bisulphite addition compound so it has a carbonyl group (*i.e.* it is an aldehyde or a ketone) since it does not reduce Fehling's solution so it is a ketone, since it gives positive iodoform test so it has $\text{CH}_3 - \text{C} -$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{O}$

grouping.

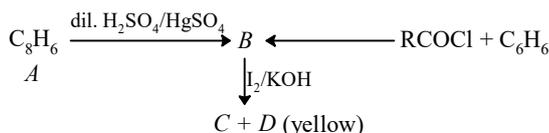
From the above we find that the compound is



Reaction of O_3 with KOH :



52. The facts given in the problem are:



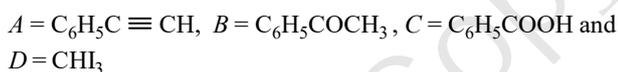
From the above it is indicated that:

(i) Since B can be obtained from benzene (C_6H_6) and RCOCl (acid chloride) in presence of anhy. AlCl_3 (Friedel Crafts reaction) so B is a ketone, $\text{C}_6\text{H}_5\text{COR}$.

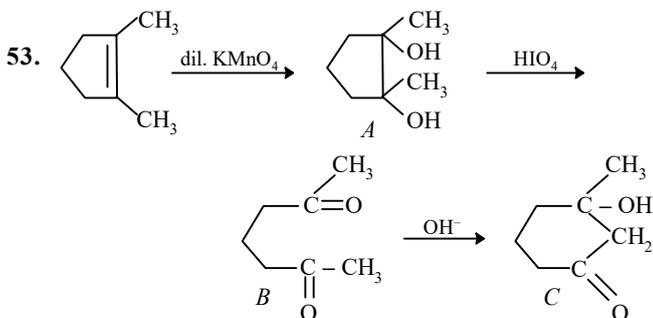
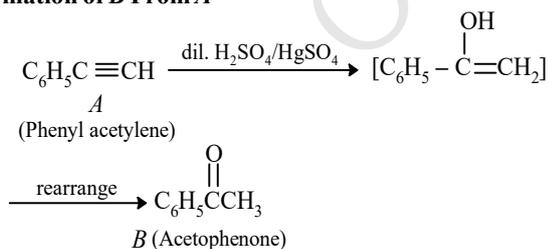
(ii) Since B (a ketone) reacts with I_2 and alkali to form yellow compound D (haloform reaction), it indicates that B contains the grouping CH_3CO - (*i.e.* R is CH_3). Thus it should be $\text{C}_6\text{H}_5\text{COCH}_3$.

(iii) Since B is also formed from A (C_8H_6) a hydrocarbon, on reaction with dil $\text{H}_2\text{SO}_4/\text{HgSO}_4$ so the compound A must have an acetylenic hydrogen atom (*i.e.* $-\text{C}\equiv\text{CH}$). Hence A must be $\text{C}_6\text{H}_5-\text{C}\equiv\text{CH}$.

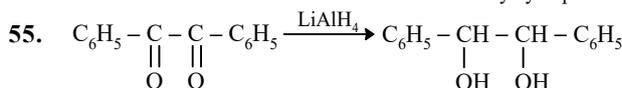
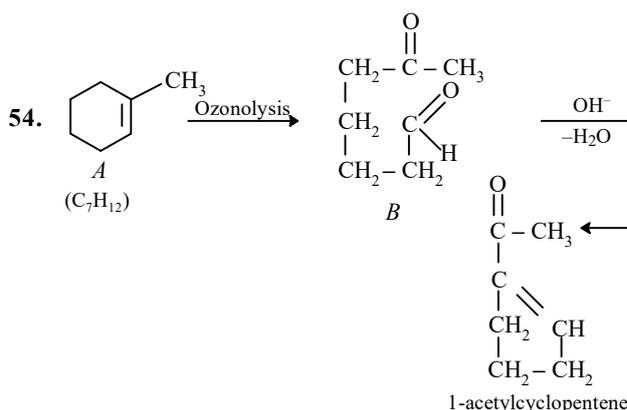
Thus compounds A , B , C and D are:



Formation of B From A

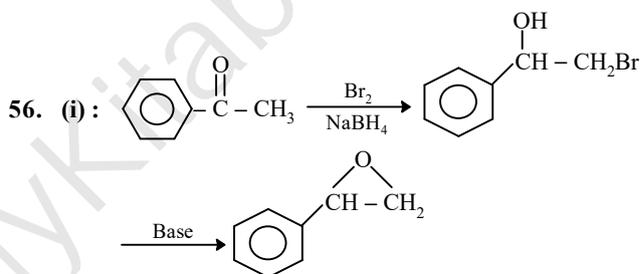


The last step is intramolecular aldol condensation.



The molecule after reduction has two asymmetric carbon atoms with symmetry in the molecule.

Thus $2 - 1 = 2^2 - 1 = 4 - 1 = 3$ stereoisomers are possible.



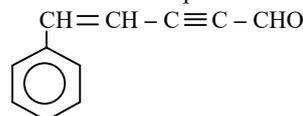
57. From the information provided in the problem following conclusions can be drawn:

(i) The aldehyde A ($\text{C}_{11}\text{H}_8\text{O}$) on ozonolysis gives $\text{C}_6\text{H}_5\text{CHO}$. This indicates the presence of a benzene ring and a side chain. The number of carbon atoms in side chain are ($\text{C}_{11} - \text{C}_6 = 5\text{C}$) and ($\text{H}_8 - \text{H}_5 = 3\text{H}$ atoms). The side chain thus have 5 carbon atoms, 3 hydrogen atoms and one oxygen atom, *i.e.*, it should be $\text{C}_5\text{H}_3\text{O}$. Since the compound A is an aldehyde (*i.e.* it contains a $-\text{CHO}$ group) so it can be written as $\text{C}_4\text{H}_2\text{CHO}$ (*i.e.* $\text{C}_5\text{H}_3\text{O}$).

(ii) On ozonolysis of one mole of A we get two moles of B . This fact indicates that there are two unsaturated linkages in the side chain and one of these must be of alkyne type (suggested by very small number of H atoms).

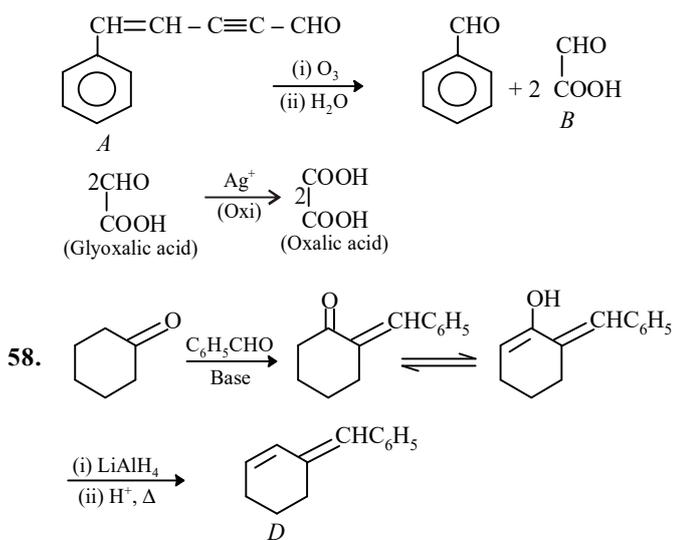
(iii) Aldehyde A does not undergo aldol condensation so it contains no α -hydrogen atom. It suggests the presence of Carbon-carbon triple bond ($-\text{C}\equiv\text{C}-$) between C_2 and C_3 . Thus the side chain $\text{C}_4\text{H}_2\text{CHO}$ may be written as $-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CHO}$

(iv) From the above considerations we conclude that the structure of compound A is



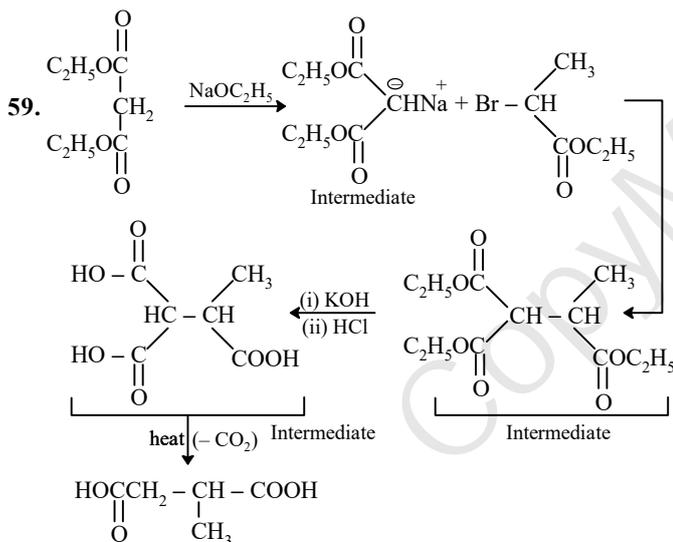
Aldehydes and Ketones

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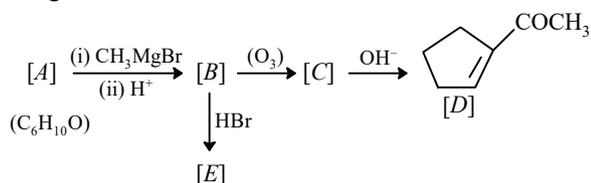


Thus $C = \text{C}_6\text{H}_5\text{CHO}$, $D =$

[LiAlH₄ reduces only 2° alcoholic group without affecting double bond].



60. The given reactions are:

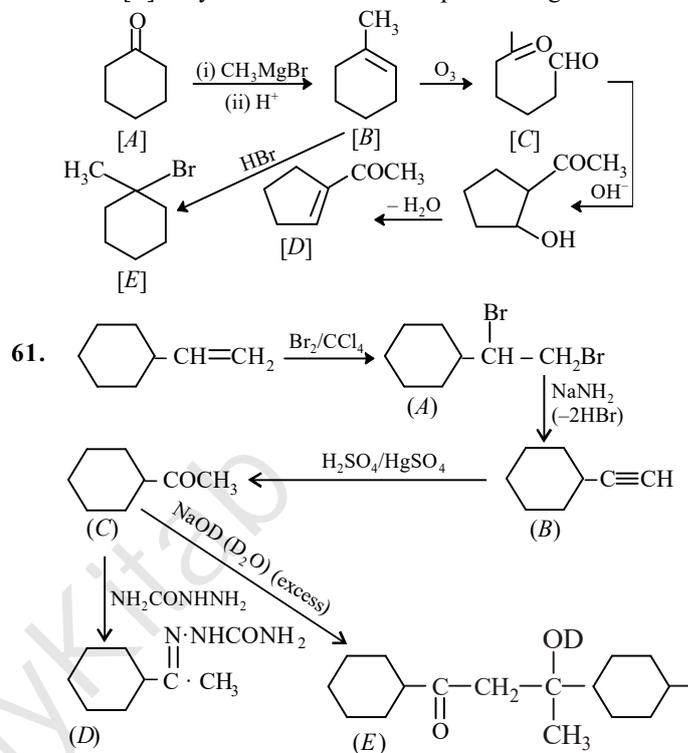


Following conclusions can be drawn:

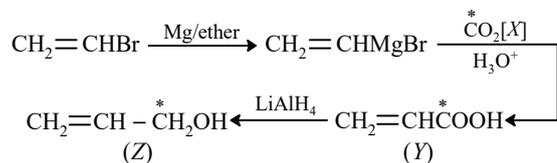
- From the ratio of carbon to hydrogen in [A] it appears to be a cyclic compound.
- [A] reacts with CH₃MgBr, it indicates that [A] contains a ketonic group.
- [B] on ozonolysis forms [C] so [B] must have a double bond and [C] must have two carbonyl groups.

(iv) [C] (a dicarbonyl compound) reacts with a base to give a cyclic compound which indicates that the intramolecular condensation has taken place during this conversion.

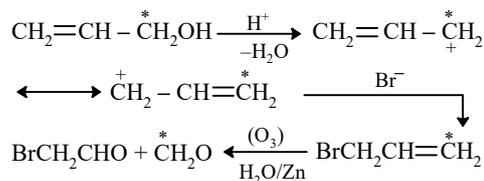
Thus [A] is cyclohexanone which explains the given reaction.



62. $\text{Ba}^*\text{CO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{CO}_2^{\uparrow}(\text{X})$



Formation of CH_2O from (Z)

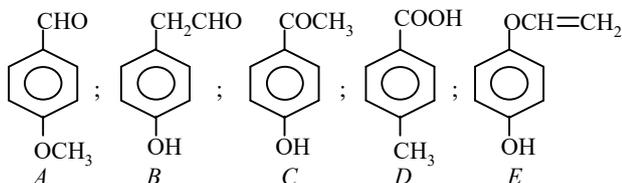


63. (i) : As both the compounds A and B form silver mirror with Tollen's reagent they have aldehydic group in their structures (i.e. A and B), B gives positive test with FeCl₃ solution which indicates that B contains phenolic group. Hence compound A is *p*-methoxybenzaldehyde and B is *p*-hydroxyphenylacetaldehyde.

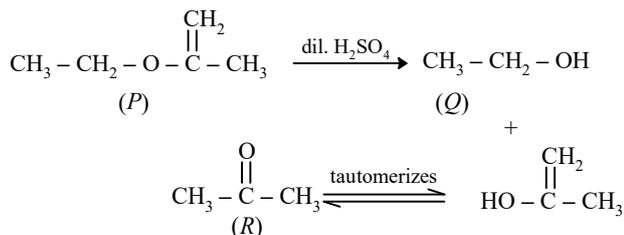
(ii) Compound C gives positive iodoform test so it must have CH₃CO group in its structure. Hence compound C is *p*-hydroxyphenylmethyl ketone.

(iii) Compound D is readily extracted in aqueous NaHCO₃, so it must have a -COOH group and therefore the compound D is *p*-methylbenzoic acid.

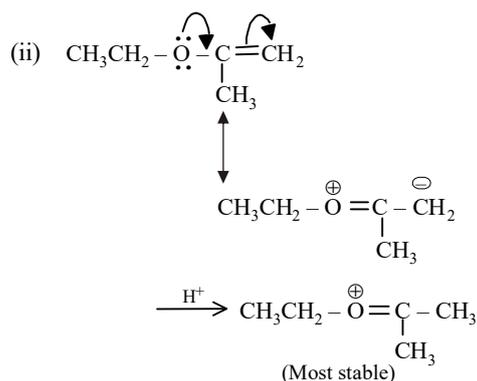
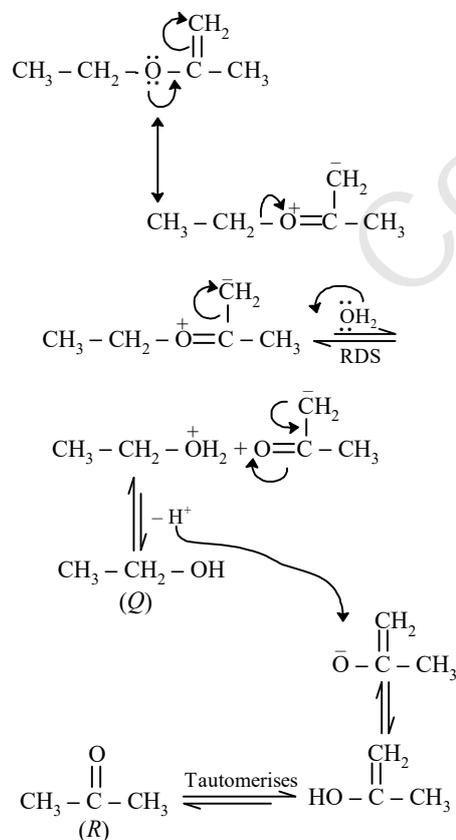
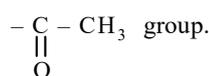
(iv) Compound *E* on hydrolysis gives 1, 4 dihydroxybenzene so compound *E* is *p*-hydroxyphenylvinyl ether. Hence the structures of compounds *A*, *B*, *C*, *D* and *E* are:



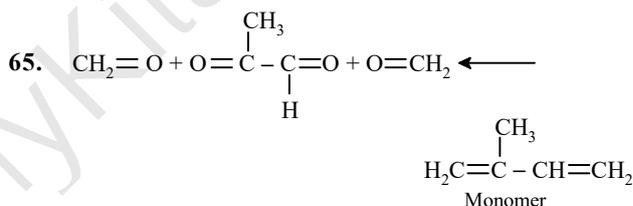
64. (i) The compound (*P*), $C_5H_{10}O$ have 1° unsaturation.



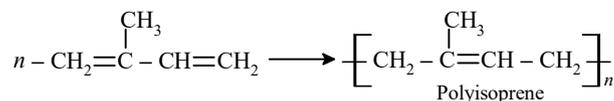
Compound (*Q*) and (*R*) both gives iodoform test since (*Q*) contains $-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{OH}$ group, while (*R*) is methyl ketone having



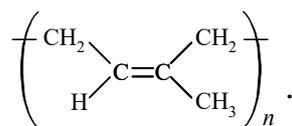
The compound (*P*) on reaction with dilute H_2SO_4 gives most stable cationic intermediate $\text{CH}_3\text{CH}_2 - \overset{\oplus}{\text{O}} = \overset{\ominus}{\text{C}} - \overset{\text{CH}_3}{\text{CH}_2}$ stabilised by completion of octet. Hence its rate of formation is higher while $\text{CH}_2 = \text{CH}_2$ gives 1° carbocation *i.e.* $\text{CH}_3 - \overset{\oplus}{\text{C}}\text{H}_2$ with dilute H_2SO_4 which is not so greatly stabilized by resonance. Hence $\text{CH}_2 = \text{CH}_2$ is very less reactive than compound (*P*).



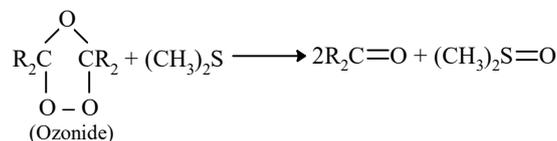
Thus the possible polymer should be



The polymer so obtained has *cis*-configuration all through



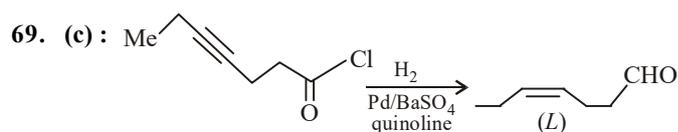
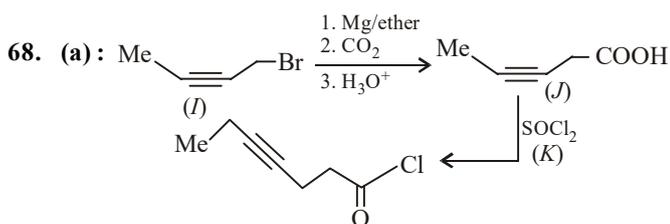
66. (a): We can reduce ozonides, by $(\text{CH}_3)_2\text{S}$, to yield carbonyl compounds and dimethyl sulphoxide.



67. (d): $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{C} - \text{CH}_2 - \text{CHO} \xrightarrow[2. \text{PBr}_3]{1. \text{NaBH}_4}$
Hex-3-ynal
 $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{C} - \text{CH}_2 - \text{CH}_2\text{Br}$
or $\text{Me} - \text{CH} = \text{CH} - \text{CH}_2 - \text{Br}$

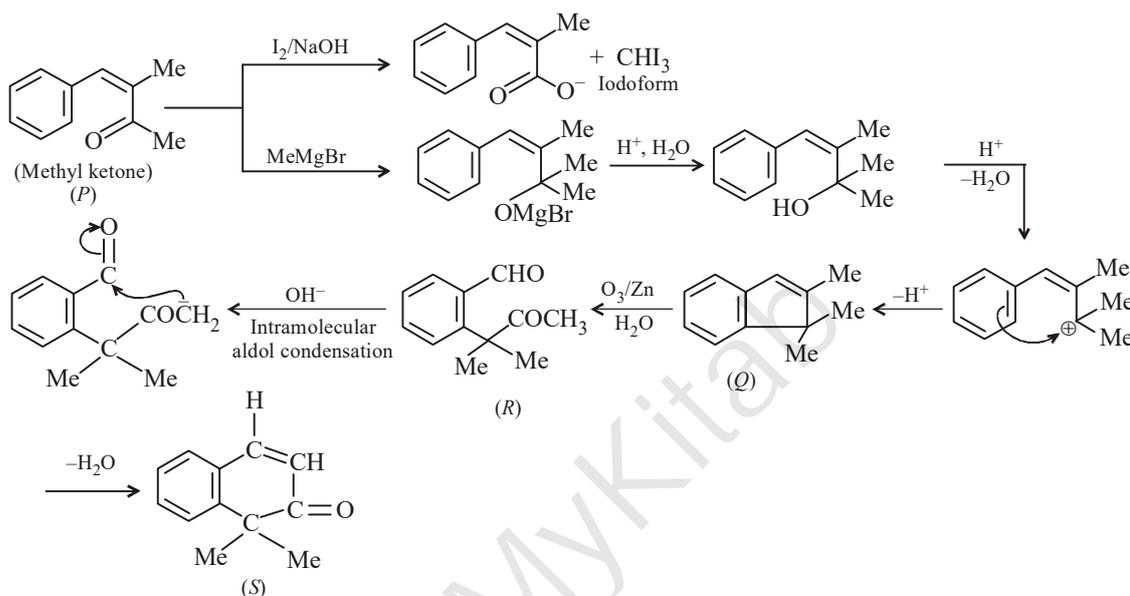
Aldehydes and Ketones

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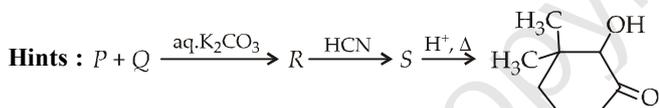


70. (b) 71. (a) 72. (b)

Hint :



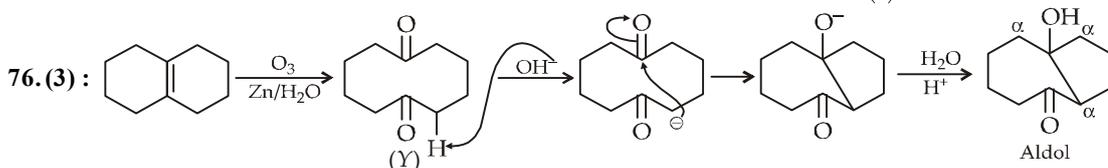
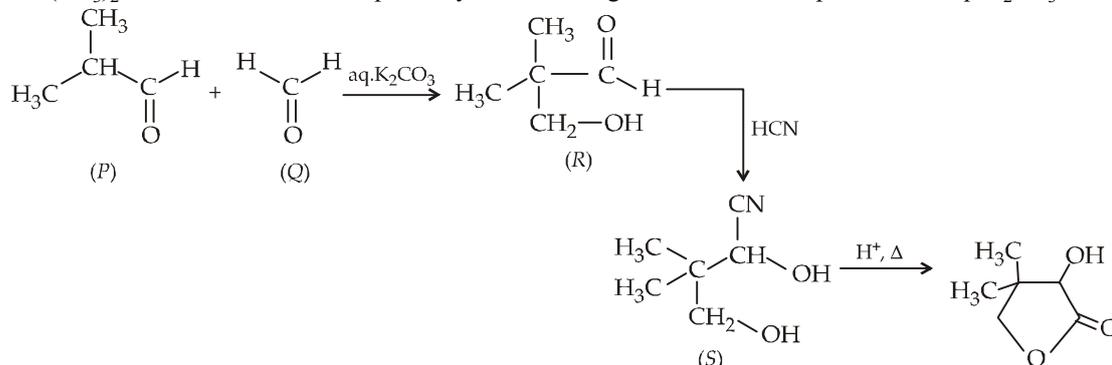
73. (b) 74. (a) 75. (d)



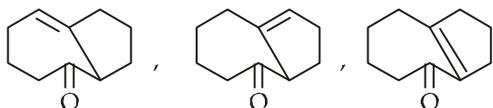
$\therefore R$ reacts with HCN, it must contain >C=O group.

Since compound S gives the given product formed on treatment with H^+ followed by heating, thus S must have one carbon more than that in R .

$\therefore P$ and Q are $(\text{CH}_3)_2\text{CHCHO}$ and HCHO respectively which undergo condensation in presence of aq. K_2CO_3 as follows :



The aldol has 3 α -hydrogen atoms and hence gives three dehydration products.

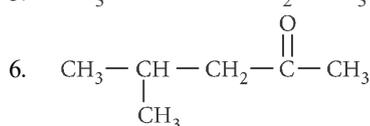
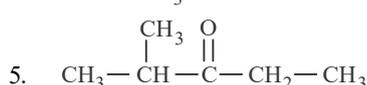
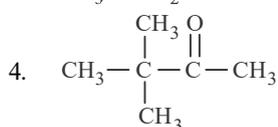
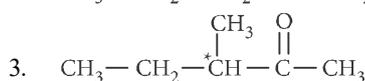
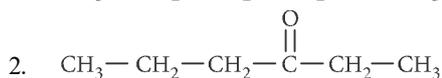
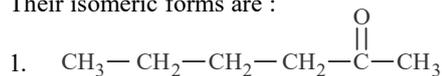


77. (5) : General formula of ketone; $C_nH_{2n}O$

$$12n + 2n + 16 = 100 \Rightarrow n = 6$$

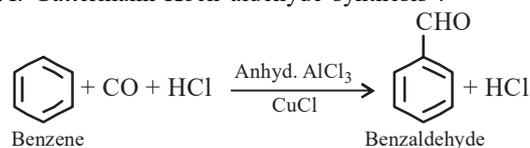
Hence, the ketone is $C_6H_{12}O$.

Their isomeric forms are :

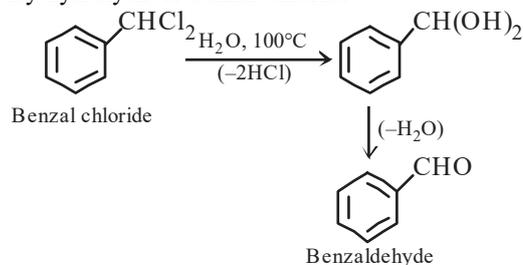


Only structure (3) will not give racemic mixture on reaction with $NaBH_4$.

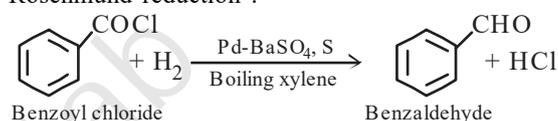
78. (4) : I. Gattermann-Koch aldehyde synthesis :



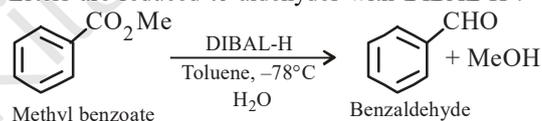
II. By hydrolysis of benzal chloride :



III. Rosenmund reduction :



IV. Esters are reduced to aldehydes with DIBAL-H :



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Carboxylic Acids and Their Derivatives

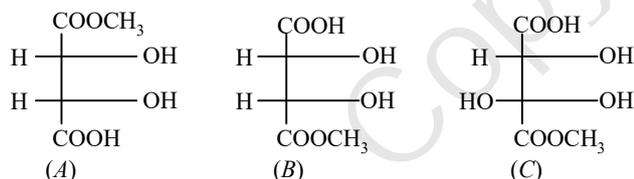
Multiple Choice Questions with ONE Correct Answer

1. Which of the following is basic?
 (a) $\text{CH}_3 - \text{CH}_2 - \text{OH}$ (b) $\text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH}$
 (c) $\text{H} - \text{O} - \text{O} - \text{H}$ (d) $\text{H}_3\text{C} - \overset{\text{O}}{\parallel}{\text{C}} - \text{OH}$ (1980)

2. Hydrogenation of benzoyl chloride in the presence of Pd on BaSO_4 gives
 (a) benzyl alcohol (b) benzaldehyde
 (c) benzoic acid (d) phenol (1992)

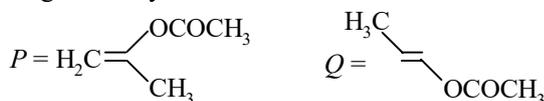
3. The organic product formed in the reaction is
 $\text{C}_6\text{H}_5\text{COOH} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) LiAlH}_4}$
 (a) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (b) $\text{C}_6\text{H}_5\text{COOH}$ and CH_4
 (c) $\text{C}_6\text{H}_5\text{CH}_3$ and CH_3OH (d) $\text{C}_6\text{H}_5\text{CH}_3$ and CH_4 (1995)

4. The correct statement about the compounds A, B and C is



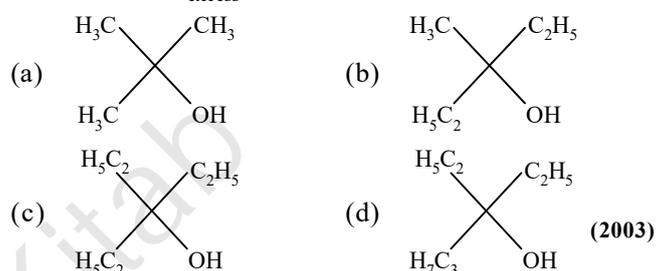
- (a) A and B are identical.
 (b) A and B are diastereomers.
 (c) A and C are enantiomers.
 (d) A and B are enantiomers. (1997)
5. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The C of CO_2 comes from
 (a) methyl group (b) carboxylic acid group
 (c) methylene group (d) bicarbonate (1999)
6. Benzoyl chloride is prepared from benzoic acid by
 (a) $\text{Cl}_2, h\nu$ (b) SO_2Cl_2 (c) SOCl_2 (d) $\text{Cl}_2, \text{H}_2\text{O}$ (2000)

7. The product of acid hydrolysis of P and Q can be distinguished by



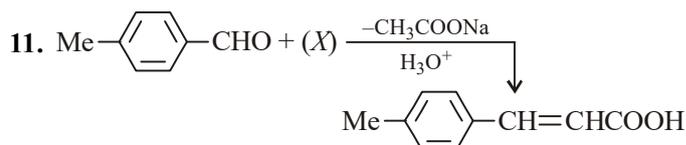
- (a) Lucas reagent (b) 2,4-DNP
 (c) Fehling's solution (d) NaHSO_3 (2003)

8. Ethyl ester $\xrightarrow[\text{excess}]{\text{CH}_3\text{MgBr}}$ P. The product P will be



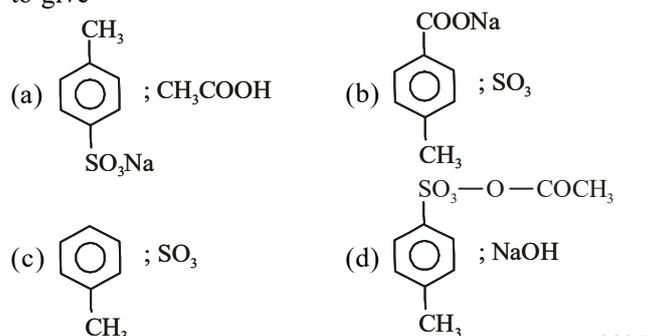
9. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be
 (a) optically active mixture (b) pure enantiomer
 (c) meso compound (d) racemic mixture (2003)

10. How will you convert butan-2-one to propanoic acid?
 (a) Tollen's reagent (b) Fehling's solution
 (c) $\text{NaOH}/\text{I}_2/\text{H}^+$ (d) $\text{NaOH}/\text{NaI}/\text{H}^+$ (2005)



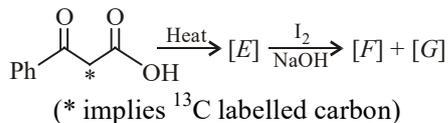
The compound (X) is

- (a) CH_3COOH (b) $\text{BrCH}_2 - \text{COOH}$
 (c) $(\text{CH}_3\text{CO})_2\text{O}$ (d) $\text{CHO} - \text{COOH}$ (2005)
12. 4-methylbenzenesulphonic acid reacts with sodium acetate to give



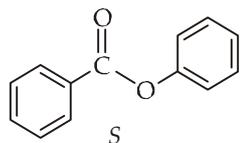
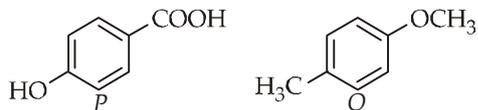
(2005)

13. In the following reaction sequence, the correct structures of *E*, *F* and *G* are

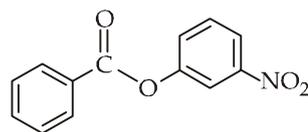
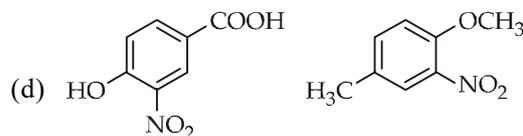
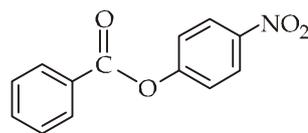
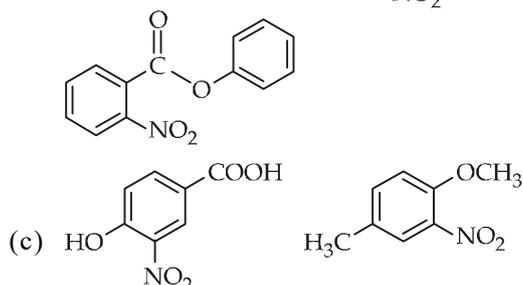
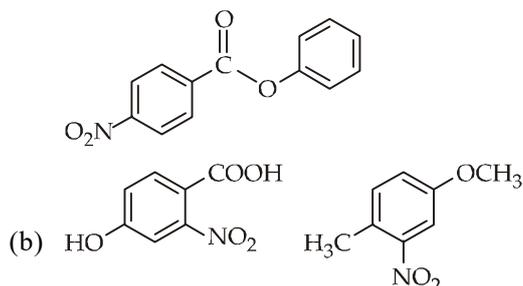
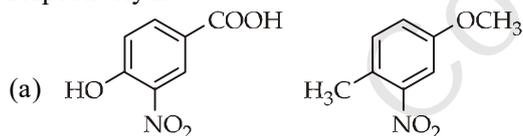


- (a) $E = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{*}{\text{C}}-\text{CH}_3$ $F = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{*}{\text{C}}-\text{O}^{\ominus}\text{Na}^{\oplus}$ $G = \text{CH}_3$
- (b) $E = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{*}{\text{C}}-\text{CH}_3$ $F = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{O}}-\text{Na}^{\oplus}$ $G = \text{CH}_3$
- (c) $E = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{*}{\text{C}}-\text{CH}_3$ $F = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{O}}-\text{Na}^{\oplus}$ $G = \overset{*}{\text{C}}\text{H}_3$
- (d) $E = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{*}{\text{C}}-\text{CH}_3$ $F = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{O}}-\text{Na}^{\oplus}$ $G = \overset{*}{\text{C}}\text{H}_3\text{I}$

14. The compounds *P*, *Q* and *S*



were separately subjected to nitration using $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture. The major product formed in each case respectively is



(2010)

15. Among the following compounds, the most acidic is

- (a) *p*-nitrophenol (b) *p*-hydroxybenzoic acid
(c) *o*-hydroxybenzoic acid (d) *p*-toluic acid

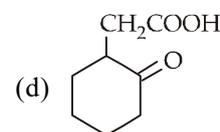
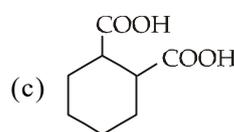
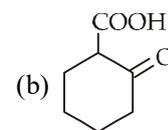
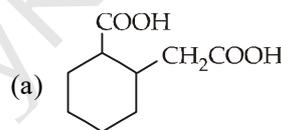
(2011)

16. The carboxyl functional group ($-\text{COOH}$) is present in

- (a) picric acid (b) barbituric acid
(c) ascorbic acid (d) aspirin

(2012)

17. The compound that undergoes decarboxylation most readily under mild condition is



(2012)

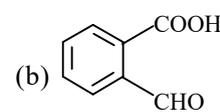
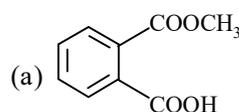
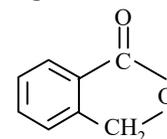
Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

18. Which of the following compounds will give a yellow precipitate with iodine and alkali?

- (a) 2-Hydroxypropane (b) Acetophenone
(c) Methyl acetate (d) Acetamide

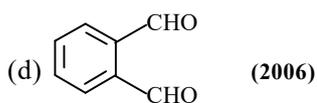
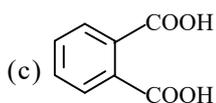
(1984)

19. Which of the following reactants on reaction with concentrated NaOH followed by acidification gives adjacent lactone as the product?

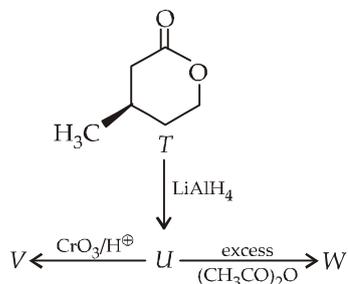


Carboxylic Acids and Their Derivatives

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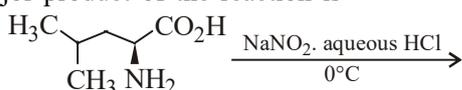
20. With reference to the scheme given, which of the given statement(s) about *T*, *U*, *V* and *W* is (are) correct?



- (a) *T* is soluble in hot aqueous NaOH.
 (b) *U* is optically active.
 (c) Molecular formula of *W* is $C_{10}H_{18}O_4$.
 (d) *V* gives effervescence on treatment with aqueous $NaHCO_3$

(2012)

21. The major product of the reaction is



- (a)
 (b)
 (c)
 (d)

(2015)

Fill in the Blanks

22. Formic acid when heated with concentrated H_2SO_4 produces

(1983)

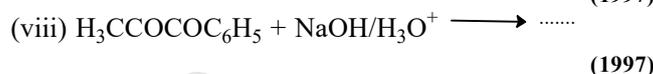
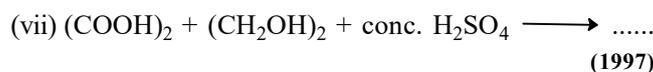
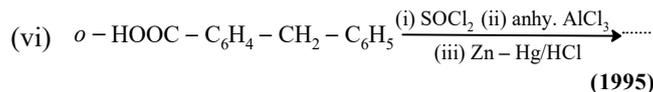
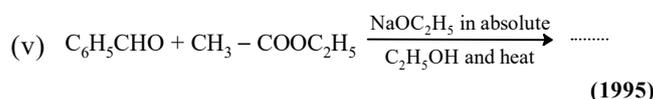
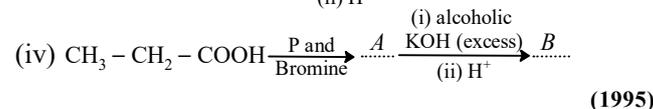
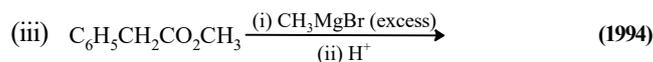
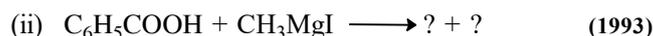
True / False

23. Hydrolysis of an ester in presence of a dilute acid is known as saponification. (1983)
 24. The boiling point of propionic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular weight. (1991)

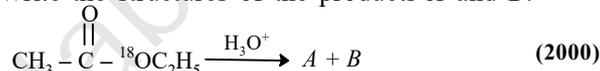
Subjective Problems

25. Write the structural formula of the main organic product formed when:

- (i) Ethyl acetate is treated with double the molar quantity of methyl magnesium bromide and the reaction mixture poured into water. (1981)



- (ix) Write the structures of the products *A* and *B*.



26. Write the chemical equation to show what happens when ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified. (1981)

27. How will you convert?

- (i) Ethyl alcohol to vinyl acetate. (in not more than 6 steps) (1986)
 (ii) Acetic acid to tertiary butyl alcohol. (1989)
 (iii) Ethanoic acid to a mixture of methanoic acid and diphenyl ketone. (1990)

28. State with balanced equation what happens when: Acetic anhydride reacts with phenol in presence of a base. (1982)

29. Give reasons for the following:

- (i) Acetic acid can be halogenated in the presence of red P and Cl_2 but formic acid cannot be halogenated in the same way. (1983)
 (ii) Formic acid is a stronger acid than acetic acid. (1985)
 (iii) In acylium ion, the structure $R - C \equiv O^+$ is more stable than $R - C^+ = O$. (1994)

30. State the conditions under which the following preparation is carried out. Give the necessary equation which need not be balanced.



31. Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis:

- Propionic anhydride from propionaldehyde
[AgNO₃/NH₄OH, P₂O₅] (1984)
32. Arrange the following in increasing ease of hydrolysis
CH₃COOC₂H₅, CH₃COCl, (CH₃CO)₂O, CH₃CONH₂.
(1986)
33. A liquid (*X*) having a molecular formula C₆H₁₂O₂ is hydrolysed with water in the presence of an acid to give a carboxylic acid (*Y*) and an alcohol (*Z*). Oxidation of (*Z*) with chromic acid gives (*Y*). What are the structures of (*X*), (*Y*) and (*Z*)?
(1986)
34. Complete the following with appropriate structures:
 $(\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{CH}_3\text{COOH} + ?$ (1986)
35. Complete the following reactions:
 $\text{CH}_3\text{COOH} \xrightarrow{?} \text{ClCH}_2\text{COOH} \xrightarrow{\text{excess ammonia}} ?$ (1988)
36. The sodium salt of a carboxylic acid, *A*, was produced by passing a gas, *B*, into an aqueous solution of caustic alkali at an elevated temperature and pressure. *A*, on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid, *C*. A sample of 0.4 g of acid *C*, on combustion gave 0.08 g of water and 0.39 g of carbon dioxide. The silver salt of the acid weighing 1.0 g on ignition yielded 0.71 g of silver as residue. Identify *A*, *B* and *C*.
(1990)
37. Compound *A* (C₆H₁₂O₂) on reduction with LiAlH₄ yielded two compounds *B* and *C*. The compound *B* on oxidation gave *D*, which on treatment with aqueous alkali and subsequent heating furnished *E*. *E* later on catalytic hydrogenation gave *C*. The compound *D* was oxidized further to give *F* which was found to be a monobasic acid (molecular formula weight = 60.0). Deduce the structures of *A*, *B*, *C*, *D* and *E*.
(1990)
38. $\text{C}_6\text{H}_5\text{COOH} \xrightarrow{\text{PCl}_5} \text{A} \xrightarrow{\text{NH}_3} \text{B}$
 $\xrightarrow{\text{P}_2\text{O}_5} \text{C}_6\text{H}_5\text{CN} \xrightarrow{\text{H}_2/\text{Ni}} \text{C}$
Identify *A*, *B* and *C*. (1991)
39. Compound *X*, containing chlorine on treatment with strong ammonia gives a solid *Y* which is free from chlorine. *Y* analysed as C = 49.31%, H = 9.59% and N = 19.18% and reacts with Br₂ and caustic soda to give a basic compound *Z*. *Z* reacts with HNO₂ to give ethanol. Suggest structures for *X*, *Y* and *Z*.
(1992)
40. An organic compound *A* on treatment with ethyl alcohol gives a carboxylic acid *B* and compound *C*. Hydrolysis of *C* under acidic conditions gives *B* and *D*. Oxidation of *D* with KMnO₄ also gives *B*. *B* on heating with Ca(OH)₂ gives *E* (molecular formula, C₃H₆O). *E* does not give Tollen's test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenyl hydrazone. Identify *A*, *B*, *C*, *D* and *E*.
(1992)
41. Which of the following carboxylic acids undergoes decarboxylation easily? Explain briefly.
(i) C₆H₅ - CO - CH₂ - COOH
(ii) C₆H₅ - CO - COOH
(iii) C₆H₅ - CH - COOH
 |
 OH
(iv) C₆H₅ - CH - COOH
 |
 NH₂ (1995)
42. A liquid *A* is reacted with hot aqueous sodium carbonate solution. A mixture of two salts *B* and *C* are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid *A* again. Identify *A*, *B* and *C* and write the equations involved.
(1997)
43. (i) Write down the structures of *E* and *F*.
 $\text{E}(\text{C}_{11}\text{H}_{14}\text{O}_2) \xrightarrow{\text{OH}^-} \text{F} + \text{CH}_3\text{CH}_2\text{COO}^-$
 $\text{F} \xrightarrow[\text{(ii) H}^+]{\text{(i) KMnO}_4/\text{OH}^-} \text{C}_6\text{H}_4(\text{COOH})_2$ (1997)
- (ii) Write down the structures of *G* and *H* where *G* is C₄H₈O₃.
Acetate ← $\text{G} \xrightarrow[\text{Pyridine}]{\text{Ac}_2\text{O}}$ Acetate
 $\text{G} \xrightarrow{\text{NaHCO}_3} \text{CO}_2$
 $\text{G} \xrightarrow{\text{CrO}_3} \text{H} \xrightarrow{\text{warm}} \text{CH}_3\text{COCH}_3 + \text{CO}_2$ (1997)
44. An ester *A* (C₄H₈O₂), on treatment with excess methyl magnesium chloride followed by acidification gives an alcohol *B* as the sole organic product. Alcohol *B*, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of *A* and *B*. Show the reactions involved.
(1998)
45. Write the structures of alanine at pH = 2 and pH = 10.
(2000)
46. An organic compound *A*, C₈H₄O₃, in dry benzene in the presence of anhydrous AlCl₃ gives compound *B*. The compound *B* on treatment with PCl₅, followed by reaction with H₂/Pd (BaSO₄) gives compound *C*, which on reaction with hydrazine gives a cyclised compound *D* (C₁₄H₁₀N₂). Identify *A*, *B*, *C* and *D*. Explain the formation of *D* from *C*.
(2000)

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47. A biologically active compound, Bombykol ($C_{16}H_{30}O$) is obtained from a natural source. The structure of the compound is determined by the following reactions.

- (a) On hydrogenation, Bombykol gives a compound *A*, $C_{16}H_{34}O$, which reacts with acetic anhydride to give an ester;
- (b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O_3/H_2O_2) gives a mixture of butanoic acid, oxalic acid and 10-acetoxydecanoic acid. Determine the number of double bonds in Bombykol. Write the structures of compound *A* and Bombykol. How many geometrical isomers are possible for Bombykol?

(2002)

48. A racemic mixture of (\pm)-2-phenylpropanoic acid on esterification with (+)-2-butanol gives two esters. Mention the stereochemistry of the two esters produced. (2003)

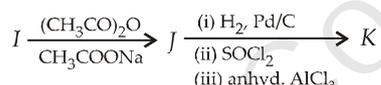
49. Compound *A* of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form *B*. On oxidation with $KMnO_4$, *A* gives *m*-chlorobenzoic acid. Identify *A* and *B*. (2003)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

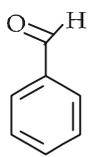
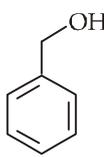
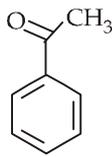
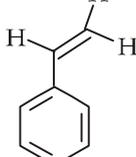
Comprehension-1

In the following reaction sequence, the compound *J* is an intermediate.

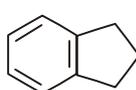
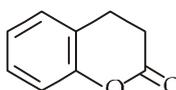


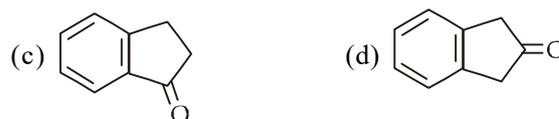
J ($C_9H_8O_2$) gives effervescence on treatment with NaHCO_3 and a positive Baeyer's test.

50. The compound *I* is

- (a) 
- (b) 
- (c) 
- (d) 

51. The compound *K* is

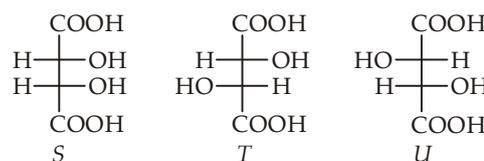
- (a) 
- (b) 



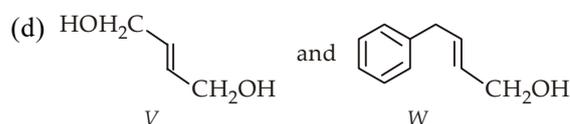
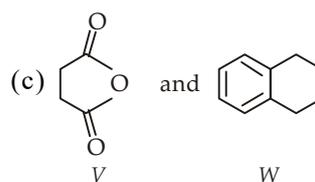
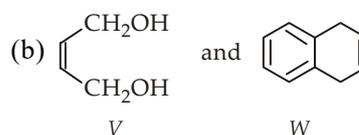
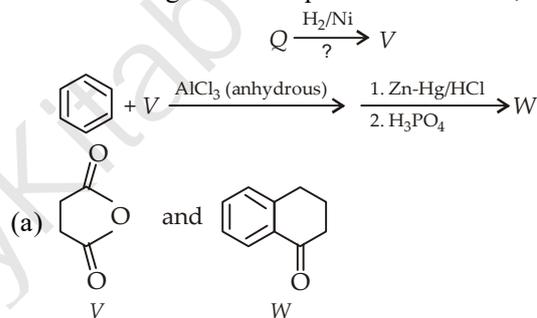
(2012)

Comprehension-2

P and *Q* are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorize $\text{Br}_2/\text{H}_2\text{O}$. On heating, *P* forms the cyclic anhydride. Upon treatment with dilute alkaline KMnO_4 , *P* as well as *Q* could produce one or more than one from *S*, *T* and *U*.



52. In the following reaction sequences *V* and *W* are, respectively



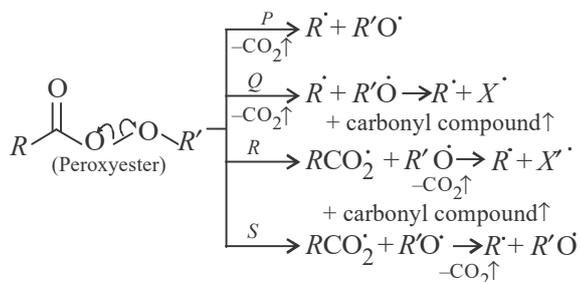
53. Compounds formed from *P* and *Q* are, respectively

- (a) optically active *S* and optically active pair (*T*, *U*)
- (b) optically inactive *S* and optically inactive pair (*T*, *U*)
- (c) optically active pair (*T*, *U*) and optically active *S*
- (d) optically inactive pair (*T*, *U*) and optically inactive *S*.

(2013)

Matching List Type

54. Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from List I with an appropriate structure from List II and select the correct answer using the code given below the lists.



List-I

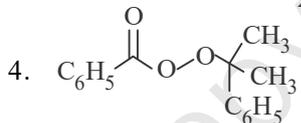
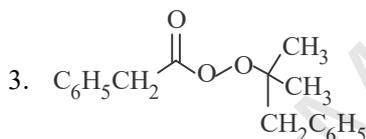
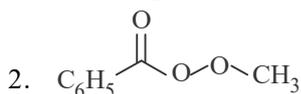
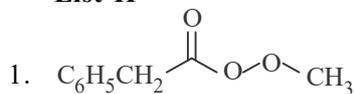
(P) Pathway P

(Q) Pathway Q

(R) Pathway R

(S) Pathway S

List-II



Code :

	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

(2014)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

55. **Statement-1** : Acetate ion is more basic than the methoxide ion.

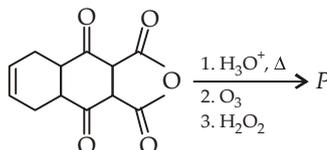
Statement-2 : The acetate ion is resonance stabilized (1994)

56. **Statement-1** : Acetic acid does not undergo haloform reaction.

Statement-2 : Acetic acid has no alpha hydrogens. (1998)

Integer Answer Type

57. The total number of carboxylic acid groups in the product P is



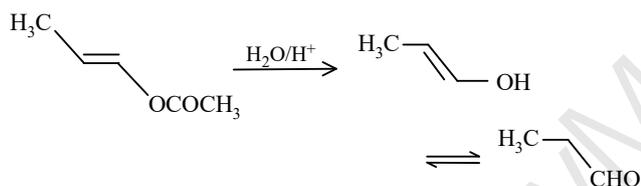
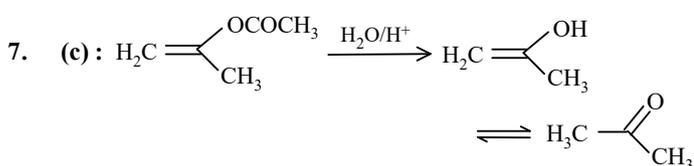
(2013)

ANSWER KEY

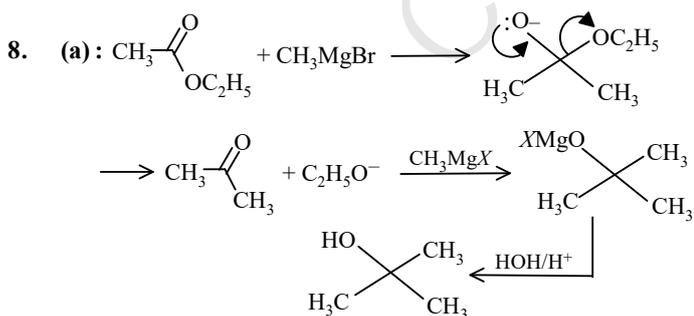
- | | | | | | |
|-----------|---------------|---------|---|-----------|------------|
| 1. None | 2. (b) | 3. (a) | 4. (d) | 5. (d) | 6. (c) |
| 7. (c) | 8. (a) | 9. (a) | 10. (c) | 11. (c) | 12. (a) |
| 13. (c) | 14. (c) | 15. (c) | 16. (d) | 17. (b) | 18. (a, b) |
| 19. (d) | 20. (a, c, d) | 21. (c) | 22. $\text{HCOOH} \xrightarrow[\Delta]{\text{H}_2\text{SO}_4} \text{CO}\uparrow + \text{H}_2\text{O}$ | 23. False | |
| 24. False | 50. (a) | 51. (c) | 52. (a) | 53. (b) | 54. (a) |
| 55. (d) | 56. (c) | 57. (2) | | | |

Explanations

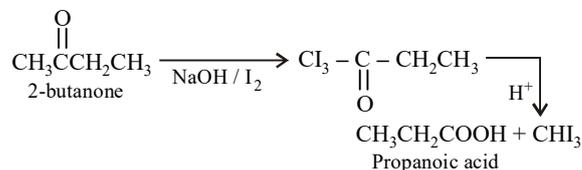
- None of these.
- (b): $C_6H_5COCl + H_2 \xrightarrow{Pd-BaSO_4} C_6H_5CHO + HCl$
- (a): $C_6H_5COOH \xrightarrow[H_3O^+]{LiAlH_4} C_6H_5CH_2OH$
- (d): Enantiomers are those optically active isomers which are mirror images to each other but not superimposable to each other.
- (d): $C_2H_5COOH + NaHCO_3 \xrightarrow{14} C_2H_5COONa + H_2O + CO_2$
- (c): $C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$



Ketone (non-reducing) and aldehyde (reducing) can be distinguished by Fehling's solution as we know that ketone does not react with Fehling's solution.

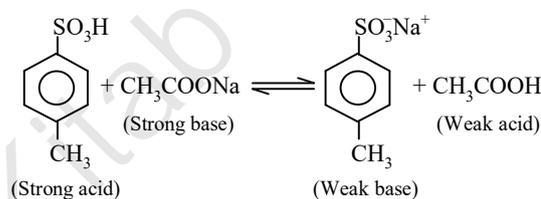


- (a): The optically active acid will react with *d*- and *l*- forms of alcohol present in the racemic mixture at different rates to form two diastereomers in unequal quantities thus the product is optically active.
- (c): Iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketone and those alcohols which possess $CH_3CH(OH)-$ group.

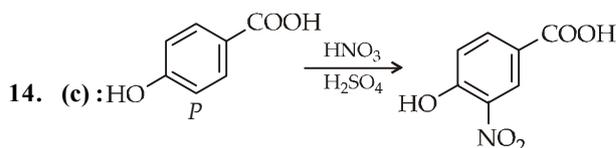
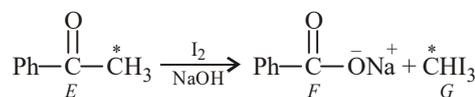


This is an example of iodoform reaction.

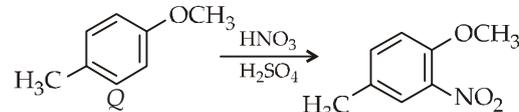
- (c): Perkin reaction involves the treatment of an aromatic aldehyde with anhydride of an aliphatic acid and the sodium salt of that acid. Products are α, β -unsaturated acids.
- (a): It is a simple acid-base reaction.



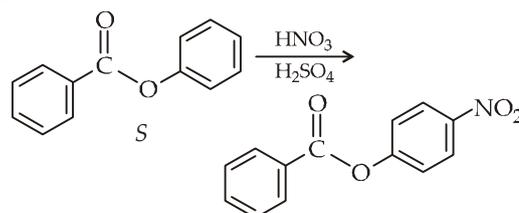
- (c): $Ph-C(=O)-CH_2-C(=O)OH \xrightarrow{\Delta} Ph-C(=O)-CH_3 + CO_2$



—OH is activating and *o*-, *p*-directing, whereas —COOH is deactivating and *m*-directing.

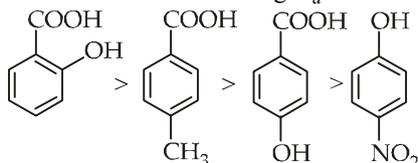


—CH₃, and —OCH₃ both are *o*-, *p*-directors. Since —OCH₃ is more activating, the substitution occurs at a position *ortho* to it.



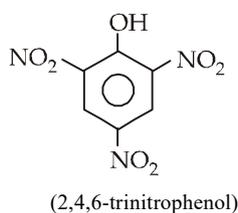
The ring attached to CO group is deactivated, so substitution takes place in the other ring and at *p*-position.

15. (c): When group has +R and -I effect. *ortho* derivative is most acidic due to *ortho* effect. Suppose acid is methoxy benzoic acid. With a methoxy substituent, the inductive effect of the oxygen withdraws electron density from the negative centre, but the resonance effect involving the nonbonding electrons on oxygen works in the opposite direction to donate electron density to carboxylate ion. Due to *ortho* effect *o*-hydroxy benzoic acid is strongest acid and correct order of decreasing K_a is :

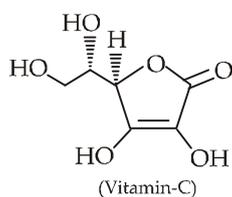


All phenols are less acidic than carboxylic acids.

16. (d): **Picric acid**



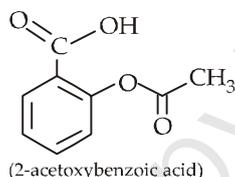
- Ascorbic acid**



- Barbituric acid**

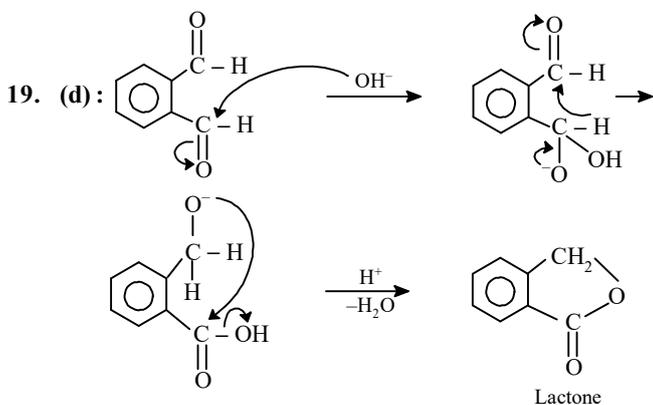


- Aspirin**

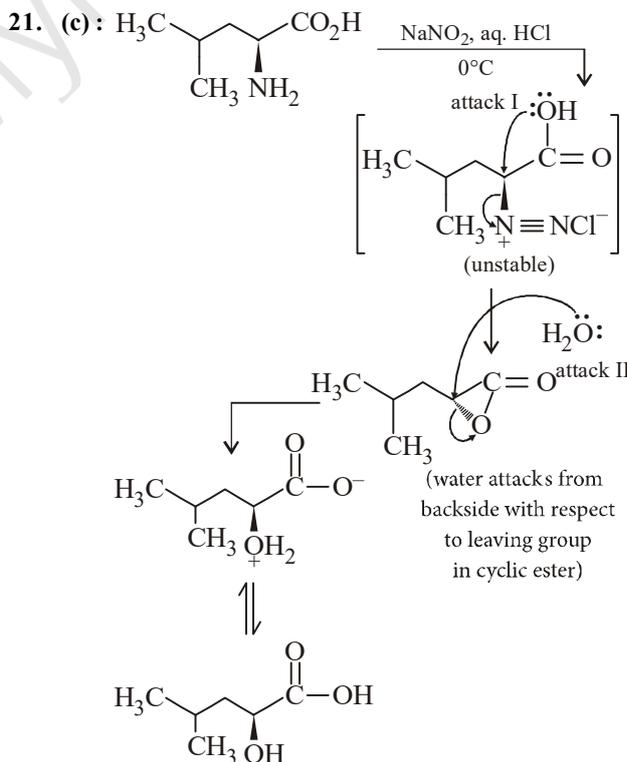
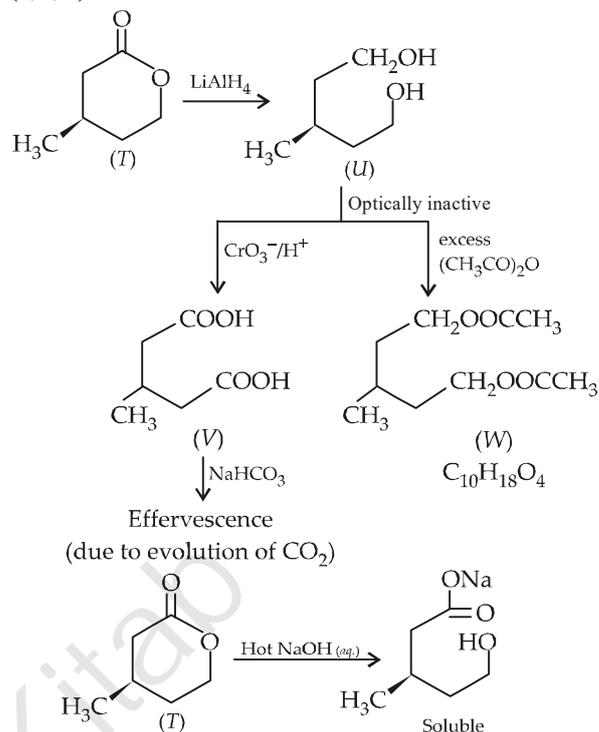


17. (b) : β -keto acids undergo decarboxylation most readily.

18. (a, b) : 2-Hydroxypropane ($\text{CH}_3\text{CH}(\text{OH})-\text{CH}_3$) contains the grouping $\text{CH}_3\text{CH}(\text{OH})-$ and the grouping $\text{CH}_3\text{CO}-$ is present in acetophenone ($\text{C}_6\text{H}_5-\text{C}(\text{O})\text{CH}_3$) so both these compounds will give iodoform test, *i.e.*, form iodoform on reaction with I_2 and alkali.



20. (a, c, d):



In attack I, inversion of configuration takes place and in IInd attack again inversion of configuration takes place which finally leads to retention of configuration.

22. $\text{HCOOH} \xrightarrow[\Delta]{\text{H}_2\text{SO}_4} \text{CO}\uparrow + \text{H}_2\text{O}$

Carboxylic Acids and Their Derivatives

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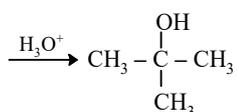
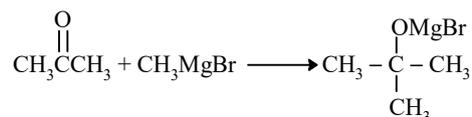
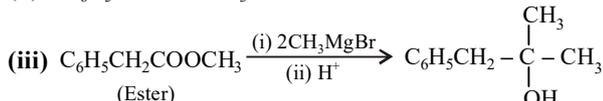
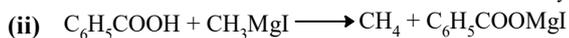
23. False

Saponification is the process of alkaline hydrolysis of esters.

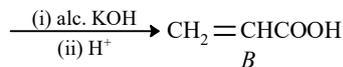
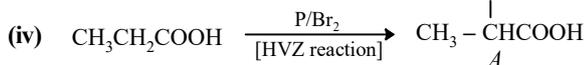
24. False

Hydrogen bonding in propionic acid is stronger than in butanol so the b.pt. of propionic acid is higher.

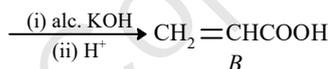
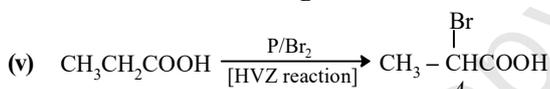
25. (i) Grignard reagent reacts with ethyl acetate and forms a ketone which at once reacts with more Grignard reagent to give
- tert*
- butyl alcohol.

*tert*-butyl alcohol

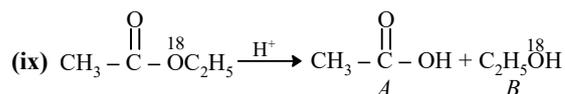
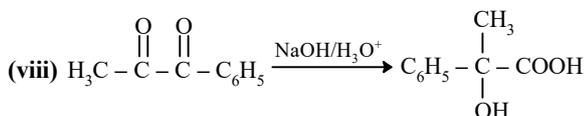
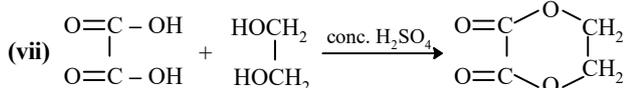
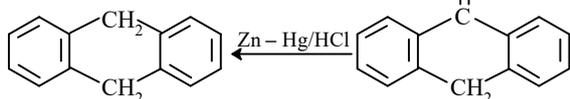
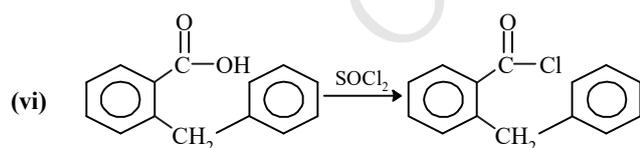
(Ester)



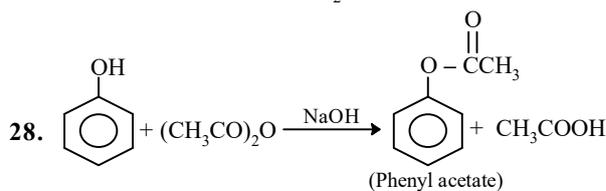
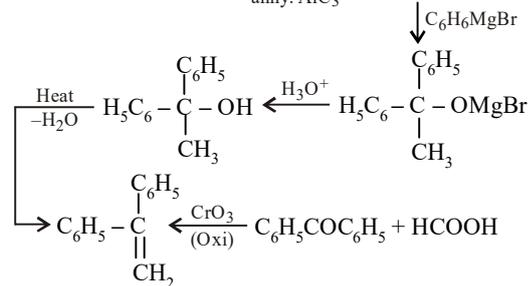
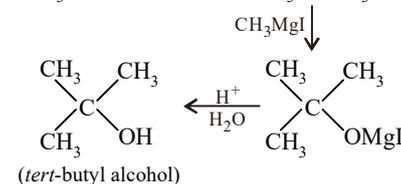
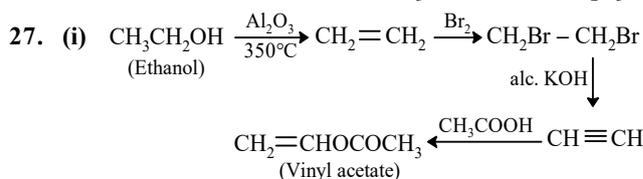
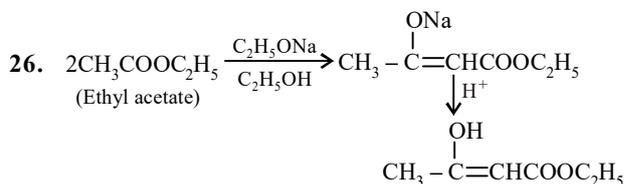
B



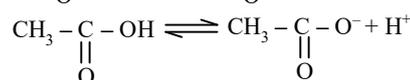
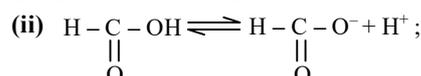
B



(In ester hydrolysis acyl-oxygen fission occurs)

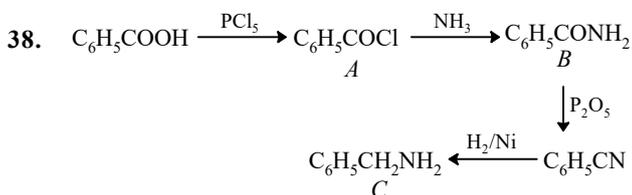
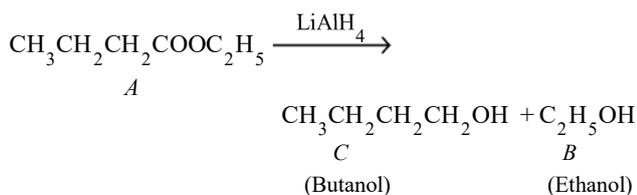


29. (i) Formic acid (HCOOH) has no
- α
- H so it does not undergo halogenation. Acetic acid (CH
- ₃
- COOH) has a methyl (-CH
- ₃
-) group on which halogenation can take place.

The presence of -CH₃ group in acetate ion shows +I effect. and so it intensifies the charge on O⁻ of acetate ion and the acetate ion gets destabilized. Thus formate ion is more stable and so HCOOH loses proton more readily than CH₃COOH.

Carboxylic Acids and Their Derivatives

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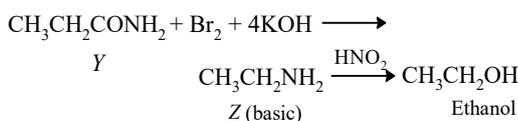


39. Calculation of empirical formula of Y

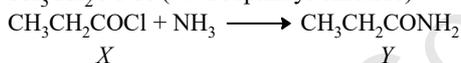
Element	% age	Relative number of atoms	Simplest ratio
C	49.31	49.31/12 = 4.10	4.10/1.37 = 3
H	9.59	9.59/1 = 9.59	9.59/1.37 = 7
N	19.18	19.18/14 = 1.37	1.37/1.37 = 1
O	21.92	21.92/16 = 1.37	1.37/1.37 = 1

Empirical formula = $\text{C}_3\text{H}_7\text{NO}$

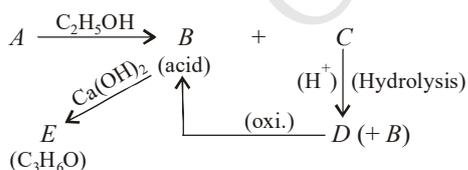
Y reacts with Br_2 and NaOH to give Z and Z reacts with HNO_2 to give ethanol. From this it appears that Y contains a $-\text{CONH}_2$ group, i.e., it is $\text{C}_2\text{H}_5\text{CONH}_2$.



Y is formed from X having Cl on treatment with NH_3 , so X is $\text{CH}_3\text{CH}_2\text{COCl}$ (i.e. Propanoyl chloride)



40. Facts given in the problem can be summarized as:



From the given facts we can conclude that:

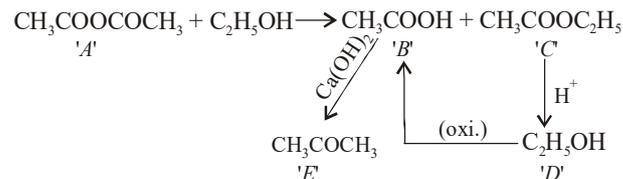
(i) E is ketone (CH_3COCH_3) because it forms a 2, 4-dinitrophenylhydrazone but it does not reduce Tollen's reagent, Fehling's solution.

(ii) Since E (a ketone) is obtained by heating compound B with Ca(OH)_2 so B must be CH_3COOH .

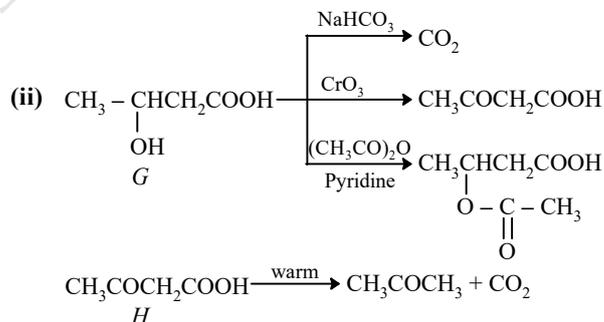
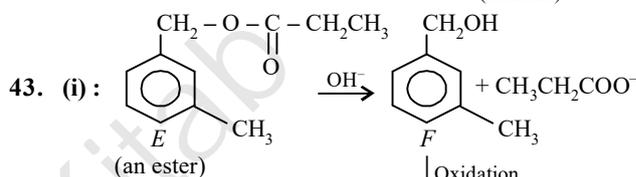
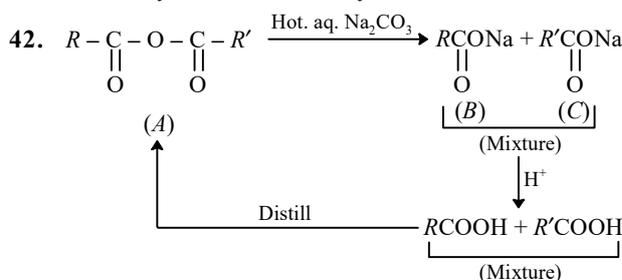
(iii) Since compound B (i.e. CH_3COOH) is obtained by oxidation of D so D must be ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) and hence C must be ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$).

(iv) Since compound A on treatment with ethyl alcohol gives acetic acid (B) and ethyl acetate (C) so A must be acetic anhydride ($\text{CH}_3\text{CO}-\text{O}-\text{OCCH}_3$).

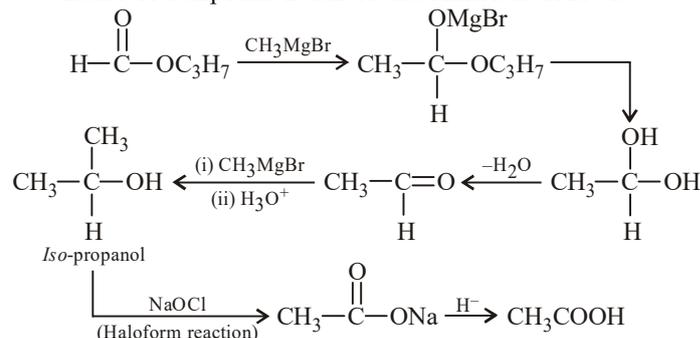
Various reactions are:



41. β -keto acids like (compound (i)) are unstable and undergo decarboxylation most readily.



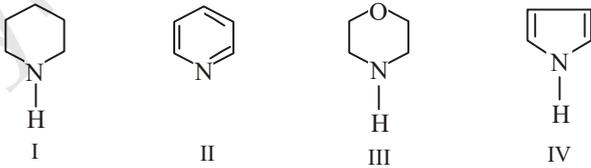
44. Esters when treated with methyl magnesium chloride either give a secondary alcohol (from alkyl formates) or tertiary alcohols (from esters other than formates). However tertiary alcohols are not easily oxidized, hence alcohol should be secondary alcohol and thus ester is alkyl formate. Hence ester A ($\text{C}_4\text{H}_8\text{O}_2$) should be HCOOC_3H_7 . Various reactions and nature of compound B can be established as follows:



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Compounds Containing Nitrogen

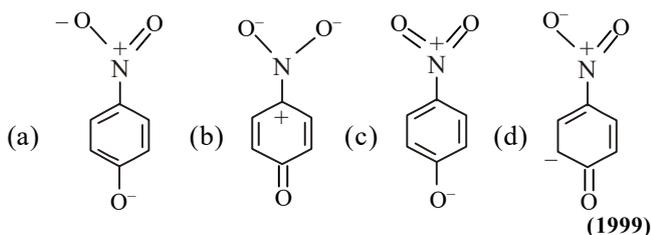
Multiple Choice Questions with ONE Correct Answer

- The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is
(a) methyl amine (b) ethyl amine
(c) diethyl amine (d) triethyl amine (1981)
- Acetamide is treated separately with the following reagents. Which one of these would give methyl amine?
(a) PCl_5 (b) $\text{NaOH} + \text{Br}_2$
(c) Sodalime (d) Hot concentrated H_2SO_4 (1983)
- Carbylamine test is performed in alcoholic KOH by heating a mixture of
(a) chloroform and silver powder
(b) trihalogenated methane and a primary amine
(c) an alkyl halide and a primary amine
(d) an alkyl cyanide and a primary amine (1984)
- The compound that is most reactive towards electrophilic nitration is
(a) toluene (b) benzene
(c) benzoic acid (d) nitrobenzene (1985)
- If two compounds have the same empirical formula but different molecular formula they must have
(a) different percentage composition
(b) different molecular weight
(c) same viscosity
(d) same vapour density (1987)
- Amongst the following, the most basic compound is
(a) benzylamine (b) aniline
(c) acetanilide (d) *p*-nitroaniline (1990)
- The formation of cyanohydrin from a ketone is an example of
(a) electrophilic addition
(b) nucleophilic addition
(c) nucleophilic substitution
(d) electrophilic substitution (1990)
- Butanenitrile may be prepared by heating
(a) propyl alcohol with KCN
(b) butyl alcohol with KCN
(c) butyl chloride with KCN
(d) propyl chloride with KCN (1992)
- Nitrobenzene can be prepared from benzene by using a mixture of concentrated HNO_3 and concentrated H_2SO_4 . In the nitrating mixture, HNO_3 acts as a
(a) base (b) acid
(c) reducing agent (d) catalyst (1997)
- In the following compounds:


The order of basicity is
(a) $\text{IV} > \text{I} > \text{III} > \text{II}$ (b) $\text{III} > \text{I} > \text{IV} > \text{II}$
(c) $\text{II} > \text{I} > \text{III} > \text{IV}$ (d) $\text{I} > \text{III} > \text{II} > \text{IV}$ (1997)
- Among the following statements on the nitration of aromatic compounds, the false one is
(a) the rate of nitration of benzene is almost the same as that of hexadeuterobenzene
(b) the rate of nitration of toluene is greater than that of benzene.
(c) the rate of nitration of benzene is greater than that of hexadeuterobenzene
(d) nitration is an electrophilic substitution reaction. (1997)
- In the reaction *p*-chlorotoluene with KNH_2 in liquid NH_3 , the major product is
(a) *o*-toluidine (b) *m*-toluidine
(c) *p*-toluidine (d) *p*-chloroaniline (1997)
- The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

Compounds Containing Nitrogen

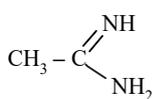
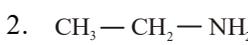
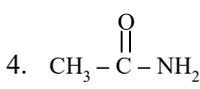
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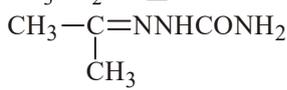
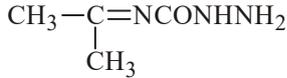
14. Among the following, the strongest base is

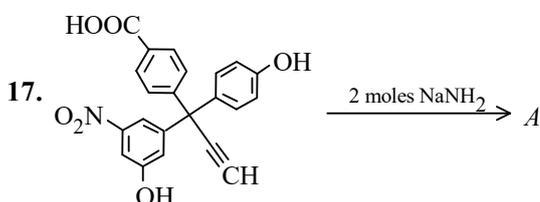
- (a) $C_6H_5NH_2$ (b) $p\text{-NO}_2.C_6H_4NH_2$
 (c) $m\text{-NO}_2.C_6H_4.NH_2$ (d) $C_6H_5CH_2NH_2$ (2000)

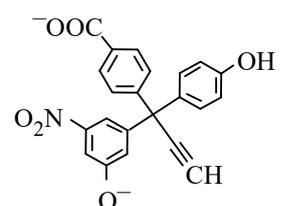
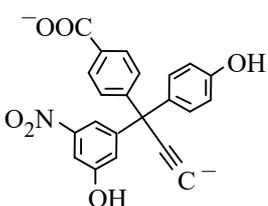
15. The correct order of basicities of the following compounds is

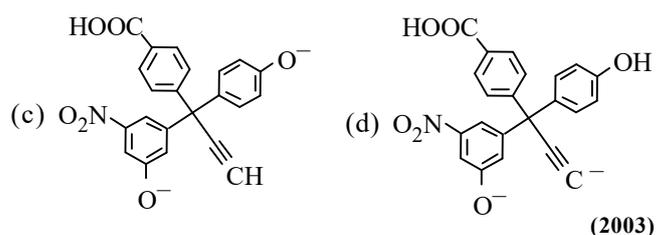
1.  2. 
 3.  4. 
 (a) $2 > 1 > 3 > 4$ (b) $1 > 3 > 2 > 4$
 (c) $3 > 1 > 2 > 4$ (d) $1 > 2 > 3 > 4$ (2001)

16. Compound *A* (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product *B* (molecular formula C_3H_6O). *B* forms a shining silver mirror on warming with ammoniacal silver nitrate. *B* when treated with an aqueous solution of $H_2NCONHNH_2$, HCl and sodium acetate gives a product *C*. Identify the structure of *C*.

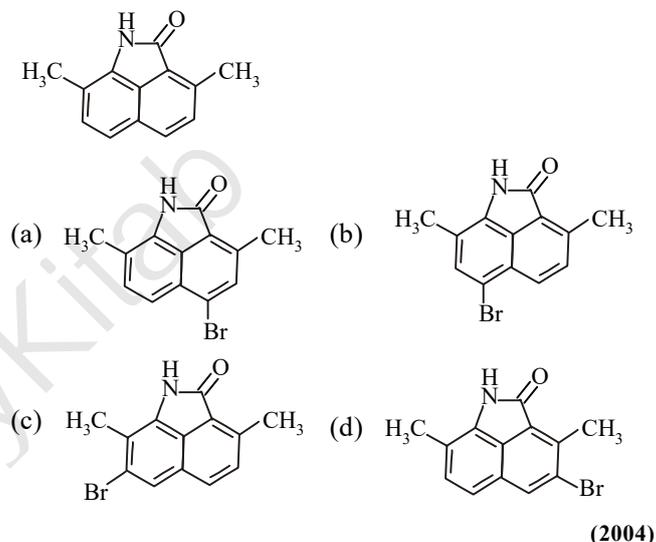
- (a) $CH_3CH_2CH=NNHCONH_2$
 (b) 
 (c) 
 (d) $CH_3CH_2CH=NCONHNH_2$ (2002)

The product (*A*) will be

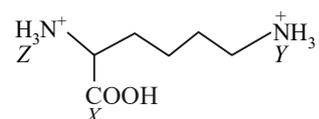
- (a)  (b) 

18. Benzamide on reaction with $POCl_3$ gives

- (a) aniline (b) chlorobenzene
 (c) benzyl amine (d) benzonitrile (2004)

19. The major product obtained when Br_2/Fe is treated with

20. In the compound given below the correct order of the acidity of the H- present on positions X, Y and Z is



- (a) $Z > X > Y$ (b) $X > Y > Z$
 (c) $X > Z > Y$ (d) $Y > X > Z$ (2004)

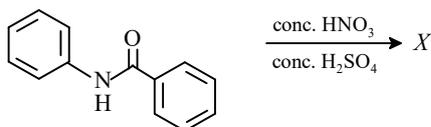
21. When benzene sulphonic acid and *p*-nitrophenol is treated with $NaHCO_3$, the gases released respectively are

- (a) SO_2, NO_2 (b) SO_2, NO
 (c) SO_2, CO_2 (d) CO_2, CO_2 (2006)

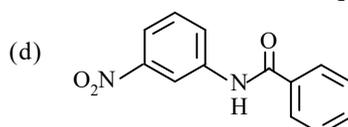
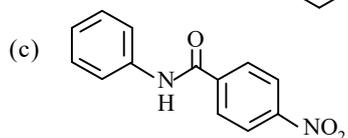
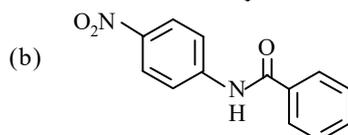
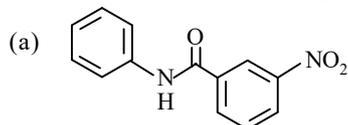
22. $CH_3NH_2 + CHCl_3 + KOH \rightarrow$ nitrogen containing compound + $KCl + H_2O$. Nitrogen containing compound is

- (a) $CH_3 - C \equiv N$ (b) $CH_3 - NH - CH_3$
 (c) $CH_3 - \bar{N} \equiv \bar{C}$ (d) $CH_3^+ \bar{N} \equiv \bar{C}$ (2006)

23. In the following reaction

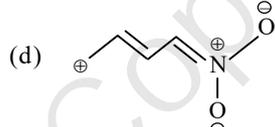
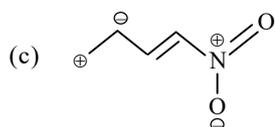
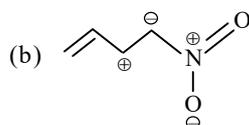
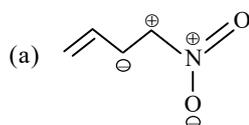


The structure of the major product X is



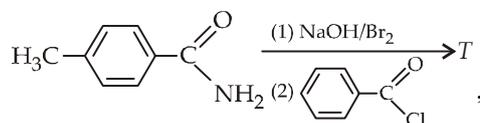
(2007)

24. Among the following, the least stable resonance structure is

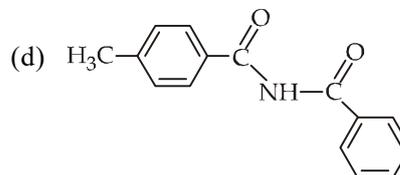
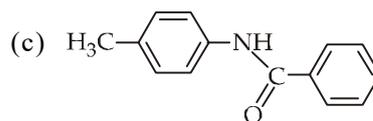
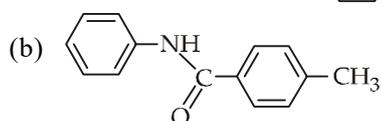
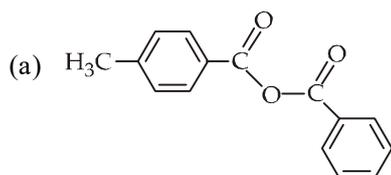


(2007)

25. In the reaction :

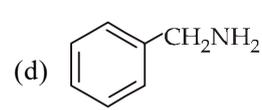
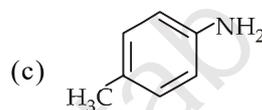
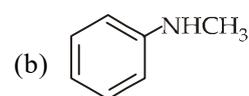
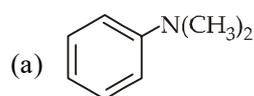


the structure of the product T is



(2010)

26. Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with NaNO_2 in dil. HCl followed by addition to an alkaline solution of β -naphthol is



(2011)

Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

27. The products of reaction of alcoholic silver nitrite with ethyl bromide are

- (a) ethane (b) ethene
(c) nitroethane (d) ethyl alcohol (1991)

28. Reaction of $R-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ with a mixture of Br_2 and KOH gives $R-\text{NH}_2$ as the main product. The intermediates involved in this reaction are:

- (a) $R-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHBr}$ (b) $R-\text{NHBr}$
(c) $R-\text{N}=\text{C}=\text{O}$ (d) $R-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}(\text{Br})_2$ (1992)

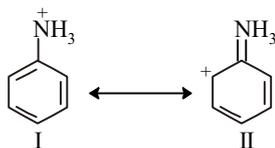
29. When nitrobenzene is treated with Br_2 in presence of FeBr_3 , the major product formed is m -bromonitrobenzene. Statements which are related to the formation of m -isomer are

- (a) The electron density on *meta* carbon is more than that on *ortho* and *para* positions
(b) The intermediate carbonium ion formed after initial attack of Br^+ at the *meta* position is least destabilised
(c) Loss of aromaticity when Br^+ attacks at the *ortho* and *para* positions and not at *meta* position
(d) Easier loss of H^+ to regain aromaticity from the *meta* position than from *ortho* and *para* positions. (1992)

Compounds Containing Nitrogen

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30. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below:



- (a) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions.
 (b) II is not an acceptable canonical structure because it is non-aromatic.
 (c) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons.
 (d) II is an acceptable canonical structure. (1998)

31. Among the following compounds, which will react with acetone to give a product containing $>C=N-$ bond?

- (a) $C_6H_5NH_2$ (b) $(CH_3)_3N$
 (c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$ (1998)

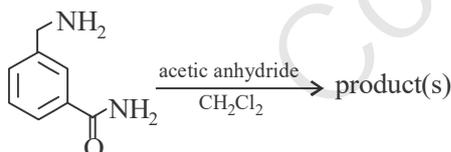
32. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives

- (a) diphenyl ether (b) *p*-hydroxyazobenzene
 (c) chlorobenzene (d) benzene (1998)

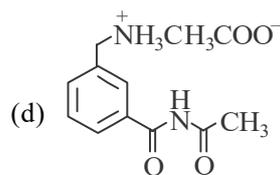
33. A positive carbylamine test is given by

- (a) *N,N*-dimethylaniline (b) 2,4-dimethylaniline
 (c) *N*-methyl-*o*-methylaniline (d) *p*-methylbenzylamine (1999)

34. In the reaction shown below, the major product(s) formed is/are

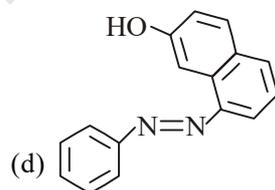
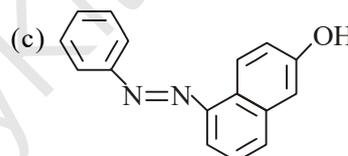
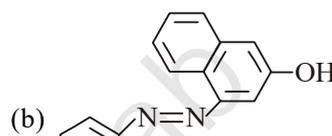
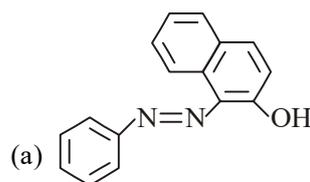
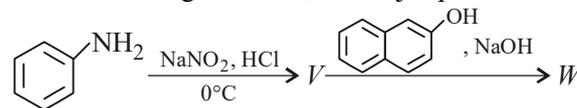


- (a) + CH_3COOH
 (b) + CH_3COOH
 (c) + H_2O



(2014)

35. In the following reactions, the major product *W* is



(2015)

Fill in the Blanks

36. In an acidic medium, behaves as the strongest base. (nitrobenzene, aniline, phenol) (1981)
 37. Amongst the three isomers of nitrophenol, the one that is least soluble in water is (1992)
 38. The high melting point and insolubility in organic solvents of sulphanic acid are due to its structure. (1994)

Subjective Problems

39. Show with equations how the following compounds are prepared (equations need not be balanced):
 (i) *n*-Propyl amine from ethyl chloride (in two steps) (1982)
 (ii) Aniline from benzene (1983)
 (iii) Acetoxime from acetaldehyde using the reagents, $[K_2Cr_2O_7/H^+, Ca(OH)_2 \text{ and } NH_2OH.HCl]$ (1984)

(iv) Aniline to chlorobenzene (1985)

(v) Benzaldehyde to cyanobenzene (in not more than 6 steps) (1986)

(vi) How will you convert toluene to *m*-nitrobenzoic acid? (1987)

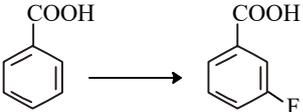
(vii) 4-Nitroaniline to 1, 2, 3-tribromobenzene. (1990)

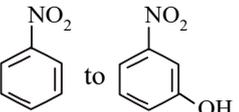
(viii) Outline a synthesis of *p*-bromonitrobenzene from benzene in two steps. (1993)

(ix) 4-Nitrobenzaldehyde from benzene (1994)

(x) Benzamide from nitrobenzene (1994)

(xi) Aniline \rightarrow Benzylamine (in 3 steps) (2003)

(xii)  (in more than 3 steps) (2003)

(xiii) Convert  (in more than 4 steps) (2004)

40. An aromatic compound contains 69.4% carbon and 5.8% hydrogen. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.05 M sulphuric acid. The excess of acid required 25 ml of 0.1 M sodium hydroxide for neutralization. Determine the molecular formula of the compound if its molecular weight is 121. Draw two possible structures for this compound. (1982)

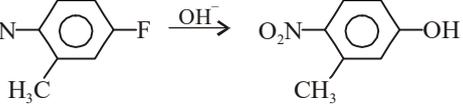
41. Give reasons for the following:

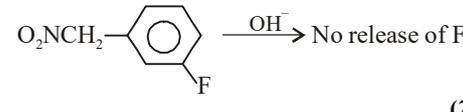
(i) Cyclohexylamine is a stronger base than aniline. (1982)

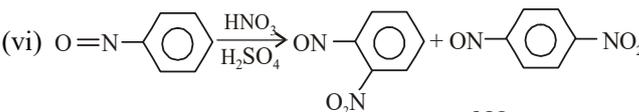
(ii) *o*-Nitrophenol is steam volatile whereas *p*-nitrophenol is not. (1985)

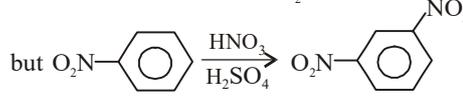
(iii) Dimethylamine is a stronger base than trimethylamine. (1998)

(iv) Nitrobenzene does not undergo Friedel-Crafts alkylation. (1998)

(v) (a) 

but (b)  (2005)

(vi) 

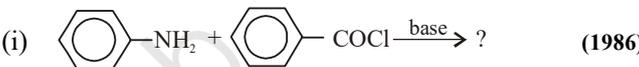
but  (2005)

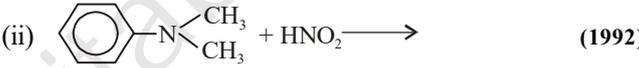
42. Arrange the following in:

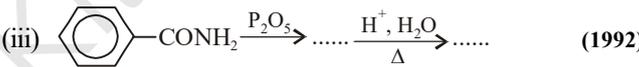
(i) increasing basicity : *p*-toluidine, *N,N*-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline. (1986)

(ii) methylamine, dimethylamine, aniline, *N*-methylamine in increasing order of base strength. (1988)

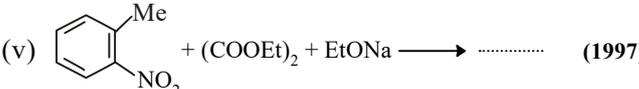
43. Complete the following with appropriate structures:

(i)  (1986)

(ii)  (1992)

(iii)  (1992)

(iv) 2, 4-Dinitroaniline $\xrightarrow[2. \text{anisole}]{1. \text{NaNO}_2 \text{ and HCl at } 5^\circ\text{C}}$ (1995)

(v)  (1997)

(vi) $\text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow[\text{heat}]{(\text{CH}_3\text{CO})_2\text{O}}$ 2 products (1998)

(vii) $\text{CH}_3\text{CONHC}_6\text{H}_5 \xrightarrow{\text{Br}_2, \text{Fe}}$ 2 products (1998)

44. Write balanced equations for the following reaction:

Acetamide is reacted with bromine in the presence of potassium hydroxide. (1987)

45. Give a chemical test and the reagent used to distinguish between the following pair of compounds:

Ethylamine and diethylamine. (1988)

46. An organic compound *A*, containing C, H, N and O, on analysis gives 49.32% carbon, 9.59% hydrogen and 19.18% nitrogen. *A* on boiling with NaOH gives off NH_3 and a salt which on acidification gives a monobasic nitrogen free acid *B*. The silver salt of *B* contains 59.67% silver. Deduce the structures of *A* and *B*. (1988)

47. A mixture of two aromatic compounds *A* and *B* was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer

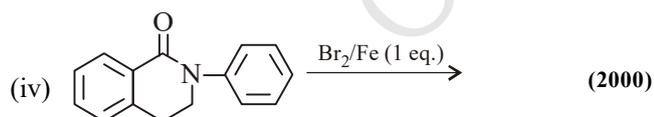
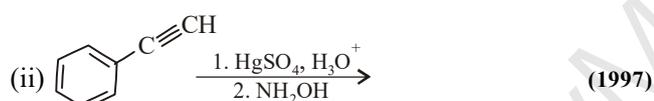
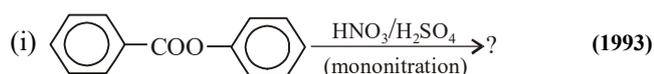
Compounds Containing Nitrogen

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containing compound *A*, when heated with alcoholic solution of KOH produced a compound *C* (C_7H_5N) associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds *D* and *E* of molecular formula $C_7H_6O_2$. Identify the compounds *A*, *B*, *C*, *D*, *E* and write their structures. (1990)

48. A basic, volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 g sample of the substance, dissolved in aqueous HCl and treated with $NaNO_2$ solution at $0^\circ C$, liberated a colourless, odourless gas whose volume corresponded to 112 ml at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule. (1993)

49. Identify the major product in the following reactions:



50. Identify, *A* (C_3H_9N) reacts with benzenesulphonyl chloride to give a solid insoluble in alkali. (1993)

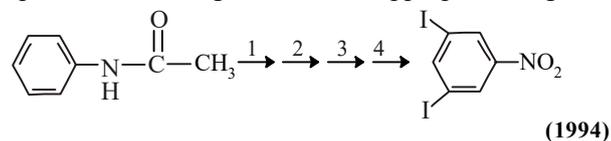
51. Write the structure of the foul-smelling compound obtained when aniline is treated with chloroform in the presence of KOH. (1996)

52. Acetophenone on reaction with hydroxylamine-hydrochloride can produce two isomeric oximes. Write structures of the oximes. (1993)

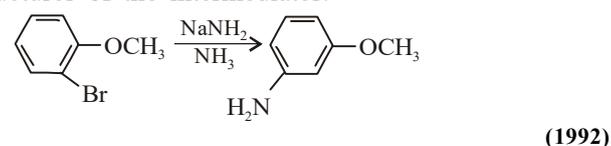
53. Compound *A* (C_8H_8O) on treatment with $NH_2OH.HCl$ gives *B* and *C*. *B* and *C* rearrange to give *D* and *E*, respectively, on treatment with acid. *B*, *C*, *D* and *E* are all isomers of molecular formula (C_8H_9NO). When *D* is boiled with

alcoholic KOH an oil *F* (C_6H_7N) separates out. *F* reacts rapidly with CH_3COCl to give back *D*. On the other hand, *E* on boiling with alkali followed by acidification gives a white solid *G* ($C_7H_6O_2$). Identify (*A-G*). (1999)

54. Complete the following reaction with appropriate reagents:

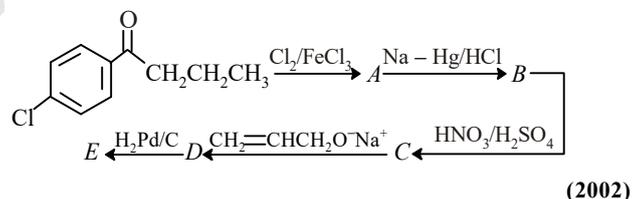


55. Explain briefly the formation of the products giving the structures of the intermediates.



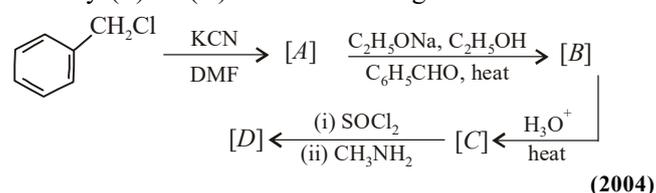
56. How would you synthesise 4-methoxyphenol from bromobenzene in NOT more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. (2001)

57. Write structures of the products *A*, *B*, *C*, *D* and *E* in the following scheme.



58. There is a solution of *p*-hydroxybenzoic acid and *p*-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory tests of the functional groups present. (2003)

59. Identify (*A*) to (*D*) in the following series of reactions.



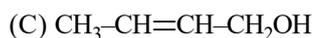
60. $C_5H_{13}N$ (optically active) $\xrightarrow[-N_2]{aq. NaNO_2/HCl}$ *X* + Some other products
Tertiary alcohol

- (i) Identify (*X*) and (*Y*).
(ii) Is (*Y*) optically active?
(iii) Give structure(s) of intermediate(s), if any, in the formation of (*Y*) from (*X*). (2005)

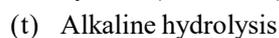
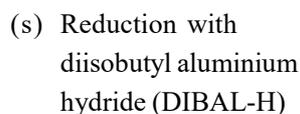
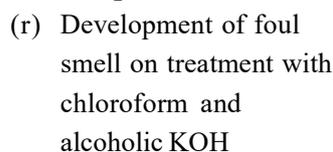
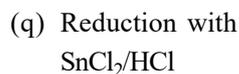
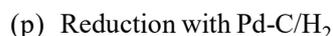
Matrix Match Type

61. Match each of the compounds in column I with its characteristic reaction(s) in column II.

Column I



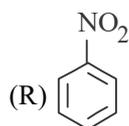
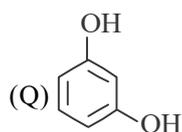
Column II



(2009)

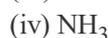
62. Match the four starting materials (P, Q, R, S) given in List-I with the corresponding reaction schemes (I, II, III, IV) provided in List-II and select the correct answer using the code given below the lists.

List-I

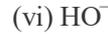
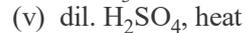
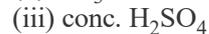


List-II

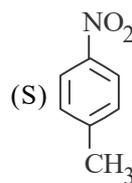
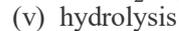
1. Scheme I



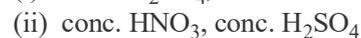
2. Scheme II



3. Scheme III



4. Scheme IV



Code :

	P	Q	R	S
(a)	1	4	2	3
(b)	3	1	4	2
(c)	3	4	2	1
(d)	4	1	3	2

(2014)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

63. **Statement-1** : *p*-Nitrophenol is a stronger acid than *o*-nitrophenol.

Statement-2 : Intramolecular hydrogen bondings make the *o*-isomer weaker than the *p*-isomer. (1989)

64. **Statement-1** : Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.

Statement-2 : Cyanide (CN^-) is a stronger nucleophile. (1998)

65. **Statement-1** : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Statement-2 : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. (2001)

66. **Statement-1** : Aniline on reaction with NaNO_2/HCl at 0°C followed by coupling with β -naphthol gives a dark blue coloured precipitate.

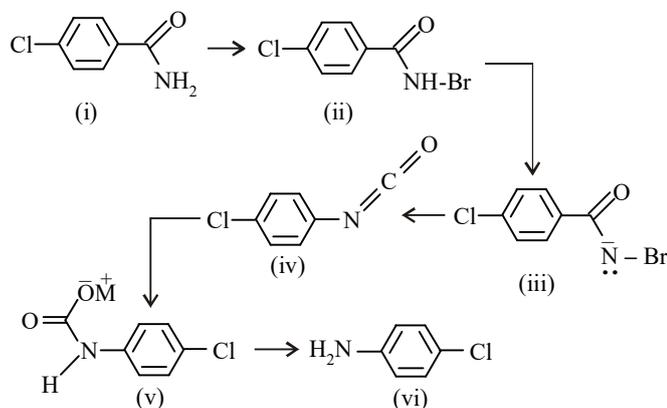
Statement-2 : The colour of the compound formed in the reaction of aniline with NaNO_2/HCl at 0°C followed by coupling with β -naphthol is due to the extended conjugation. (2008)

Comprehension Based Questions

Read the passage given below and answer the questions that follow

Comprehension - 1

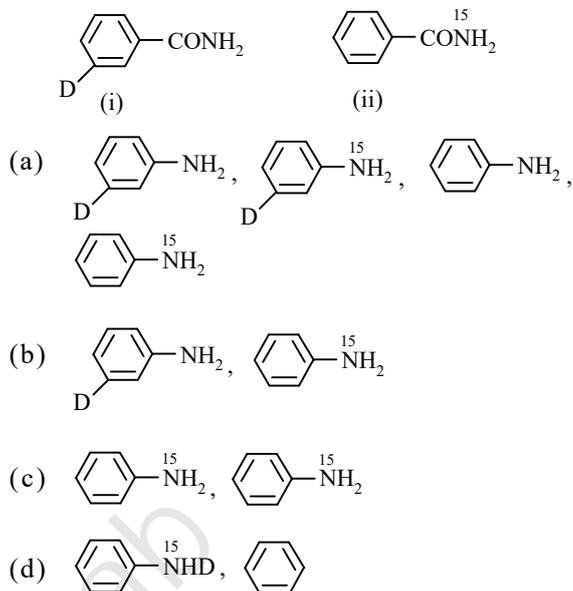
$RCONH_2$ is converted into RNH_2 by means of Hofmann bromamide degradation.



In this reaction, $RCONHBr$ is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an intramolecular reaction.

67. How can the conversion of (i) to (ii) be brought about?
 (a) KBr (b) $KBr + CH_3ONa$
 (c) $KBr + KOH$ (d) $Br_2 + KOH$.

68. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation?



69. Which is the rate determining step in Hofmann bromamide degradation?

- (a) formation of (i) (b) formation of (ii)
 (c) formation of (iii) (d) formation of (iv).
 (2006)

ANSWER KEY

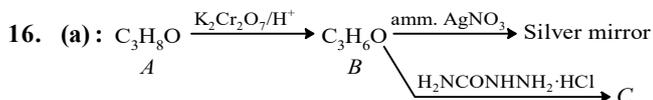
- | | | | | | |
|---------------------------|-----------------|---|------------|------------|-------------|
| 1. (c) | 2. (b) | 3. (b) | 4. (a) | 5. (b) | 6. (a) |
| 7. (b) | 8. (d) | 9. (a) | 10. (d) | 11. (c) | 12. (b) |
| 13. (c) | 14. (d) | 15. (b) | 16. (a) | 17. (a) | 18. (d) |
| 19. (b) | 20. (c) | 21. (d) | 22. (d) | 23. (b) | 24. (a) |
| 25. (c) | 26. (c) | 27. (c) | 28. (a, c) | 29. (a, d) | 30. (c) |
| 31. (a, d) | 32. (b) | 33. (b, d) | 34. (a) | 35. (a) | 36. Aniline |
| 37. <i>o</i> -Nitrophenol | 38. Dipolar ion | 61. $A \rightarrow (p, q, s, t); B \rightarrow (p, s, t); C \rightarrow (p); D \rightarrow (r)$ | 62. (c) | | |
| 63. (a) | 64. (d) | 65. (d) | 66. (d) | 67. (d) | 68. (b) |
| 69. (d) | | | | | |

Compounds Containing Nitrogen

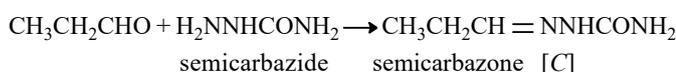
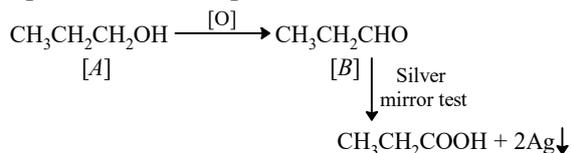
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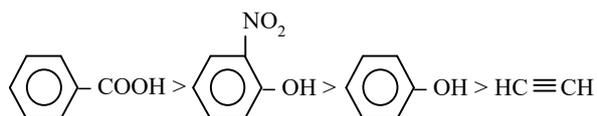
Thus the order of basic strength would be $1 > 3 > 2 > 4$.



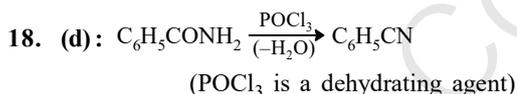
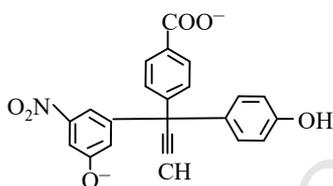
Reaction of B indicates that B is an aldehyde thus B should be $\text{C}_2\text{H}_5\text{CHO}$ or $\text{CH}_3\text{CH}_2\text{CHO}$ and therefore C should be $\text{CH}_3\text{CH}_2\text{CH} = \text{NNHCONH}_2$.



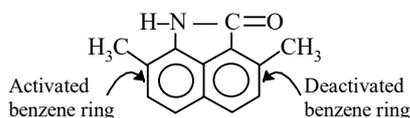
17. (a): The acidic strength of the attached groups is in the following order.



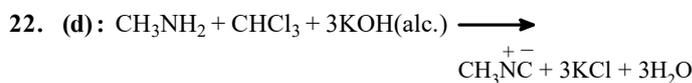
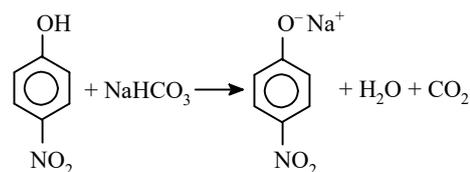
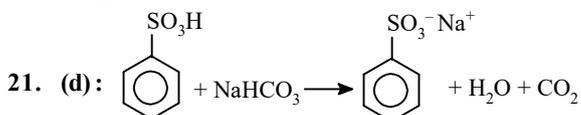
Two moles of amide ions will attract two moles of most acidic hydrogen and the obtained product will be



19. (b): We find that in one benzene ring the key group is $>\text{NH}$ which is an activating group while in other the key group is $>\text{C}=\text{O}$ which is a deactivating group. Hence electrophilic substitution will be governed by the ring having $>\text{N} - \text{H}$ group.



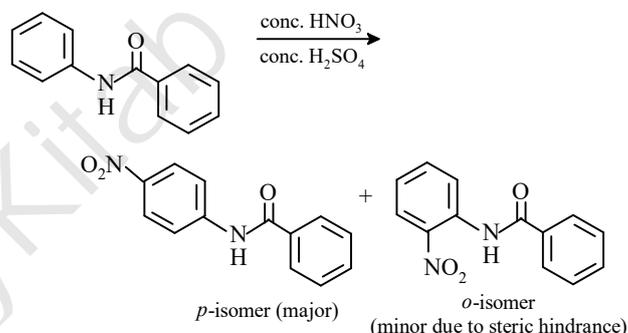
20. (c): The position (X) is most acidic due to $-\text{COOH}$ group. $-\text{NH}_3^+$ group at position Z is more acidic than at Y because of presence of electron withdrawing $-\text{COOH}$ group in close proximity. Hence $-\text{NH}_3^+$ group at position Z is least acidic.



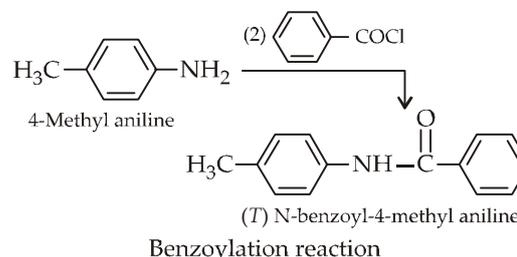
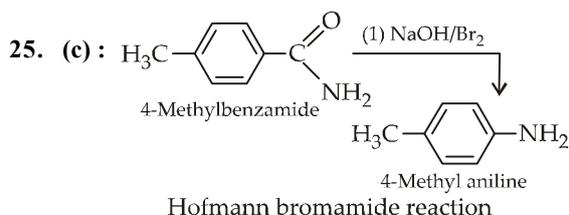
This is known as carbylamine reaction.

23. (b): $-\ddot{\text{N}}\text{H}-$ group is activating and *ortho-para* directing whereas $-\overset{\text{O}}{\parallel}{\text{C}}-$ is deactivating and *meta* directing.

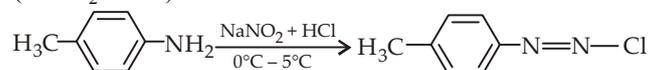
When the two groups present in the benzene ring direct differently, *i.e.* one is *ortho-para* and the other is *meta* directing, then *ortho-para* directing group takes precedence.

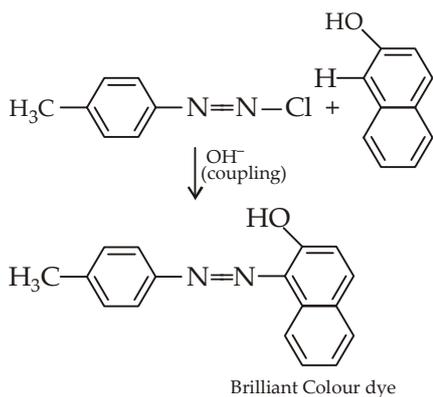


24. (a): In (a), due to similar charges (two positive charges) on adjacent atom, the structure is expected to be least stable.

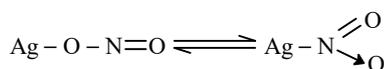


26. (c): For formation of colour dye, reaction should take place between diazonium salt and β -naphthol. Diazonium salt is prepared by reaction between aromatic amine and HNO_2 . ($\text{NaNO}_2 + \text{HCl}$).

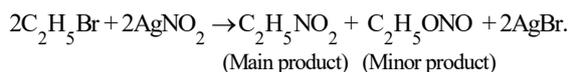




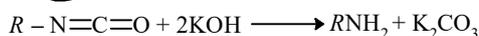
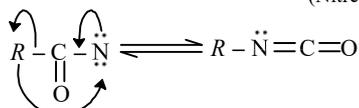
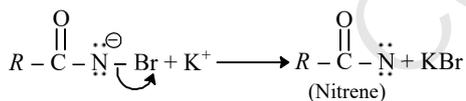
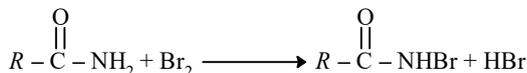
27. (c) : Silver nitrite, AgNO_2 (a salt of nitrous acid, HNO_2) occurs in two tautomeric forms



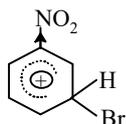
Thus NO_2^- ion from AgNO_2 may exist either as $-\text{O}-\text{N}=\text{O}$ (nitrite ion, NO_2^-) forming alkyl nitrites or in $-\text{N} \begin{array}{l} \text{O} \\ \text{O} \end{array}$ (nitro group) forming nitroalkanes.



28. (a, c) : This is Hoffmann bromamide degradation reaction.

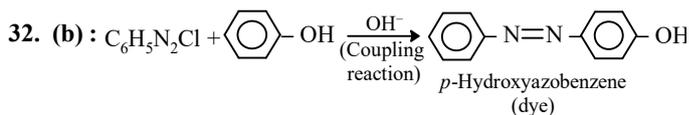
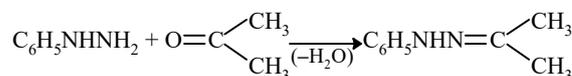
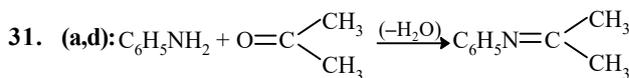


29. (a, d) : $-\text{NO}_2$ group decreases the density of electrons at *meta*-position as compared to that at *ortho* and *para* position. This is because of $-I$ and $-M$ effects.



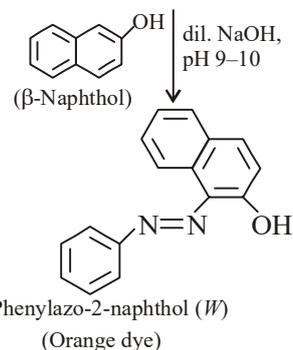
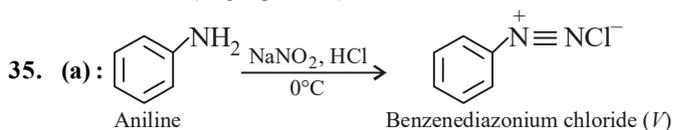
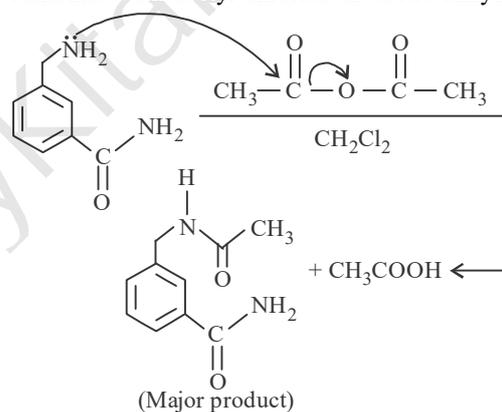
The above intermediate is a resonance hybrid of three structures so it is more stable than the corresponding intermediates from *ortho*- and *para*-attack.

30. (c) : In it we find 1 double and 3 single bonds of N *i.e.* a total of 10 electrons in valence shell of N which is not acceptable.



33. (b,d) : The carbylamine reaction is given by only primary amines. Hence 2, 4-dimethylaniline and *p*-methyl benzyl amine will give this test.

34. (a) : Acetylation takes place when amine (not amide) combines with acetyl chloride or acetic anhydride.



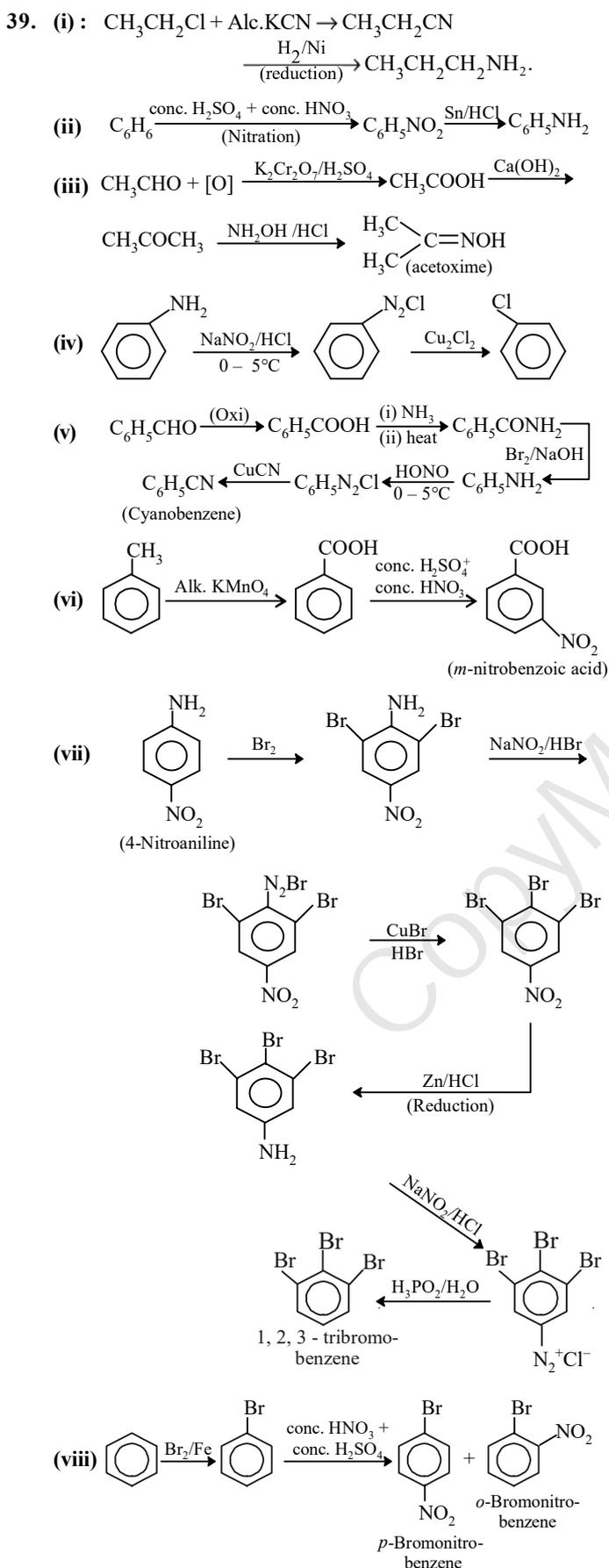
36. Aniline;

37. *o*-Nitrophenol; In this isomer intramolecular H-bonding takes place. Due to intramolecular H-bonding *o*-nitrophenol is less polar and hence least soluble in water (a polar solvent).

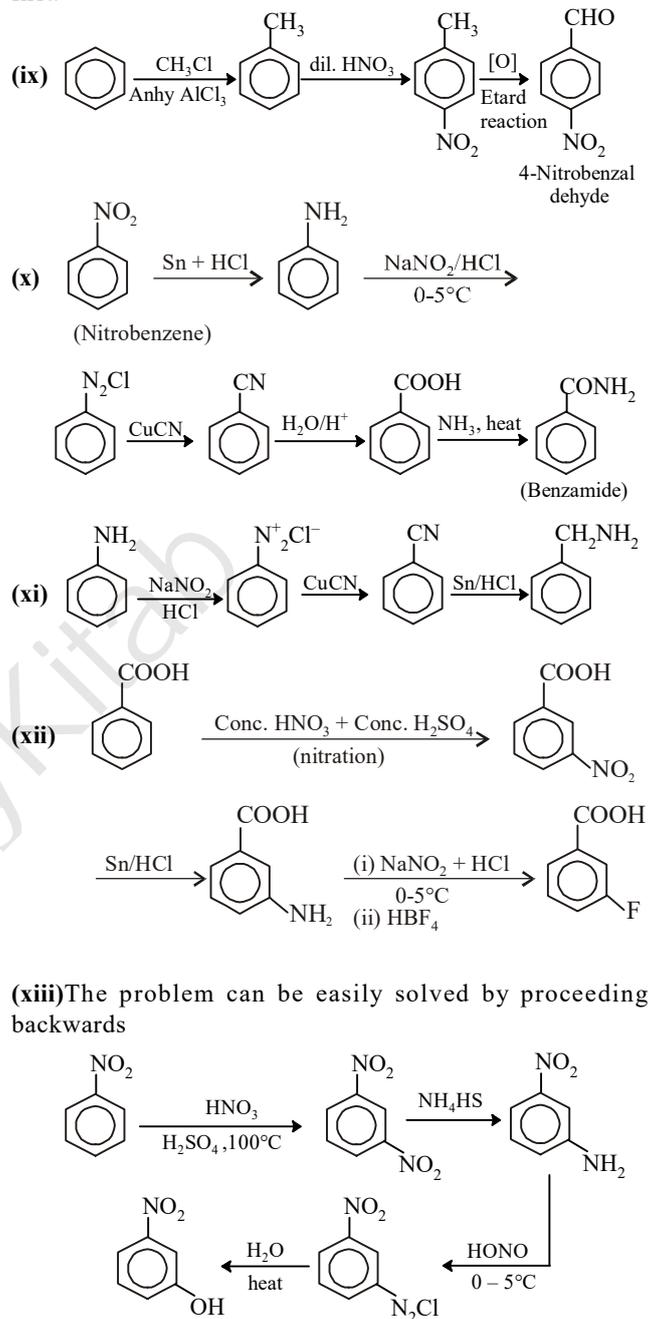
38. Dipolar ion; salt like

Compounds Containing Nitrogen

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On fractional crystallisation, crystals of *para*-isomer appear first.



(xiii) The problem can be easily solved by proceeding backwards

40. To calculate percentage of nitrogen :

$$50 \text{ ml of } 0.05 \text{ M H}_2\text{SO}_4 = 50 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4 \quad [\because N = 2 \times M]$$

Excess of acid required 25 ml of 0.1 M or 0.1 N NaOH

$$[\because N = M]$$

$$25 \text{ ml of } 0.1 \text{ N NaOH} = 25 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4 \quad [N_1V_1 = N_2V_2]$$

\therefore Volume of 0.1 N H₂SO₄ used for neutralization of NH₃

$$= 50 - 25 = 25 \text{ ml}$$

$$\begin{aligned} \text{Hence \% age of N} &= \frac{1.4 \times \text{normality of acid} \times \text{volume of acid}}{\text{weight of the compound}} \\ &= \frac{1.4 \times 0.1 \times 25}{0.303} = 11.55\% \end{aligned}$$

Percentage of oxygen :

$$\text{percentage of oxygen} = 100 - (69.4 + 5.8 + 11.55) = 13.25\%$$

Empirical formula:

Element	%	Relative number	Simplest ratio of atoms
C	69.4	69.4/12 = 5.8	5.8/0.825 = 7
H	5.8	5.8/1 = 5.8	5.8/0.825 = 7
N	11.55	11.55/14 = 0.825	0.825/0.825 = 1
O	13.25	13.25/16 = 0.828	0.825/0.828 = 1

Hence empirical formula of the aromatic compound = C_7H_7NO

Molecular formula :

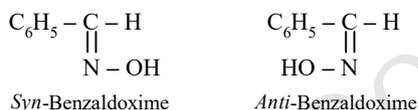
$$\begin{aligned} \text{Empirical formula weight} &= 7 \times 12 + 7 \times 1 + 1 \times 14 + 1 \times 16 \\ &= 84 + 7 + 14 + 16 = 121 \end{aligned}$$

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}} = \frac{121}{121} = 1$$

Hence molecular formula = C_7H_7NO .

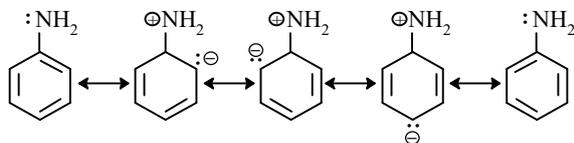
Structure of the compound

Since the compound is aromatic so we can write its formula as $C_6H_5CH_2NO$ or $C_6H_5CH = NOH$ (benzaldoxime). It can exist in following two isomeric structures.

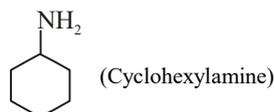


41. (i): Aniline is a weaker base than cyclohexylamine because of resonance.

Resonance structures of aniline are:

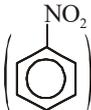


In case of cyclohexylamine there is no resonance.



- (ii) In *o*-nitrophenol the intramolecular H-bonding occurs hence it exists as single molecule and in *p*-nitrophenol the intermolecular H-bonding occurs hence it exists as associated molecule. Because of this difference in H-bonding *o*-nitrophenol has low b.p. and is steam volatile whereas *p*-nitrophenol is not.

- (iii) The alkyl groups, which are electron releasing groups, increase the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or Lewis acids and making the amine more basic. Thus, it is expected that the basic nature of amines should be in the order tertiary > secondary > primary, but the observed order in the case of lower members is found to be as secondary > primary > tertiary. This anomalous behaviour of tertiary amines is due to steric factors, *i.e.*, crowding of alkyl groups cover nitrogen atom from all sides and thus makes the approach and bonding by a proton relatively difficult, resulting the reduction in its basicity.

- (iv) The nitro ($-NO_2$) group in nitrobenzene 

strongly deactivates the benzene ring due to its $-I$ and $-M$ effects. Due to this, the reactivity of benzene ring towards Friedel-Craft's alkylation decreases.

- (v) Given compound is activated aryl halide hence it undergoes aromatic nucleophilic substitution reaction by S_NAr mechanism due to presence of very strong electron withdrawing group ($-NO_2$) at *para* position and electron releasing group ($-CH_3$) at *meta* position of fluorine atom.

While O_2NCH_2-  is not reactive towards aromatic

nucleophilic substitution reaction as the ring is not highly deactivated because $-NO_2$ group is not directly attached to the benzene ring.

- (vi) (a) $-\ddot{N}=\overset{\ominus}{O}$ group is electron releasing, hence *o*-, *p*-directing

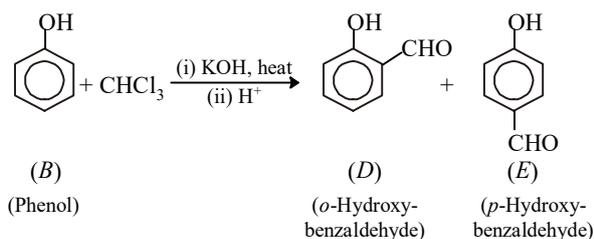
- (b) $-NO_2$ group is electron withdrawing hence *meta*-directing.

42. (i): N,N -dimethyl-*p*-toluidine > *p*-toluidine > aniline > *p*-nitrophenol.

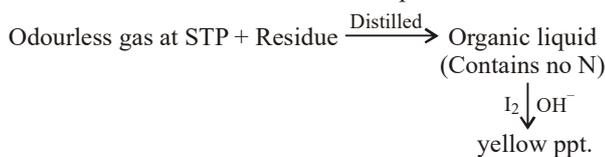
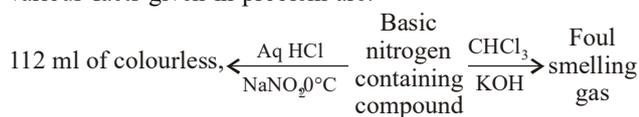
Presence of $+I$ group (like alkyl group) in the benzene nucleus of aniline increases the basicity. The effect is more when the alkyl group is in *o*- and *p*-position than in *m*-position.

Presence of $-I$ group (like $-NO_2$) in the benzene nucleus of aniline decreases the basicity. The effect is much more in *o*- and *p*- position than in *m*-position.

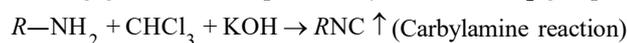
- (ii) Aniline < *N*-Methylamine < Methylamine < Dimethylamine. The ease with which the lone pair of N-atom coordinates with a proton determines the relative basic strength of amines. Moreover $-C_6H_5$ is an electron attracting group hence aniline is least basic. $-CH_3$ is electron repelling group and so we get the above order.



48. Various facts given in problem are:



Since the basic organic compound containing nitrogen on reaction with alc. KOH and chloroform produces a foul smelling gas so the compound may contain $-\text{NH}_2$ group.



Molecular weight of amine (RNH_2)

112 ml of gas is evolved at STP by amine = 0.295 g

$$\therefore 22400 \text{ ml of gas at NTP is given by amine} = \frac{0.295}{112} \times 22400 \text{ g} = 59 \text{ g}$$

Hence mol. wt. of amine = 59

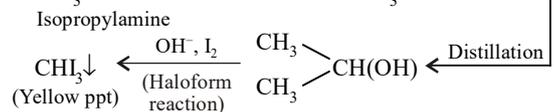
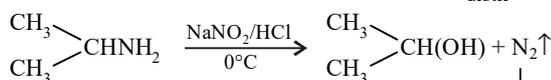
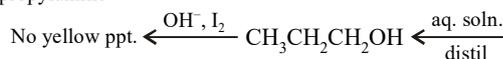
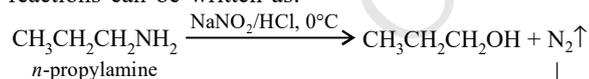
Molecular weight of alkyl group R = 59 - 16 = 43

Nature of Alkyl group with mol. wt. 43

It is C_3H_7 - (mol. wt. = 43)

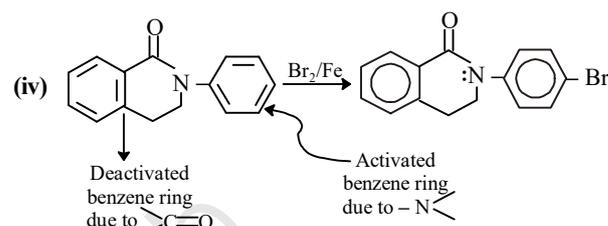
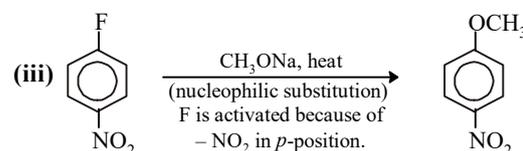
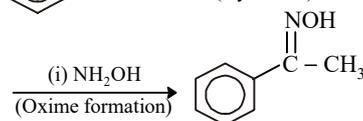
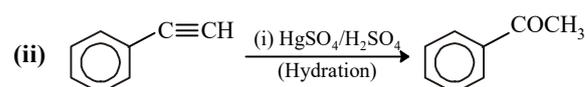
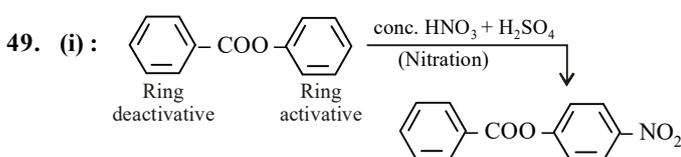
So the amine may be either $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ or $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array} \text{CHNH}_2$

The reaction of amine with NaNO_2 at 0°C and all other reactions can be written as:

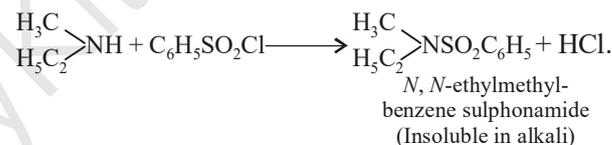


Since the given reactions correspond to isopropylamine,

the original compound is isopropylamine, $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array} \text{CHNH}_2$.

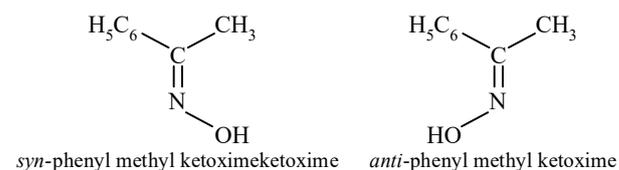


50. $\text{A}(\text{C}_3\text{H}_9\text{N})$ is a secondary (2°) amine $\text{CH}_3-\text{NH}-\text{C}_2\text{H}_5$ i.e. ethyl-methylamine.

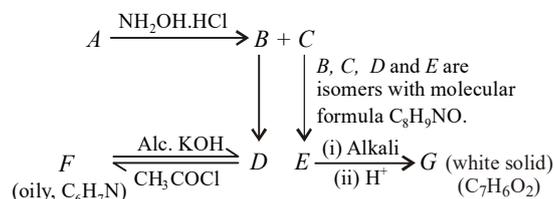


51. The foul smelling compound is phenyl isocyanide i.e. $\text{C}_6\text{H}_5\text{NC}$. $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{C}_6\text{H}_5\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$ (Alc)

52. The structure of two isomeric oximes is



53. The facts given in the problem can be summarized as:

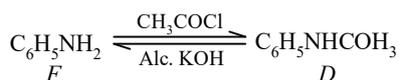


Following conclusions can be drawn from the set of reactions given above:

(i) Since only *F* reacts with acetyl chloride so it must have $-\text{NH}_2$ or $>\text{NH}$ group. Thus (*F*) i.e. $\text{C}_6\text{H}_7\text{N}$ can be written as $\text{C}_6\text{H}_5\text{NH}_2$ or $\text{C}_6\text{H}_5\text{NH}$. Hence it is $\text{C}_6\text{H}_5\text{NH}_2$ and therefore *D* is $\text{C}_6\text{H}_5\text{NHCOCH}_3$

Compounds Containing Nitrogen

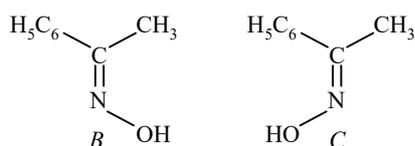
331



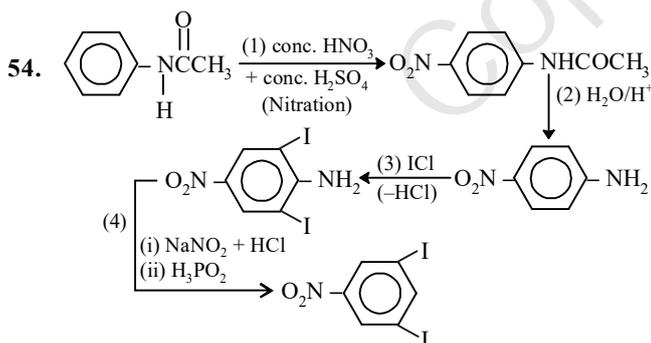
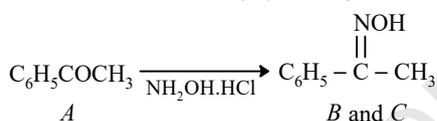
(ii) When *E* is treated with alkali followed by acidification yields a white solid compound (*G*) with formula $\text{C}_7\text{H}_6\text{O}_2$ thus *G* seems to be an acid, so it is $\text{C}_6\text{H}_5\text{COOH}$.

(iii) Since *D* and *E* are isomers ($\text{C}_8\text{H}_9\text{ON}$) and they form $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{COOH}$ respectively so both *D* and *E* should be amides with different alkyl or aryl groups. Since *D* is $\text{C}_6\text{H}_5\text{NHCOCH}_3$, so *E* must be $\text{CH}_3\text{NHCOC}_6\text{H}_5$.

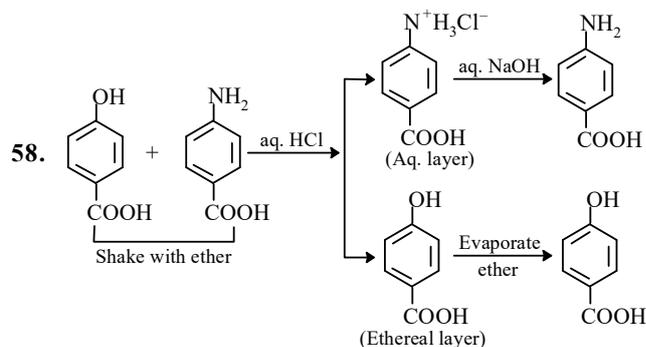
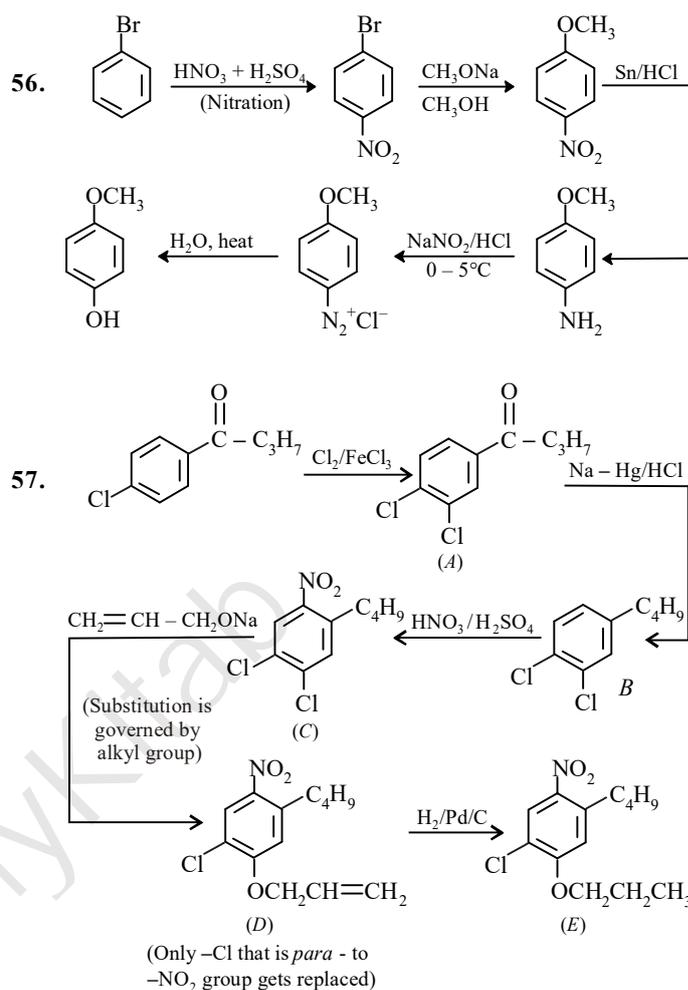
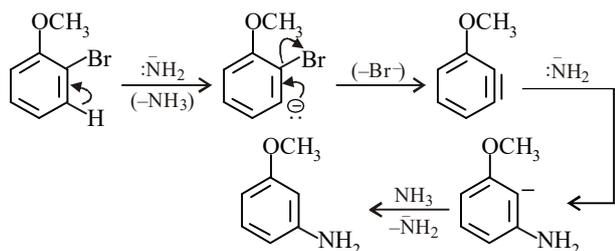
(iv) Since compounds *D* and *E* are formed by rearrangement of compounds *B* and *C* respectively, compounds *B* and *C* should be oximes >C=NOH (oximes rearrange to amides - Beckmann Rearrangement). Moreover oximes having different alkyl (or aryl) groups show geometrical isomerism (*Syn* and *Anti*). In view of above the compounds *B* and *C* must have the following structures.



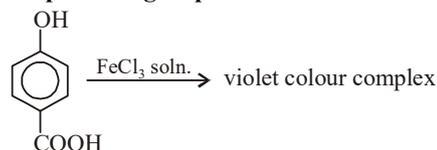
(v) Since oximes *B* and *C* are formed from *A* therefore *A* should be a ketone with formula $\text{C}_6\text{H}_5\text{COCH}_3$.



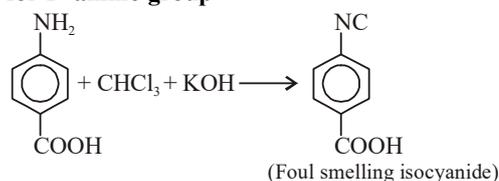
55. This reaction proceeds *via* benzyne formation.



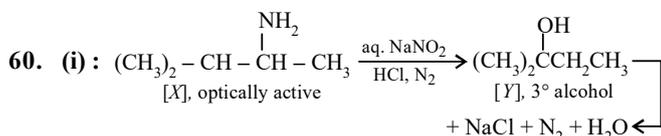
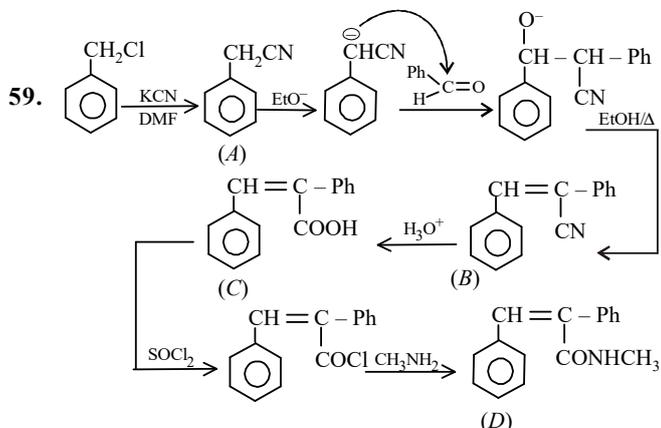
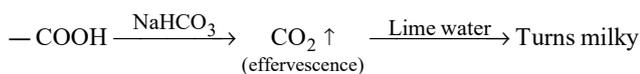
Test for phenolic group



Test for 1° amino group

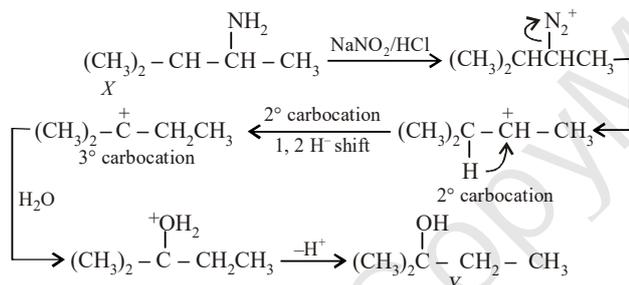


Test for -COOH group

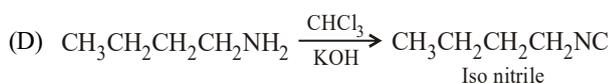
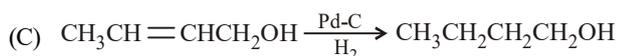
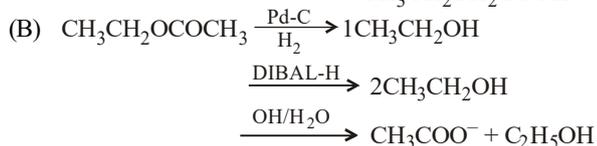
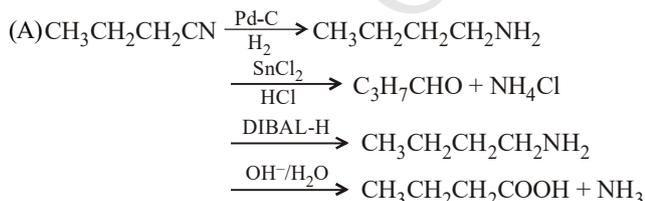


(ii) [Y], a 3° alcohol is optically inactive.

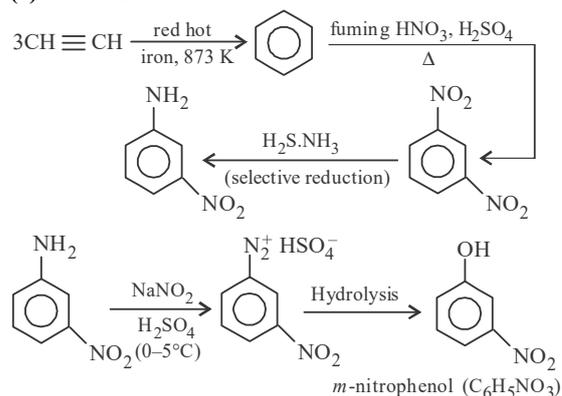
(iii) Formation of [Y] from [X]



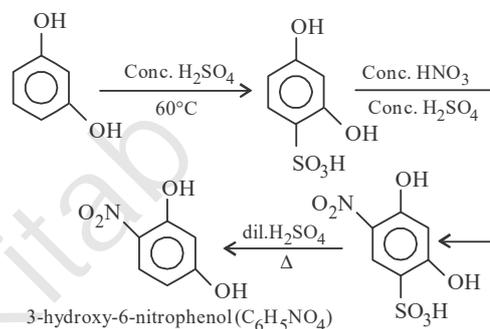
61. A \rightarrow (p, q, s, t); B \rightarrow (p, s, t); C \rightarrow (p); D \rightarrow (r) :



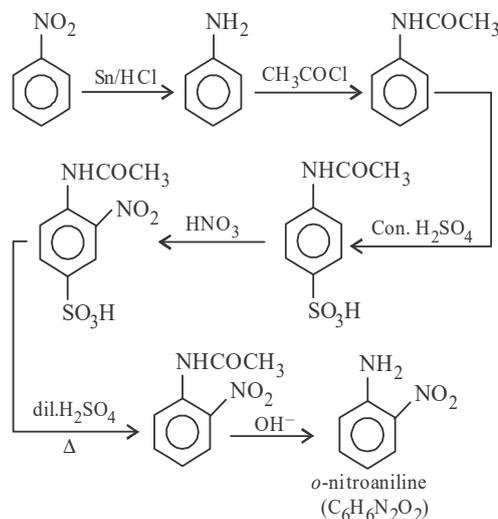
62. (c) : P : Scheme III



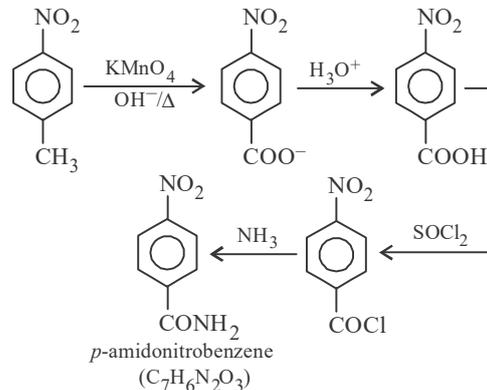
Q : Scheme IV



R : Scheme II



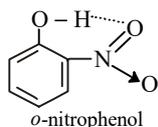
S : Scheme I



Compounds Containing Nitrogen

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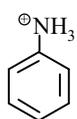
63. (a): Both statements are correct.



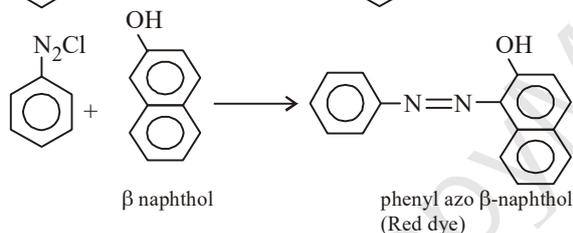
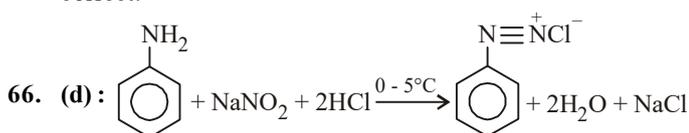
Due to the presence of intramolecular H-bonding in *o*-nitrophenol, release of H^+ becomes difficult, as a result, it acts as a weaker acid than *p*-nitrophenol.

64. (d): Aryl halides (chlorobenzene) do not undergo nucleophilic substitution with KCN because of low reactivity of Cl atom, which is due to resonance in chlorobenzene. So statement-1 is wrong, but statement-2 is correct.

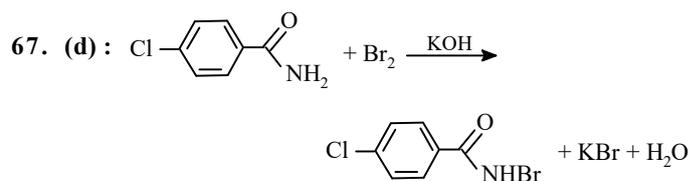
65. (d): In strongly acidic medium, aniline gets protonated and so the lone pair of electrons is not available to produce $+E$ or $+M$ effects. On the other hand, the —NH_3^+ group exerts strong $-I$ effect and thus it causes the deactivation of the ring.



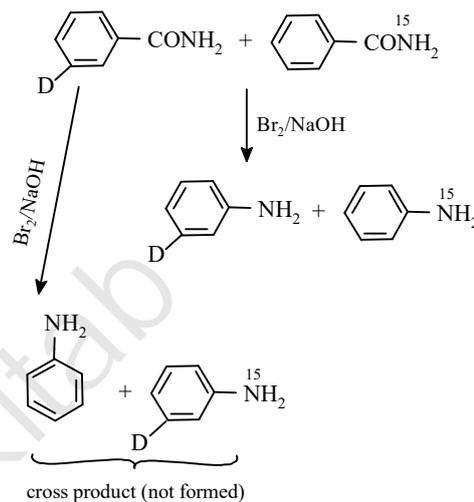
. Thus statement-1 is incorrect but statement-2 is correct.



This is an example of coupling reaction.



68. (b): Since the overall reaction is intramolecular, hence there will be no effect on product formation.



69. (d): The rate limiting step is probably loss of Br^- to form isocyanates as this is the slowest step.

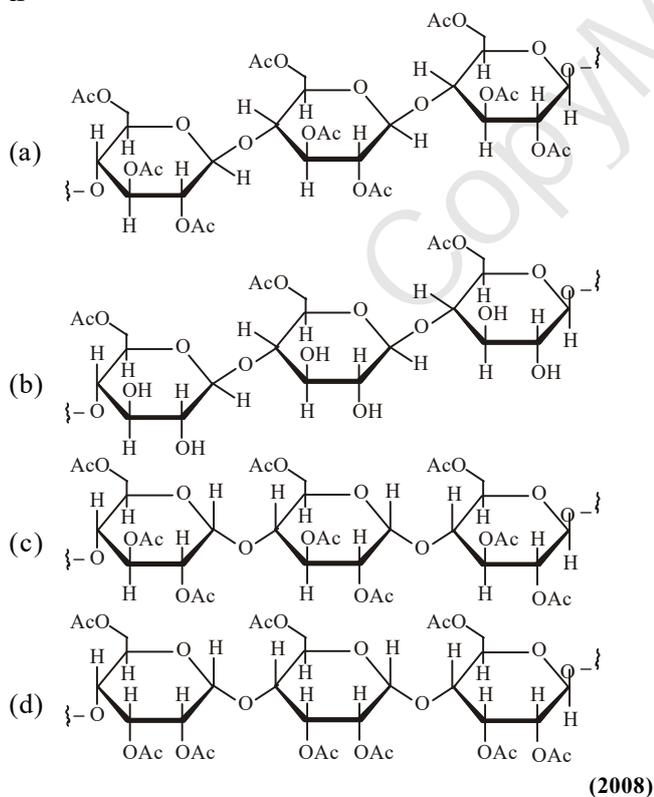


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Biomolecules and Chemistry in Everyday Life

Multiple Choice Questions with ONE Correct Answer

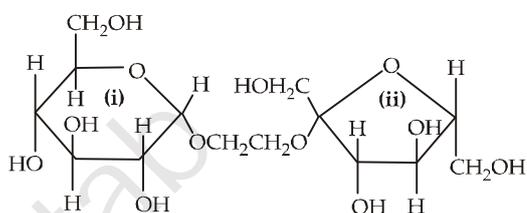
- The pair of compounds in which both the compounds give positive test with Tollen's reagent is
 - glucose and sucrose
 - fructose and sucrose
 - acetophenone and hexanal
 - glucose and fructose
 (2004)
- The two forms of *D*-glucopyranose obtained from the solution of *D*-glucose are called
 - isomers
 - anomers
 - epimers
 - enantiomers
 (2005)
- Cellulose upon acetylation with excess acetic anhydride/ H_2SO_4 (catalytic) gives cellulose triacetate whose structure is



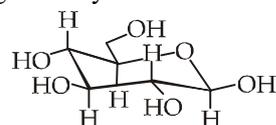
- Among cellulose, poly(vinylchloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is

- nylon
- poly(vinyl chloride)
- cellulose
- natural rubber. (2009)

- The correct statement about the following disaccharide is



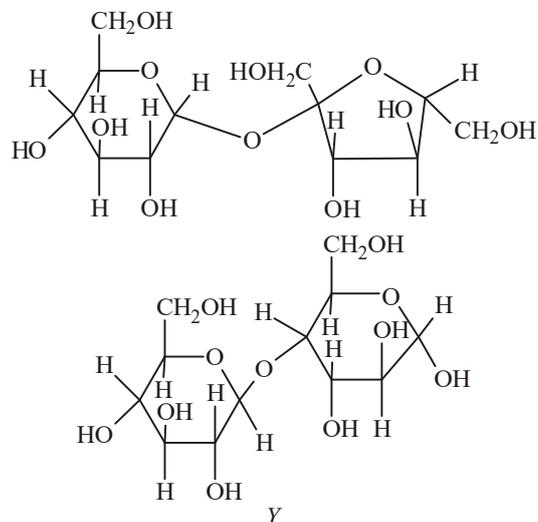
- Ring (i) is pyranose with α -glycosidic link
 - Ring (i) is furanose with α -glycosidic link
 - Ring (ii) is furanose with α -glycosidic link
 - Ring (ii) is pyranose with β -glycosidic link
- (2010)
- The following carbohydrate is



- a ketohexose
 - an aldohexose
 - an α -furanose
 - an α -pyranose
- (2011)

Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

- The correct statement(s) about the following sugars *X* and *Y* is(are)

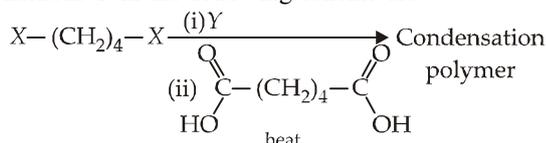


Biomolecules and Chemistry in Everyday Life

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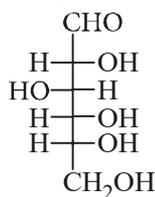
- (a) X is a reducing sugar and Y is a non-reducing sugar
 (b) X is a non-reducing sugar and Y is a reducing sugar
 (c) the glycosidic linkages in X and Y are α and β respectively
 (d) the glycosidic linkages in X and Y are β and α respectively. (2009)

8. The correct functional group X and the reagent/reaction conditions Y in the following scheme are



- (a) $X = \text{COOCH}_3$, $Y = \text{H}_2/\text{Ni}/\text{heat}$
 (b) $X = \text{CONH}_2$, $Y = \text{H}_2/\text{Ni}/\text{heat}$
 (c) $X = \text{CONH}_2$, $Y = \text{Br}_2/\text{NaOH}$
 (d) $X = \text{CN}$, $Y = \text{H}_2/\text{Ni}/\text{heat}$. (2011)

9. The structure of D -(+)-glucose is

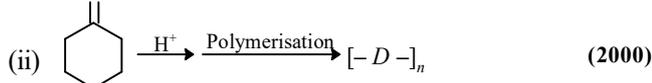
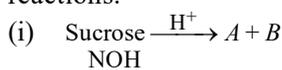


The structure of L -(-)-glucose is

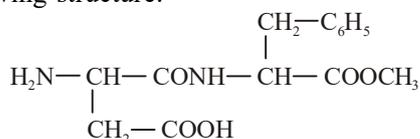
- (a) $\begin{array}{c} \text{CHO} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{CH}_2\text{OH} \end{array}$ (b) $\begin{array}{c} \text{CHO} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{CH}_2\text{OH} \end{array}$
 (c) $\begin{array}{c} \text{CHO} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{CH}_2\text{OH} \end{array}$ (d) $\begin{array}{c} \text{CHO} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ (2015)

Subjective Problems

10. Give the structures of the products in each of the following reactions.

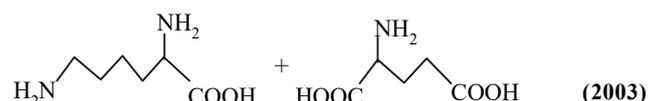


11. Aspartame, an artificial sweetener, is a peptide and has the following structure:

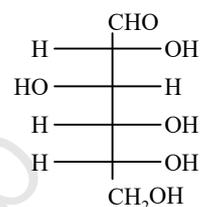


- (i) Identify the four functional groups.
 (ii) Write the zwitter ion structure.
 (iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
 (iv) Which of the two amino acids is more hydrophobic? (2001)

12. Following two amino acids lysine and glutamic acid form dipeptide linkage. What are two possible dipeptides?

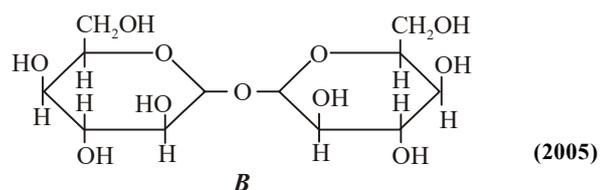
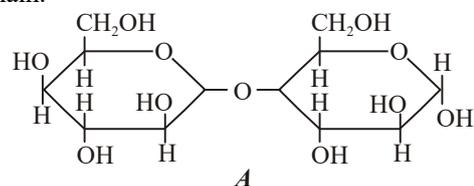


13. The Fisher projection of D -glucose is drawn below:



- (i) Draw the Fisher projection of L -glucose.
 (ii) Give the reaction of L -glucose with Tollen's reagent. (2004)

14. Which of the following will reduce Tollen's reagent? Explain.



Matrix Match Type

15. Match the chemical substances in Column I with type of polymers/type of bonds in Column II.

Column I	Column II
(A) cellulose	(p) natural polymer
(B) nylon-6,6	(q) synthetic polymer
(C) protein	(r) amide linkage
(D) sucrose	(s) glycoside linkage

(2007)

Reasoning Type

This section contains reasoning type questions. Each Question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

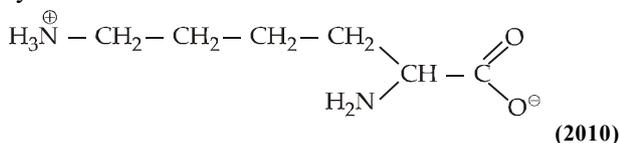
- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
 (b) Statement-1 is true; statement-2 is true; statement-2 is NOT a correct explanation for statement-1.
 (c) Statement-1 is true, statement-2 is false.
 (d) Statement-1 is false, statement-2 is true.

16. Statement-1 : Glucose gives a reddish-brown precipitate with Fehling's solution.

Statement-2 : Reaction of glucose with Fehling's solution gives CuO and gluconic acid. (2007)

Integer Answer Type

17. The total number of basic groups in the following form of lysine is



18. A decapeptide (Mol. Wt. 796) on complete hydrolysis gives glycine (Mol. wt. 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is (2011)

19. The substituents R_1 and R_2 for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0?



Peptide	R_1	R_2
I	H	H
II	H	CH_3
III	CH_2COOH	H

IV	CH_2CONH_2	$(\text{CH}_2)_4\text{NH}_2$
V	CH_2CONH_2	CH_2CONH_2
VI	$(\text{CH}_2)_4\text{NH}_2$	$(\text{CH}_2)_4\text{NH}_2$
VII	CH_2COOH	CH_2CONH_2
VIII	CH_2OH	$(\text{CH}_2)_4\text{NH}_2$
IX	$(\text{CH}_2)_4\text{NH}_2$	CH_3

(2012)

20. When the following aldohexose exists in its *D*-configuration, the total number of stereoisomers in its pyranose form is

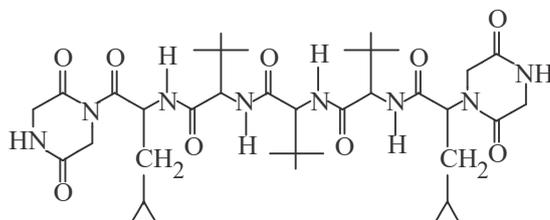


(2012)

21. A tetrapeptide has $-\text{COOH}$ group on alanine. This produces glycine (Gly), valine (Val), phenyl-alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with $-\text{NH}_2$ group attached to a chiral center is (JEE 2013)

22. The total number of lone-pairs of electrons in melamine is (JEE 2013)

23. The total number of distinct naturally occurring amino acids obtained by complete acidic hydrolysis of the peptide shown below is



(2014)

ANSWER KEY

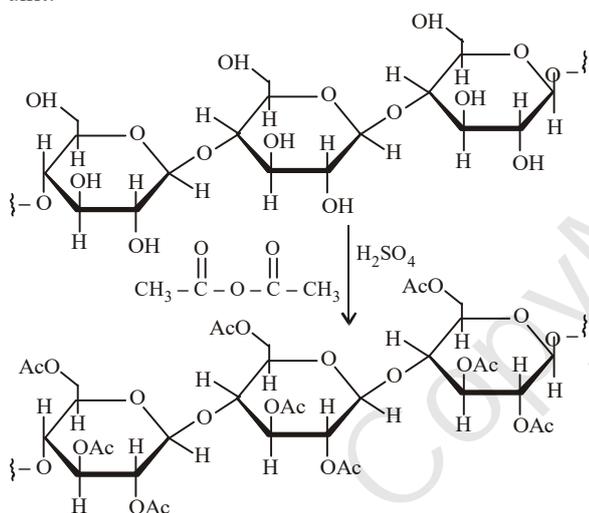
- | | | | | | |
|-----------|-----------------|---------|---|---------|---------|
| 1. (d) | 2. (b) | 3. (a) | 4. (d) | 5. (a) | 6. (b) |
| 7. (b, c) | 8. (a, b, c, d) | 9. (a) | 15. (A) \rightarrow (p, s); (B) \rightarrow (q, r); (C) \rightarrow (p, r); (D) \rightarrow (s) | 20. (8) | 21. (4) |
| 16. (c) | 17. (2) | 18. (6) | 19. (4) | | |
| 22. (6) | 23. (1) | | | | |

Explanations

1. **(d)**: Glucose is an aldose containing an aldehydic group ($-\text{CHO}$) so it responds to Tollen's test. Fructose is a ketose contains a ketonic group ($>\text{C}=\text{O}$) and it undergoes rearrangement in presence of basic medium (provided by Tollen's reagent) to form glucose (containing $-\text{CHO}$ group), it (*i.e.* fructose) therefore undergoes Tollen's test in basic medium.

2. **(b)**: The two isomeric forms (α - and β -) of *D*-glucopyranose differ in their configuration only at C-1 so they are called anomers.

3. **(a)**: Cellulose is a straight chain polysaccharide composed of *D*-glucose units which are joined by β -glycosidic linkages between C-1 of one glucose unit and C-4 of the next glucose unit.



4. **(d)**: Cellulose and nylon are fibres and thus their intermolecular forces are the strongest. Poly (vinyl chloride) is a thermoplastic, the intermolecular forces in them are neither strong nor weak.

Natural rubber has weak van der Waals forces, which are the weakest forces.

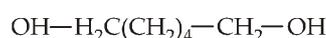
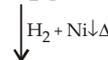
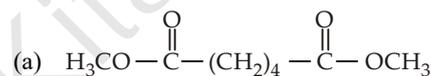
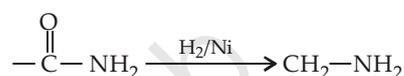
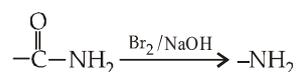
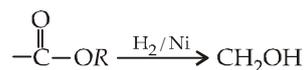
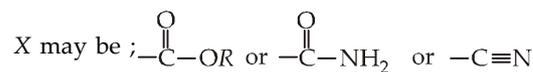
5. **(a)**: The disaccharide is sucrose, with ring (i) having 6-members and hence is a pyranose and ring (ii) has 5-members and hence is a furanose. C-1 of ring (i) has an α -glycosidic linkage.

6. **(b)**: This structure is an example of pyranose and aldohexose. Here the carbohydrate's structure is of the β -pyranose form.

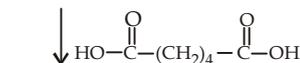
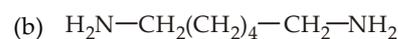
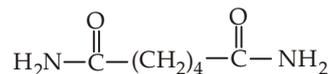
7. **(b, c)**: In *X* reducing ends of both the sugars are not free whereas in *Y* reducing end at C-1 is free. So, *Y* is a reducing sugar.

The glycosidic linkage is α in *X* and β in *Y*.

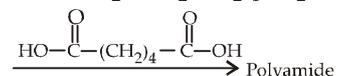
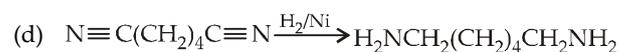
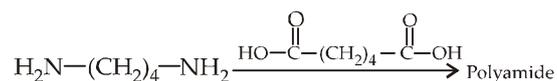
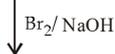
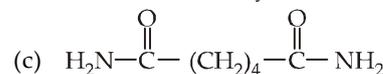
8. **(a, b, c, d)**: Condensation polymers are formed by condensation of diols or diamine with dicarboxylic acids. Therefore,

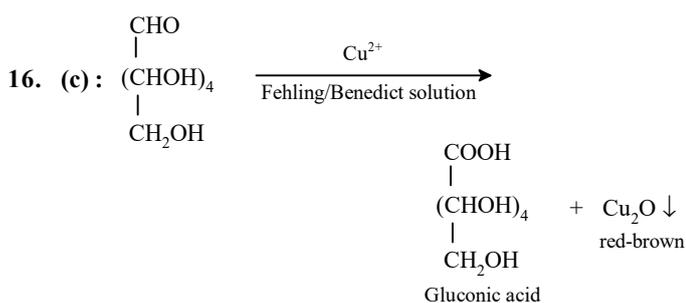


Polyester

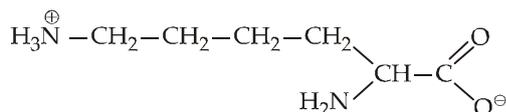


Polyamide





17. (2) : The given form of lysine has two basic groups, i.e., —NH₂ group and —COO[−] group.



18. (6) : Decapeptide + 9 H₂O → Glycine + Alanine + Phenylalanine.

Total wt. of amino acids after addition of 9 mol of H₂O
= 796 + (9 × 18) = 958

For *n*-units of glycine, $\frac{n \times 75}{958} \times 100 = 47 \Rightarrow n = 6$

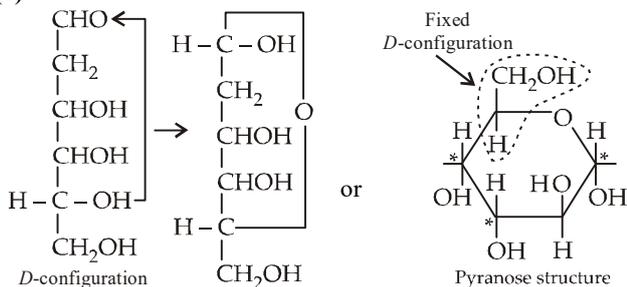
19. (4)

I	H	H	Neutral	0
II	H	CH ₃	Neutral	0
III	CH ₂ COOH	H	Acidic	(−)ve charge
IV	CH ₂ CONH ₂	(CH ₂) ₄ NH ₂	Basic	(+)ve charge
V	CH ₂ CONH ₂	CH ₂ CONH ₂	Neutral	0
VI	(CH ₂) ₄ NH ₂	(CH ₂) ₄ NH ₂	Basic	(+)ve charge
VII	CH ₂ COOH	CH ₂ CONH ₂	Acidic	(−)ve charge
VIII	CH ₂ OH	(CH ₂) ₄ NH ₂	Basic	(+)ve charge
IX	(CH ₂) ₄ NH ₂	CH ₃	Basic	(+)ve charge

Hence IV, VI, VIII and IX are positively charged at pH = 7.0

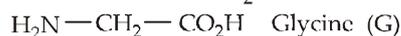
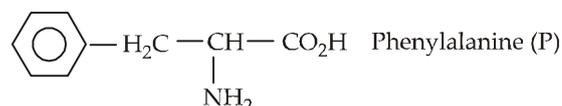
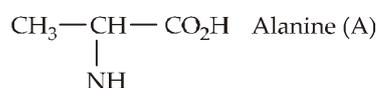
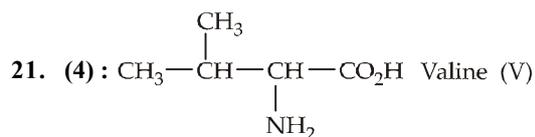
Groups like —CH₂OH, amides —CH₂C(=O)—NH₂, are neutral.

20. (8) :



Chiral centres in pyranose structure, *n* = 3.

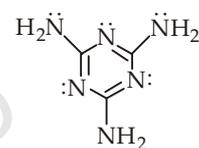
Total stereoisomers = 2^{*n*} = 2³ = 8.



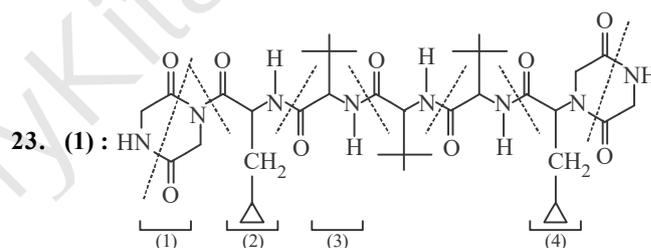
As (A) is at the end so options possible with —NH₂ at beginning are

(i) VPGA, (ii) VGPA, (iii) PVGA, and (iv) PGVA

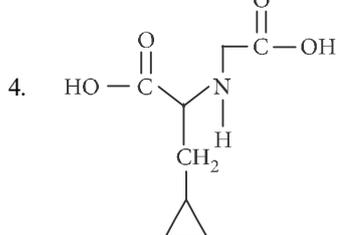
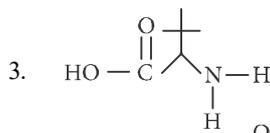
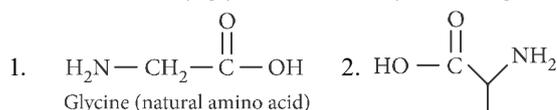
22. (6) : Structure of melamine is



Total no. of lone pair of electrons = 6.



On acidic hydrolysis, 4 distinct amino acids were produced out of which only glycine is naturally occurring amino acid.



28

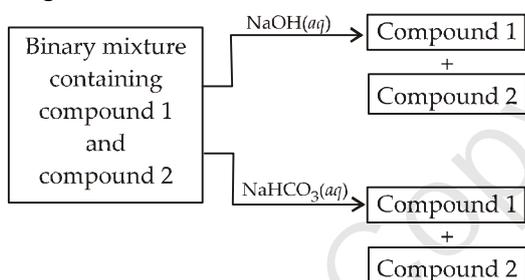
Practical Organic Chemistry

Only One Option Correct Type

1. For the identification of β -naphthol using dye test, it is necessary to use
- dichloromethane solution of β -naphthol
 - acidic solution of β -naphthol
 - neutral solution of β -naphthol
 - alkaline solution of β -naphthol.
- (2014)

Multiple Choice Questions with ONE or MORE THAN ONE Correct Answer

2. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme.



- C_6H_5OH and C_6H_5COOH
 - C_6H_5COOH and $C_6H_5CH_2OH$
 - $C_6H_5CH_2OH$ and C_6H_5OH
 - $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$
- (2012)

Matrix Match Type

3. Match the compounds in Column I with their characteristic test(s)/reaction(s) given in Column II.

Column I

Column II

- | | |
|-----------------------|--|
| (A) $H_2N-NH_3^+Cl^-$ | (p) sodium fusion extract of the compound gives prussian blue colour with $FeSO_4$ |
| (B) | (q) gives positive $FeCl_3$ test |
| (C) | (r) gives white precipitate with $AgNO_3$ |
| (D) | (s) reacts with aldehydes to form the corresponding hydrazone derivatives. |

(2008)

ANSWER KEY

1. (d) 2. (b, d) 3. (A) \rightarrow (r, s), (B) \rightarrow (p, q), (C) \rightarrow (p, q, r), (D) \rightarrow (p, s)

Explanations

1. **(d)** : In dye test, phenolic $-OH$ is converted into $-O^-$ ion, which activates the ring for further reaction. This is possible only in alkaline solution of β -naphthol. It dissolves poorly in aq. acidic solution.

Only those compounds having both alcoholic $-OH$ group and $-COOH$ group can be separated by $NaOH$ and $NaHCO_3$ solutions. Phenol does not react with $NaHCO_3$ solution.

2. **(b, d)** : (a) $C_6H_5OH, C_6H_5COOH \rightarrow$ separated by $NaHCO_3$ only but not by $NaOH$.
 (b) $C_6H_5COOH, C_6H_5CH_2OH \rightarrow$ separated by $NaHCO_3$ and $NaOH$ both.
 (c) $C_6H_5CH_2OH, C_6H_5OH \rightarrow$ separated by $NaOH$ only but not by $NaHCO_3$.
 (d) $C_6H_5CH_2OH, C_6H_5CH_2COOH \rightarrow$ separated by $NaHCO_3$ and $NaOH$ both.

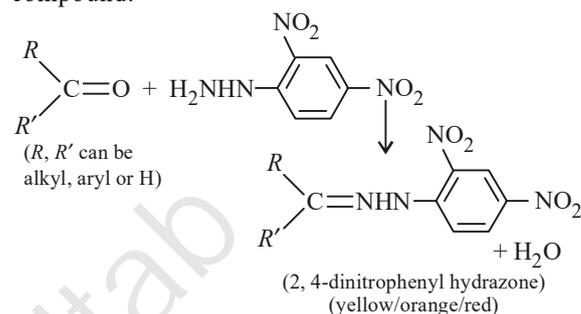
3. **(A)** \rightarrow **(r, s)**; **(B)** \rightarrow **(p, q)**; **(C)** \rightarrow **(p, q, r)**; **(D)** \rightarrow **(p, s)**

Phenolic group forms coloured iron complex when treated with neutral $FeCl_3$ solution. The formation of the iron complex is attributed to the existence of keto-enol tautomerism in

phenol. Phenol predominantly exists in enolic form, hence colour formation is used to identify phenol.

In (A) and (C), terminal chloride ion is capable of forming white precipitate of $AgCl$ with $AgNO_3$.

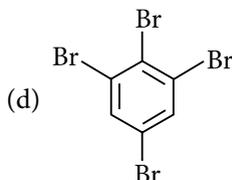
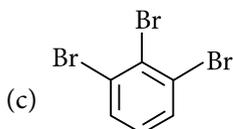
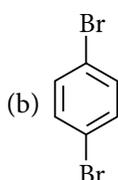
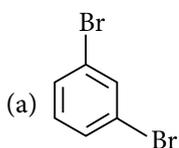
Aldehyde or ketone gives orange/yellow/red colour crystalline products with 2,4-dinitrophenyl hydrazine compound.



Sodium fusion extract of the compound containing C, N gives prussian blue colour with $FeSO_4$.

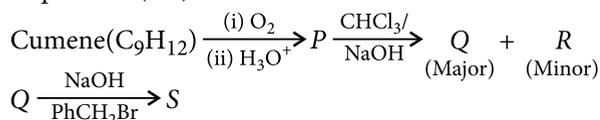
This is the detection of element (C and N) by Lassaigne's method.





[Compounds Containing Nitrogen]

7. The correct statement(s) about the following reaction sequence is(are)



- (a) R is steam volatile
 (b) Q gives dark violet colouration with 1% aqueous FeCl₃ solution
 (c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine
 (d) S gives dark violet colouration with 1% aqueous FeCl₃ solution.

[Aldehydes and Ketones]

8. The crystalline form of borax has
 (a) tetranuclear [B₄O₅(OH)₄]²⁻ unit
 (b) all boron atoms in the same plane
 (c) equal number of sp² and sp³ hybridized boron atoms
 (d) one terminal hydroxide per boron atom.

[The p-Block Elements]

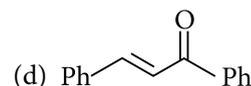
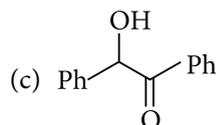
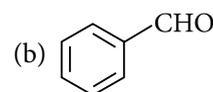
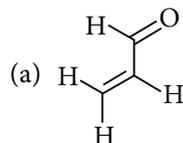
9. The reagent(s) that can selectively precipitate S²⁻ from a mixture of S²⁻ and SO₄²⁻ in aqueous solution is (are)
 (a) CuCl₂
 (b) BaCl₂
 (c) Pb(OOCCH₃)₂
 (d) Na₂[Fe(CN)₅NO]

[Analytical Chemistry]

10. A plot of the number of neutrons (N) against the number of protons (P) of stable nuclei exhibits upward deviation from linearity for atomic number, Z > 20. For an unstable nucleus having N/P ratio less than 1, the possible mode(s) of decay is(are)
 (a) β⁻-decay (β emission)
 (b) orbital or K-electron capture
 (c) neutron emission
 (d) β⁺-decay (positron emission).

[Nuclear Chemistry]

11. Positive Tollens' test is observed for



[Aldehydes and Ketones]

12. The compound(s) with two lone pairs of electrons on the central atom is(are)

- (a) BrF₅ (b) ClF₃
 (c) XeF₄ (d) SF₄

[Chemical Bonding]

13. According to the Arrhenius equation,

- (a) a high activation energy usually implies a fast reaction
 (b) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy
 (c) higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant
 (d) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

[Chemical Kinetics]

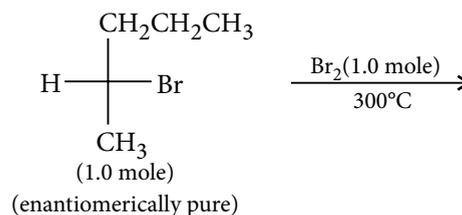
SECTION 3 (Maximum Marks : 15)

- This section contains FIVE questions.
- The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive.
- For each question, darken the bubble corresponding to the correct integer in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks : +3 If only the bubble corresponding to the correct answer is darkened.

Zero Marks : 0 In all other cases.

14. In the following monobromination reaction, the number of possible chiral products is



[General Organic Chemistry]

15. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm^{-3} . The ratio of the molecular weights of the solute and solvent, $\left(\frac{MW_{\text{solute}}}{MW_{\text{solvent}}}\right)$, is

[Solutions and Colligative Properties]

16. The number of geometric isomers possible for the complex $[\text{CoL}_2\text{Cl}_2]^-$ ($L = \text{H}_2\text{NCH}_2\text{CH}_2\text{O}^-$) is

[Coordination Compounds]

17. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. The magnitude of X is

[The Transition Elements]

18. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The value of x is

[Gaseous and Liquid States]

PAPER - 2

SECTION 1 (Maximum Marks : 18)

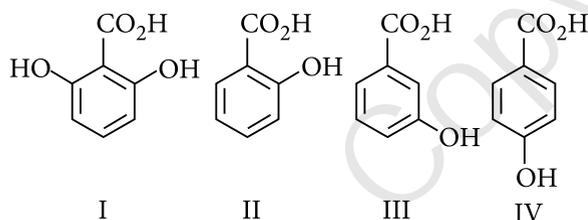
- This section contains SIX questions.
- Each question has FOUR options (a), (b), (c) and (d). ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks : +3 If only the bubble corresponding to the correct option is darkened.

Zero Marks : 0 If none of the bubbles is darkened.

Negative Marks : -1 In all other cases.

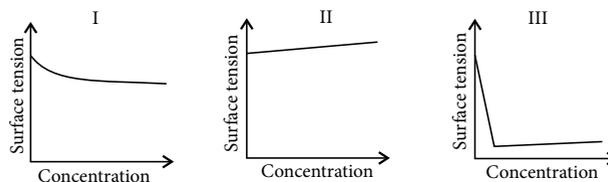
1. The correct order of acidity for the following compounds is



- (a) I > II > III > IV (b) III > I > II > IV
 (c) III > IV > II > I (d) I > III > IV > II

[Carboxylic Acids and Their Derivatives]

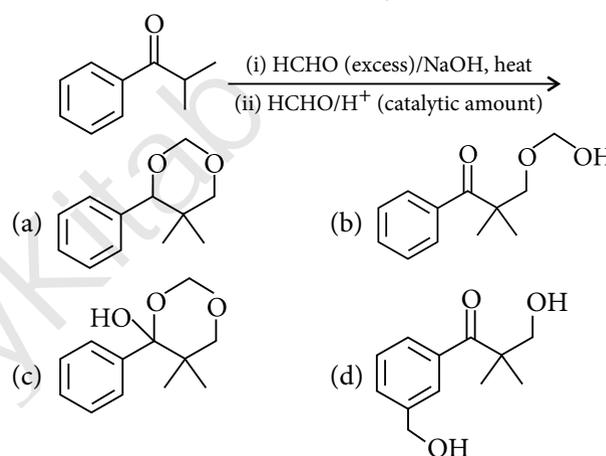
4. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions KCl, CH_3OH and $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$ at room temperature. The correct assignment of the sketches is



- (a) I : KCl II : CH_3OH III : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$
 (b) I : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$ II : CH_3OH III : KCl
 (c) I : KCl II : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$ III : CH_3OH
 (d) I : CH_3OH II : KCl III : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$

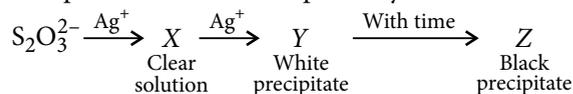
[Gaseous and Liquid States]

2. The major product of the following reaction sequence is



[Aldehydes and Ketones]

3. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively,



- (a) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$, $\text{Ag}_2\text{S}_2\text{O}_3$, Ag_2S
 (b) $[\text{Ag}(\text{S}_2\text{O}_3)_3]^{5-}$, Ag_2SO_3 , Ag_2S
 (c) $[\text{Ag}(\text{SO}_3)_2]^{3-}$, $\text{Ag}_2\text{S}_2\text{O}_3$, Ag
 (d) $[\text{Ag}(\text{SO}_3)_3]^{3-}$, Ag_2SO_4 , Ag

[Analytical Chemistry]

5. The geometries of the ammonia complexes of Ni^{2+} , Pt^{2+} and Zn^{2+} , respectively, are
- octahedral, square planar and tetrahedral
 - square planar, octahedral and tetrahedral
 - tetrahedral, square planar and octahedral
 - octahedral, tetrahedral and square planar.

[Coordination Compounds]

6. For the following electrochemical cell at 298 K,
 $\text{Pt}_{(s)}|\text{H}_{2(g)}(1\text{ bar})|\text{H}^+_{(aq)}(1\text{ M})||\text{M}^{4+}_{(aq)}, \text{M}^{2+}_{(aq)}|\text{Pt}_{(s)}$

$$E_{\text{cell}} = 0.092\text{ V when } \frac{[\text{M}^{2+}_{(aq)}]}{[\text{M}^{4+}_{(aq)}]} = 10^x$$

$$\text{Given : } E^\circ_{\text{M}^{4+}/\text{M}^{2+}} = 0.151\text{ V; } 2.303 \frac{RT}{F} = 0.059\text{ V}$$

The value of x is

- 2
- 1
- 1
- 2

[Redox Reactions and Electrochemistry]**SECTION 2 (Maximum Marks : 32)**

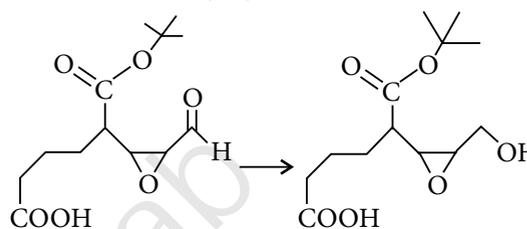
- This section contains EIGHT questions.
 - Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct.
 - For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.
 - For each question, marks will be awarded in one of the following categories :
 Full Marks : +4 If only the bubble(s) corresponding to all the correct option(s) is(are) darkened.
 Partial Marks : +1 For darkening a bubble corresponding to each correct option, provided NO incorrect option is darkened.
 Zero Marks : 0 If none of the bubbles is darkened.
 Negative Marks : -2 In all other cases.
 - For example, if (a), (c) and (d) are all the correct options for a question, darkening all these three will result in +4 marks; darkening only (a) and (d) will result in +2 marks; and darkening (a) and (b) will result in -2 marks, as a wrong option is also darkened.
7. According to molecular orbital theory,
- C_2^{2-} is expected to be diamagnetic
 - O_2^{2+} is expected to have a longer bond length than O_2
 - N_2^+ and N_2^- have the same bond order
 - He_2^+ has the same energy as two isolated He atoms.

[Chemical Bonding]

8. The correct statement(s) for cubic close packed (ccp) three dimensional structure is(are)
- the number of the nearest neighbours of an atom present in the topmost layer is 12
 - the efficiency of atom packing is 74%
 - the number of octahedral and tetrahedral voids per atom are 1 and 2, respectively
 - the unit cell edge length is $2\sqrt{2}$ times the radius of the atom.

[Solid State]

9. Reagent(s) which can be used to bring about the following transformation is(are)



- LiAlH_4 in $(\text{C}_2\text{H}_5)_2\text{O}$
- BH_3 in THF
- NaBH_4 in $\text{C}_2\text{H}_5\text{OH}$
- Raney Ni/ H_2 in THF.

[Aldehydes and Ketones]

10. Extraction of copper from copper pyrite (CuFeS_2) involves
- crushing followed by concentration of the ore by froth-floatation
 - removal of iron as slag
 - self-reduction step to produce 'blister copper' following evolution of SO_2
 - refining of 'blister copper' by carbon reduction.
11. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10}
- can also be prepared by reaction of P_4 and HNO_3
 - is diamagnetic
 - contains one N—N bond
 - reacts with Na metal producing brown gas.

[Metallurgy]**[The p-Block Elements]**

12. Mixture(s) showing positive deviation from Raoult's law at 35°C is(are)
- carbon tetrachloride + methanol
 - carbon disulphide + acetone
 - benzene + toluene
 - phenol + aniline.

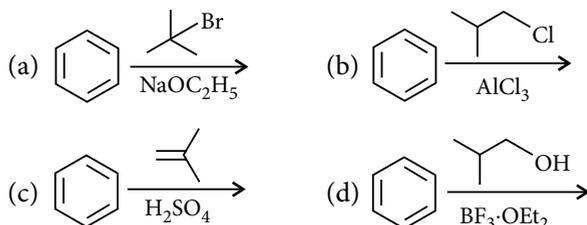
[Solutions and Colligative Properties]

13. For 'invert sugar', the correct statement(s) is(are)
 (Given : specific rotations of (+)-sucrose, (+)-maltose, L-(-)-glucose and L-(+)-fructose in aqueous solution are $+66^\circ$, $+140^\circ$, -52° and $+92^\circ$, respectively)

- (a) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose
 (b) 'invert sugar' is an equimolar mixture of *D*-(+)-glucose and *D*-(-)-fructose
 (c) specific rotation of 'invert sugar' is -20°
 (d) on reaction with Br_2 water, 'invert sugar' forms saccharic acid as one of the products

[Biomolecules and Chemistry in Everyday Life]

14. Among the following, reaction(s) which gives(give) *tert*-butyl benzene as the major product is(are)



[Hydrocarbons]

SECTION 3 (Maximum Marks : 12)

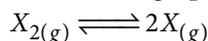
- This section contains TWO paragraphs.
- Based on each paragraph, there are Two questions.
- Each question has FOUR options (a), (b), (c) and (d). ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks : +3 If only the bubble corresponding to the correct option is darkened.

Zero Marks : 0 In all other cases.

PARAGRAPH 1

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation :



The standard reaction Gibbs energy, $\Delta_r G^\circ$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X . As the reaction proceeds, the number of moles of X formed is given by β . Thus, $\beta_{\text{equilibrium}}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given : $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$)

15. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{\text{equilibrium}}$, is

- (a) $\frac{8\beta_{\text{equilibrium}}^2}{2 - \beta_{\text{equilibrium}}}$ (b) $\frac{8\beta_{\text{equilibrium}}^2}{4 - \beta_{\text{equilibrium}}^2}$
- (c) $\frac{4\beta_{\text{equilibrium}}^2}{2 - \beta_{\text{equilibrium}}}$ (d) $\frac{4\beta_{\text{equilibrium}}^2}{4 - \beta_{\text{equilibrium}}^2}$

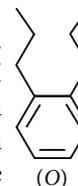
16. The incorrect statement among the following, for this reaction, is

- (a) decrease in the total pressure will result in formation of more moles of gaseous X
 (b) at the start of the reaction, dissociation of gaseous X_2 takes place spontaneously
 (c) $\beta_{\text{equilibrium}} = 0.7$
 (d) $K_c < 1$

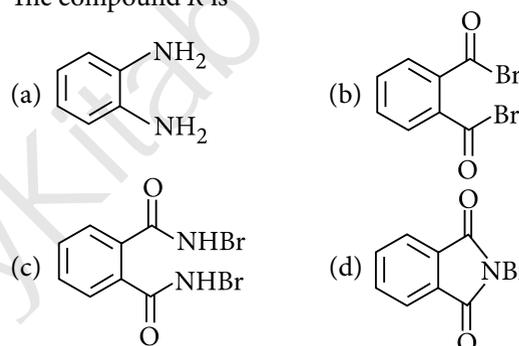
[Equilibrium]

PARAGRAPH 2

Treatment of compound *O* with KMnO_4/H^+ gave *P*, which on heating with ammonia gave *Q*. The compound *Q* on treatment with Br_2/NaOH produced *R*. On strong heating, *Q* gave *S*, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound *T*.



17. The compound *R* is



18. The compound *T* is

- (a) glycine (b) alanine
 (c) valine (d) serine.

[Compounds Containing Nitrogen]

SOLUTIONS

PAPER-1

1. (c) : Probability of finding 1s electron is maximum near the nucleus and goes on increasing till it reaches a maximum value at a distance 52.9 pm and then begins to decrease abruptly. Even at large distance from the nucleus, there is a finite though small probability of finding an electron of a given energy.

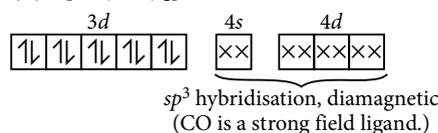
2. (c) : For isothermal expansion, $\Delta U = 0$
 As pressure is constant therefore, process is irreversible.

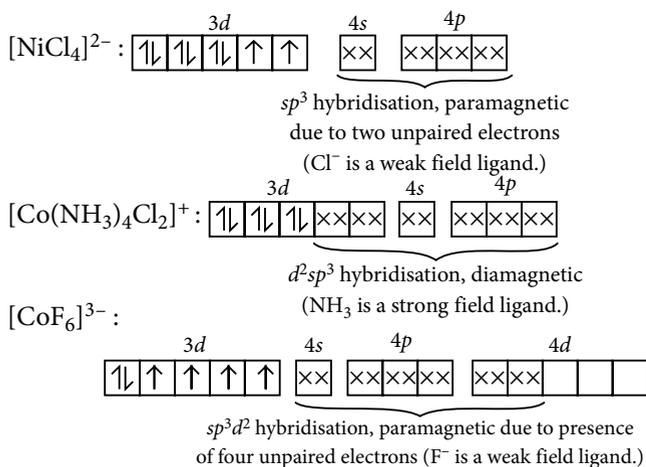
$$\Rightarrow q_{\text{irrev}} = -w_{\text{irrev}}$$

$$= -(-P\Delta V) = -[-3(2 - 1)] = 3 \text{ L atm} = 3 \times 101.3 \text{ J}$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irrev}}}{T} = -\frac{3 \times 101.3 \text{ J}}{300 \text{ K}} = -1.013 \text{ J K}^{-1}$$

3. (b) : $[\text{Ni}(\text{CO})_4]$:



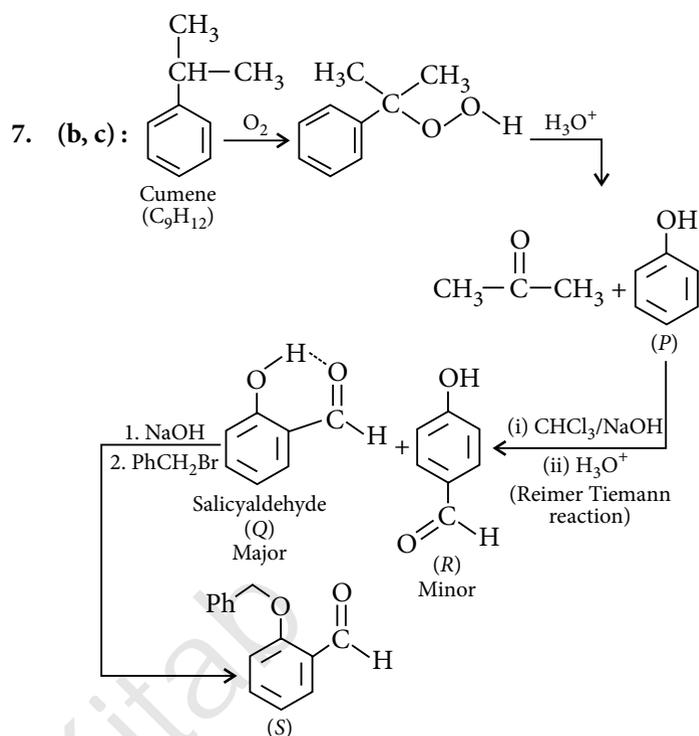
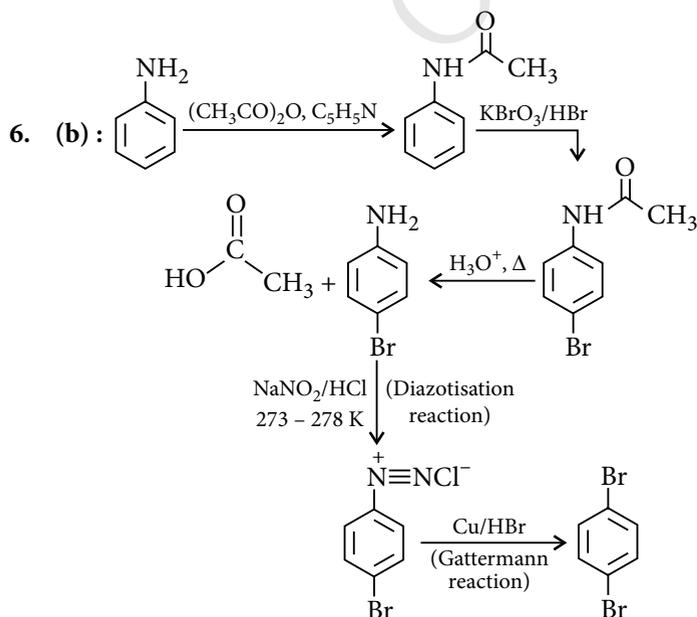
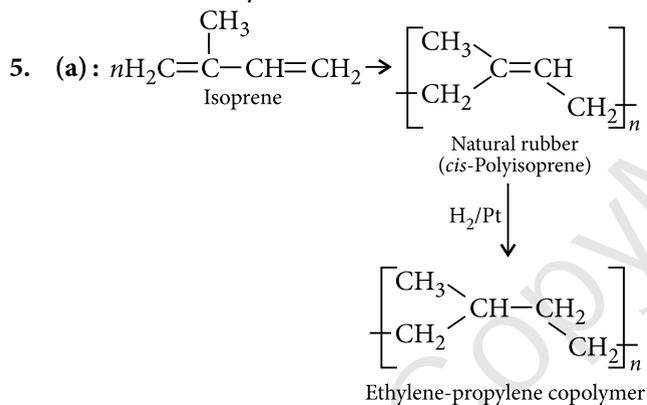


Na_2O_2 ; O_2^{2-} (peroxide ion) is diamagnetic.

CsO_2 ; O_2^- (superoxide ion) is paramagnetic.

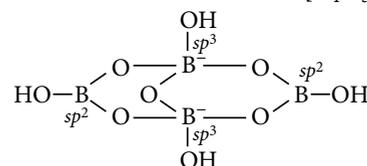
4. (b): The increasing order of atomic radii of group 13 elements is Ga < Al < In < Tl.

Atomic radius of Ga is slightly lower than that of Al due to the presence of *d*-electrons in Ga which do not shield the nucleus effectively.



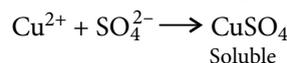
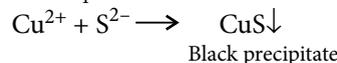
'Q' is steam volatile due to intramolecular hydrogen bonding while 'R' undergoes intermolecular hydrogen bonding hence, has higher boiling point. 'Q' gives dark violet colouration with 1% aqueous FeCl_3 solution due to the presence of phenolic group while 'S' gives yellow precipitate with 2, 4-dinitrophenyl hydrazine due to the presence of aldehydic group ($-\text{CHO}$).

8. (a, c, d): The formula of borax is $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ which contains the tetranuclear unit $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$.

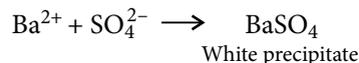
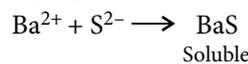


Only two B atoms lie in the same plane as two B atoms are sp^2 hybridized and other two B atoms are sp^3 hybridized.

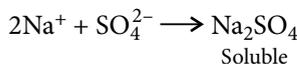
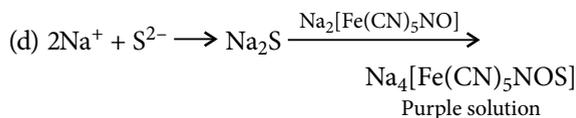
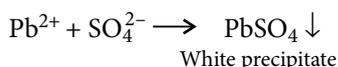
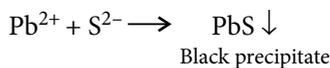
9. (a): (a) Cu^{2+} will give black precipitate of CuS while CuSO_4 is soluble.



(b) Ba^{2+} will give white precipitate of BaSO_4 while BaS is soluble.



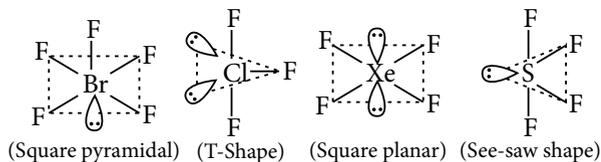
(c) Pb^{2+} will give precipitate with both S^{2-} and SO_4^{2-} .



10. (b, d) : Nuclides with $Z > 20$ lying below the stability belt decay by β^+ (positron) emission or K -electron capture so, that N/P ratio increases to $(N + 1)/(Z - 1)$.

11. (a, b, c) : Aldehydes and α -hydroxyketones reduce Tollens' reagent.

12. (b, c) :



13. (b, c, d) : According to Arrhenius equation, $k = Ae^{-E_a/RT}$

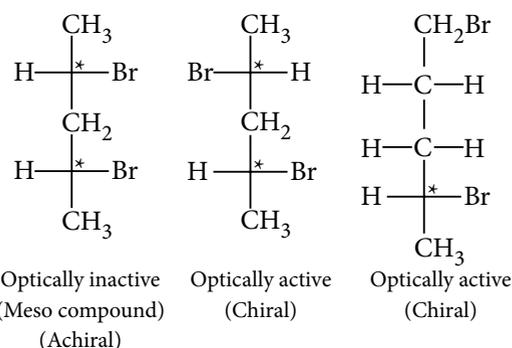
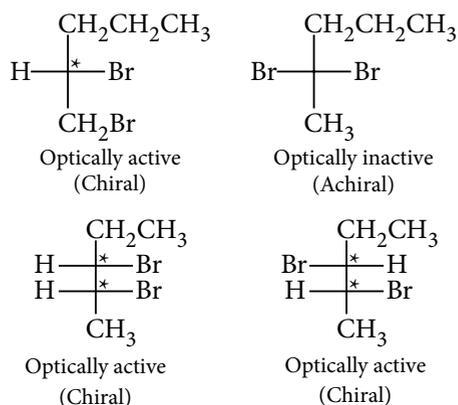
(a) Higher activation energy means slower reaction or lower value of k .

(b) On increasing the temperature rate constant increases due to increase in the number of effective collisions (*i.e.*, collisions whose energy exceeds the activation energy).

(c) High activation energies have a stronger temperature dependence than those with low activation energies.

(d) Pre-exponential factor A is called frequency factor as it gives the frequency of binary collisions of the reacting molecules per second per litre. Thus, the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

14. (5) : Total five products are formed.



$$15. (9) : \text{Molality } (m) = \frac{x_2 \times 1000}{x_1 \times M_1} = \frac{0.1 \times 1000}{0.9 \times M_1} = \frac{1000}{9M_1}$$

$$\Rightarrow M_1 = \frac{1000}{9m} \quad \dots (i)$$

$$\text{Also, } m = \frac{1000M}{1000d - M_2 \times M} \Rightarrow \frac{m}{M} = \frac{1000}{1000 \times 2 - M_2 \times M}$$

$$\Rightarrow 1 = \frac{1000}{2000 - M_2 \times M} \quad [\because m = M \text{ given}]$$

$$\Rightarrow M \times M_2 = 1000$$

$$\Rightarrow M_2 = \frac{1000}{M} \quad \dots (ii)$$

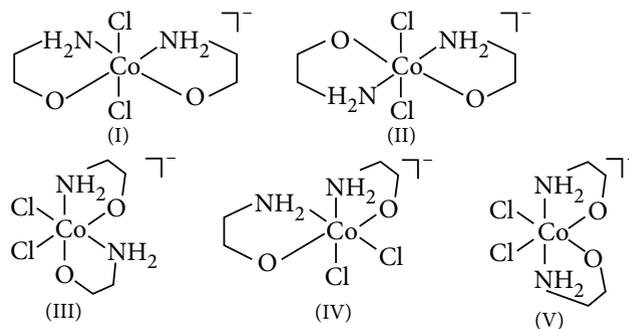
On dividing equation (ii) by (i), we get

$$\frac{M_2}{M_1} = \frac{1000}{M} \times \frac{9m}{1000}$$

$$\Rightarrow \frac{M_2}{M_1} = 9 \quad [\because m = M]$$

$$\text{or } \frac{M_{\text{solute}}}{M_{\text{solvent}}} = 9$$

16. (5) : Total five isomers are possible :



17. (6) : In neutral or faintly alkaline solution, thiosulphate is oxidized to sulphate by permanganate,
 $8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \longrightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$

18. (4) : Diffusion coefficient $\propto \lambda C_{\text{mean}}$

$$\lambda \propto \frac{T}{P} \text{ and } C_{\text{mean}} \propto \sqrt{T}$$

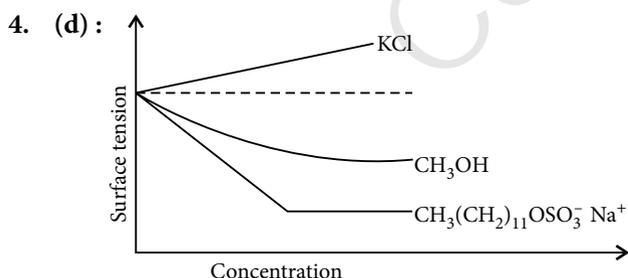
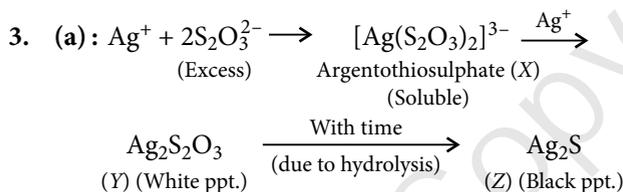
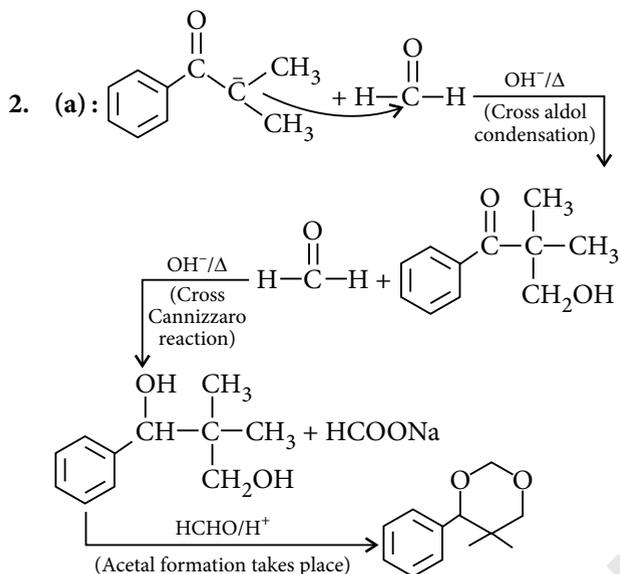
$$\text{Diffusion coefficient} \propto \frac{T}{P} \sqrt{T}$$

$$\text{Diffusion coefficient} \propto \frac{T^{3/2}}{P}$$

If T is increased four times and pressure is increased two times diffusion coefficient will become 4 times.

PAPER-2

1. (a): Due to *ortho*-effect, (I) and (II) are stronger acid than (III) and (IV). Due to two *ortho* hydroxyl groups in (I), it is stronger acid than (II). (III) is a stronger acid than (IV) because at *m*-position, $-OH$ group cannot exert its $+R$ effect but can only exert its $-I$ effect while at *p*-position, $-OH$ group exerts its strong $+R$ effect. Thus, the correct order of acidity is : $I > II > III > IV$



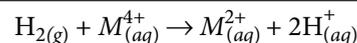
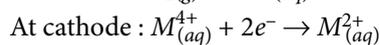
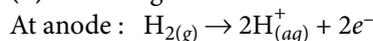
For KCl curve — Increase of surface tension for inorganic salts.

For CH_3OH curve — Decrease of surface tension progressively for alcohols.

For $CH_3(CH_2)_{11}OSO_3^- Na^+$ curve — Decrease of surface tension before CMC (Critical Micelle Concentration) and then almost unchanged.

5. (a): $[Ni(NH_3)_6]^{2+}$: sp^3d^2 hybridisation, octahedral
 $[Pt(NH_3)_4]^{2+}$: dsp^2 hybridisation, square planar
 $[Zn(NH_3)_4]^{2+}$: sp^3 hybridisation, tetrahedral

6. (d): For the given electrochemical cell, the reactions are



$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{[M^{2+}][H^+]^2}{[M^{4+}]}$$

$$0.092 = \left(E_{M^{4+}/M^{2+}}^\circ - E_{H^+/H_2}^\circ \right) - \frac{0.059}{2} \log(10^x [H^+]^2)$$

$$0.092 = (0.151 - 0) - \frac{0.059}{2} \log(10^x \times 1^2)$$

$$0.092 = 0.151 - 0.0295 \log 10^x$$

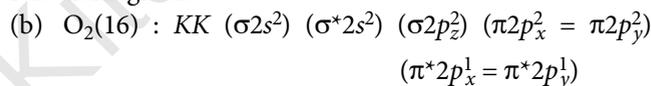
$$0.0295 \log 10^x = 0.151 - 0.092$$

$$\log 10^x = \frac{0.059}{0.0295} = 2$$

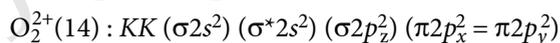
$$10^x = \text{Antilog } 2 = 10^2$$

$$\therefore x = 2$$

7. (a, c): (a) $C_2^-(14)$: $KK(\sigma 2s^2)(\sigma^* 2s^2)(\pi 2p_x^2 = \pi 2p_y^2)\sigma 2p_z^2$
 It is diamagnetic.

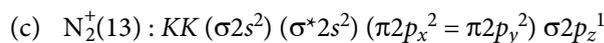


$$B.O. = \frac{1}{2}(8 - 4) = \frac{4}{2} = 2$$

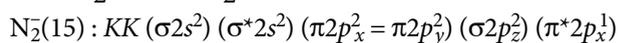


$$B.O. = \frac{1}{2}(8 - 2) = \frac{6}{2} = 3$$

As bond order of O_2^{2+} is greater than that of O_2 so, O_2^{2+} is expected to have a shorter bond length than O_2 .



$$B.O. = \frac{1}{2}(7 - 2) = \frac{5}{2} = 2.5$$



$$B.O. = \frac{1}{2}(8 - 3) = \frac{5}{2} = 2.5$$

Thus, N_2^+ and N_2^- have the same bond order.

(d) He_2^+ has lesser energy than two isolated He atoms as some energy is released during formation of He_2^+ .

8. (b,c,d): (a) The number of the nearest neighbours of an atom present in the topmost layer is 9 as a sphere is in contact with 6 other spheres in its own layer and it also touches directly 3 spheres in the layer below.

(b) For *ccp*, packing fraction = 74%.

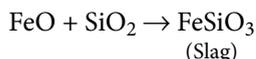
(c) In *ccp*, there are two tetrahedral voids per sphere and one octahedral void per sphere.

(d) For *ccp*, $a = \frac{4}{\sqrt{2}}r = 2\sqrt{2}r$

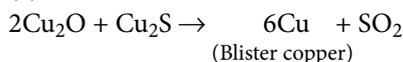
9. (c) : NaBH_4 in $\text{C}_2\text{H}_5\text{OH}$ reduces specifically aldehyde to alcohol and do not reduce acid, ester and epoxide.

10. (a, b, c) : (a) In the extraction of copper from copper pyrite (CuFeS_2), after crushing, concentration of ore is done by froth floatation process.

(b) Iron is removed as slag.



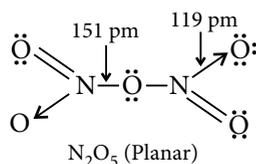
(c) Auto-reduction :



(d) Blister copper is finally purified by electrolytic refining.

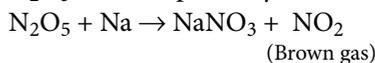
11. (b, d) : $\text{P}_4\text{O}_{10} + 4\text{HNO}_3 \rightarrow 2\text{N}_2\text{O}_5 + 4\text{HPO}_3$

N_2O_5 cannot be obtained by reaction of P_4 and HNO_3 .



Hence, it is diamagnetic and does not have N-N bond.

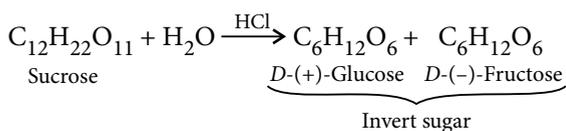
N_2O_5 is decomposed by alkali metals.



12. (a, b) : $\text{CCl}_4 + \text{CH}_3\text{OH}$ and $\text{CS}_2 + (\text{CH}_3)_2\text{CO}$

(A-B interactions are weaker than A-A and B-B interactions) shows positive deviation from Raoult's law. Benzene + toluene forms an ideal solution. Phenol + aniline (A-B interactions are stronger than A-A and B-B interactions) shows negative deviation from Raoult's law.

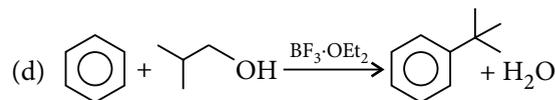
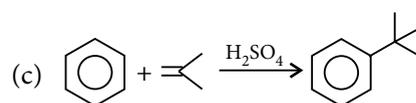
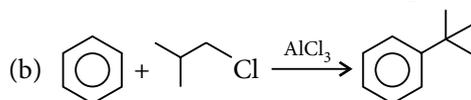
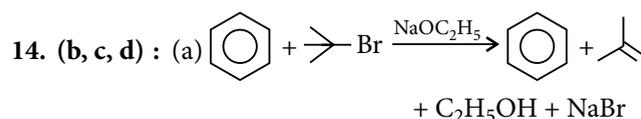
13. (b, c) : Invert sugar is prepared by acid catalyzed hydrolysis of sucrose.



Specific rotation of invert sugar is

$$[\alpha]_{\text{mix}} = 0.5 \times (+52) + 0.5 \times (-92) = +26 - 46 = -20^\circ$$

On reaction with Br_2 water, invert sugar forms gluconic acid as one of the products. Br_2 water oxidises glucose into gluconic acid and fructose is not oxidised by it.



15. (b) : $X_{2(g)} \rightleftharpoons 2X_{(g)}$

At $t = 0$, $\frac{1}{1} \rightleftharpoons \frac{0}{0}$

At eq. $1 - \frac{\beta_{eq}}{2} \rightleftharpoons \beta_{eq}$

$$K_p = \frac{(p_X)^2}{(p_{X_2})}$$

$$p_X = \left(\frac{\beta_{eq}}{1 - \frac{\beta_{eq}}{2} + \beta_{eq}} \right) P_{\text{total}} = \left(\frac{\beta_{eq}}{1 + \frac{\beta_{eq}}{2}} \right) P_{\text{total}}$$

$$p_{X_2} = \left(\frac{1 - \frac{\beta_{eq}}{2}}{1 + \frac{\beta_{eq}}{2}} \right) P_{\text{total}}$$

$$K_p = \frac{\left[\left(\frac{\beta_{eq}}{1 + \frac{\beta_{eq}}{2}} \right) P_{\text{total}} \right]^2}{\left(\frac{1 - \frac{\beta_{eq}}{2}}{1 + \frac{\beta_{eq}}{2}} \right) P_{\text{total}}} = \left(\frac{\beta_{eq}^2}{1 - \frac{\beta_{eq}^2}{4}} \right) P_{\text{total}}$$

$$= \left(\frac{4\beta_{eq}^2}{4 - \beta_{eq}^2} \right) P_{\text{total}} = \left(\frac{4\beta_{eq}^2}{4 - \beta_{eq}^2} \right) \times 2 = \frac{8\beta_{eq}^2}{4 - \beta_{eq}^2}$$

16. (c) : (a) If the pressure on the system is decreased, the equilibrium will shift in the direction in which pressure increases *i.e.*, increase in no. of moles takes place *i.e.*, in forward direction.

(b) At the start of the reaction, $Q < K$ thus, the reaction will proceed in the forward direction *i.e.*, reaction is spontaneous.

(c) If $\beta_{eq} = 0.7$ then, $K_p = \frac{8 \times (0.7)^2}{4 - (0.7)^2} > 1$

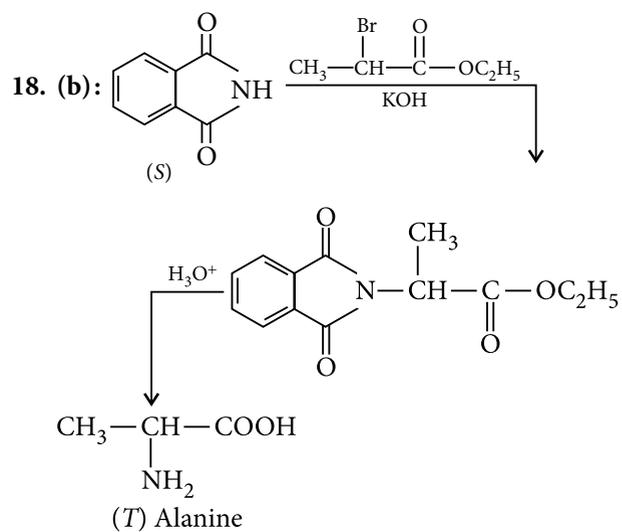
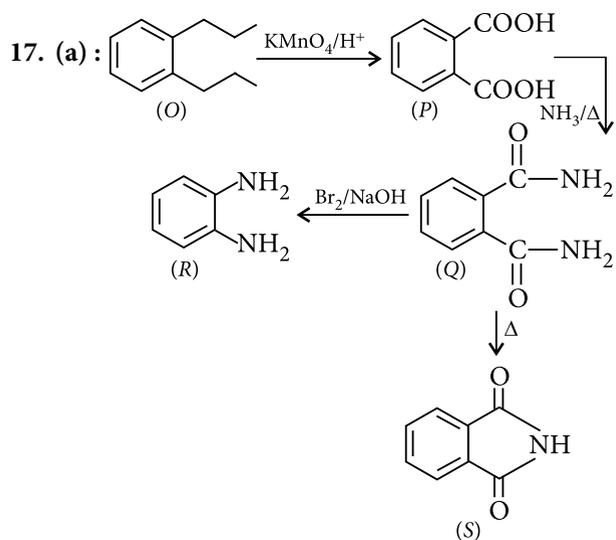
$\Delta G^\circ = -RT \ln K_p$ so, $\Delta G^\circ = -ve$ but given $\Delta G^\circ = +ve$ so, K_p should be less than 1 hence, $\beta_{eq} \neq 0.7$.

(d) $K_p = K_c (RT)^{\Delta n}$

$K_c < K_p$

($\because RT > 1$)

If $K_p < 1$ then $K_c < 1$



SOLVED PAPER

JEE Advanced 2017

PAPER - 1

SECTION 1 (Maximum Marks : 28)

- This section contains SEVEN questions.
- Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four options is (are) correct.
- For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks : +4 If only the bubble(s) corresponding to all the correct option(s) is(are) darkened.

Partial Marks : +1 For darkening a bubble corresponding to each correct option, provided NO incorrect option is darkened.

Zero Mark : 0 If none of the bubbles is darkened.

Negative Marks : -2 In all other cases.

- For example, if (a), (c), and (d) are all the correct options for a question, darkening all these three will get +4 marks; darkening only (a) and (d) will get +2 marks; and darkening (a) and (b) will get -2 marks, as a wrong option is also darkened.

1. The colour of the X_2 molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to
 - (a) the physical state of X_2 at room temperature changes from gas to solid down the group
 - (b) decrease in HOMO-LUMO gap down the group
 - (c) decrease in $\pi^*-\sigma^*$ gap down the group
 - (d) decrease in ionization energy down the group.

[The p-Block Elements]

2. Addition of excess aqueous ammonia to a pink coloured aqueous solution of $MCl_2 \cdot 6H_2O$ (X) and NH_4Cl gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1:3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. Among the following options, which statement(s) is(are) correct?

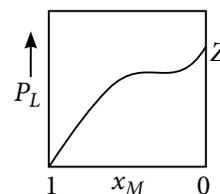
- (a) The hybridization of the central metal ion in Y is d^2sp^3 .
- (b) When X and Z are in equilibrium at $0^\circ C$, the colour of the solution is pink.
- (c) Z is a tetrahedral complex.
- (d) Addition of silver nitrate to Y gives only two equivalents of silver chloride.

[The Transition Elements]

3. An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is(are)
 - (a) if the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic.
 - (b) the work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions
 - (c) the work done on the gas is maximum when it is compressed irreversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1
 - (d) the change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$.

[Chemical Energetics]

4. For a solution formed by mixing liquids L and M, the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure. Here x_L and x_M represent mole fractions of L and M, respectively, in the solution. The correct statement(s) applicable to this system is(are)

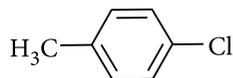


- (a) attractive intermolecular interactions between L-L in pure liquid L and M-M in pure liquid M are stronger than those between L-M when mixed in solution
- (b) the point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \rightarrow 0$

- (c) the point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from $x_L = 0$ to $x_L = 1$
 (d) the point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \rightarrow 1$

[Solutions and Colligative Properties]

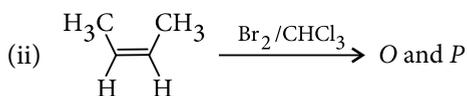
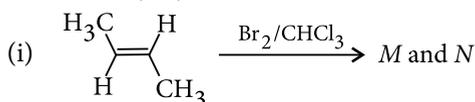
5. The IUPAC name(s) of the following compound is(are)



- (a) 1-chloro-4-methylbenzene
 (b) 4-chlorotoluene
 (c) 1-methyl-4-chlorobenzene
 (d) 4-methylchlorobenzene.

[Halogen Derivatives]

6. The correct statement(s) for the following addition reactions is(are)



- (a) O and P are identical molecules
 (b) bromination proceeds through *trans*-addition in both the reactions
 (c) (M and O) and (N and P) are two pairs of enantiomers
 (d) (M and O) and (N and P) are two pairs of diastereomers.

[Hydrocarbons]

7. The correct statement(s) about the oxoacids, HClO_4 and HClO , is(are)
 (a) the conjugate base of HClO_4 is weaker base than H_2O
 (b) the central atom in both HClO_4 and HClO is sp^3 hybridized
 (c) HClO_4 is formed in the reaction between Cl_2 and H_2O
 (d) HClO_4 is more acidic than HClO because of the resonance stabilization of its anion.

[The p-Block Elements]**SECTION 2 (MAXIMUM MARKS : 15)**

- This section contains FIVE questions.
- The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive.
- For each question, darken the bubble corresponding the correct integer in the ORS.
- For each question, marks will be awarded in one of the following categories :
 Full Marks : +3 If only the bubble corresponding to the correct answer is darkened.
 Zero Marks : 0 In all other cases.

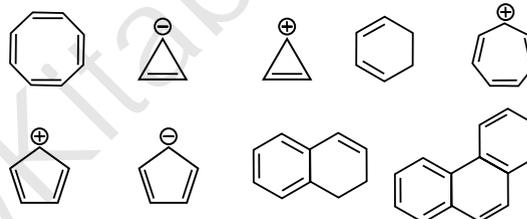
8. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm^2 . The conductance of this solution was found to be $5 \times 10^{-7} \text{ S}$. The pH of the solution is 4. The value of limiting molar conductivity (Λ_m^0) of this weak monobasic acid in aqueous solution is $Z \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$. The value of Z is

[Redox Reactions and Electrochemistry]

9. The sum of the number of lone pairs of electrons on each central atom in the following species is $[\text{TeBr}_6]^{2-}$, $[\text{BrF}_2]^+$, SNF_3 , and $[\text{XeF}_3]^-$
 (Atomic numbers: N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54)

[Chemical Bonding]

10. Among the following, the number of aromatic compound(s) is

**[Hydrocarbons]**

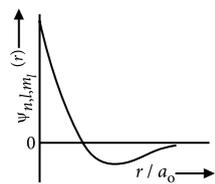
11. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm^{-3} , then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value of N is
12. Among H_2 , He_2^+ , Li_2 , Be_2 , B_2 , C_2 , N_2 , O_2^- , and F_2 the number of diamagnetic species is (Atomic numbers: H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, F = 9)

[Solid State]**[Chemical Bonding]****SECTION 3 (MAXIMUM MARKS : 18)**

- This section contains SIX questions of matching type.
- This section contains TWO tables (each having 3 columns and 4 rows)
- Based on each table, there are THREE questions
- Each question has FOUR options (a), (b), (c) and (d). ONLY ONE of these four options is correct
- For each question, darken the bubble corresponding to the correct option in the ORS
- For each question, marks will be awarded in one of the following categories :
 Full Marks : +3 If only the bubble corresponding to the correct option is darkened.
 Zero Marks : 0 If none of the bubbles is darkened
 Negative Marks : -1 In all other cases.

Answer Q. 13, Q. 14 and Q. 15 by appropriately matching the information given in the three columns of the following table.

The wave function, Ψ_{n,l,m_l} is a mathematical function whose value depends upon spherical polar coordinates (r, θ, ϕ) of the electron and characterized by the quantum numbers n, l and m_l . Here r is distance from nucleus, θ is colatitude and ϕ is azimuth. In the mathematical functions given in the table, Z is atomic number and a_0 is Bohr radius.

Column 1	Column 2	Column 3
(I) 1s orbital	(i) $\Psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$	(P) 
(II) 2s orbital	(ii) One radial node	(Q) Probability density at nucleus $\propto \frac{1}{a_0^3}$
(III) 2p _z orbital	(iii) $\Psi_{n,l,m_l} \propto \left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r e^{-\left(\frac{Zr}{2a_0}\right)} \cos\theta$	(R) Probability density is maximum at nucleus
(IV) 3d _{z²} orbital	(iv) xy - plane is a nodal plane	(S) Energy needed to excite electron from $n = 2$ state to $n = 4$ state is $\frac{27}{32}$ times the energy needed to excite electron from $n = 2$ state to $n = 6$ state

13. For He⁺ ion, the only incorrect combination is

- (a) (I) (i) (R)
- (b) (II) (ii) (Q)
- (c) (I) (i) (S)
- (d) (I) (iii) (R)

14. For the given orbital in Column 1, the only correct combination for any hydrogen-like species is

- (a) (I) (ii) (S)
- (b) (IV) (iv) (R)
- (c) (III) (iii) (P)
- (d) (II) (ii) (P)

15. For hydrogen atom, the only correct combination is

- (a) (II) (i) (Q)
- (b) (I) (iv) (R)
- (c) (I) (i) (P)
- (d) (I) (i) (S)

[Atomic Structure]

Answer Q. 16, Q. 17 and Q. 18 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2, and 3 contain starting materials, reaction conditions, and type of reactions, respectively.

Column 1	Column 2	Column 3
(I) Toluene	(i) NaOH/ Br ₂	(P) Condensation
(II) Acetophenone	(ii) Br ₂ /hν	(Q) Carboxylation
(III) Benzaldehyde	(iii) (CH ₃ CO) ₂ O/ CH ₃ COOK	(R) Substitution
(IV) Phenol	(iv) NaOH/ CO ₂	(S) Haloform

16. The only correct combination in which the reaction proceeds through radical mechanism is

- (a) (II) (iii) (R)
- (b) (III) (ii) (P)
- (c) (IV) (i) (Q)
- (d) (I) (ii) (R)

17. For the synthesis of benzoic acid, the only correct combination is

- (a) (III) (iv) (R)
- (b) (IV) (ii) (P)
- (c) (II) (i) (S)
- (d) (I) (iv) (Q)

18. The only correct combination that gives two different carboxylic acids is

- (a) (IV) (iii) (Q)
- (b) (I) (i) (S)
- (c) (III) (iii) (P)
- (d) (II) (iv) (R)

[Carboxylic Acids and Their Derivatives]

SECTION 2 (MAXIMUM MARKS : 28)

- This section contains SEVEN questions.
- Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct.
- For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks : +4 If only the bubble(s) corresponding to all the correct option(s) is(are) darkened.

Partial Marks : +1 For darkening a bubble corresponding to each correct option, provided NO incorrect option is darkened.

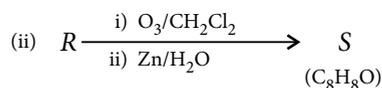
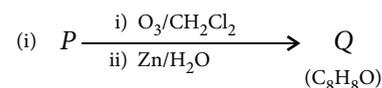
Zero Marks : 0 If none of the bubbles is darkened.
Negative Marks : -2 In all other cases.

- For example, if (a), (c), and (d) are all the correct options for a question, darkening all these three will get +4 marks; darkening only (a) and (d) will get +2 marks; and darkening (a) and (b) will get -2 marks, as a wrong option is also darkened.

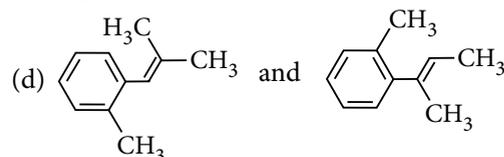
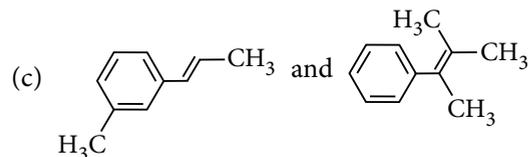
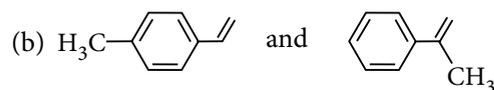
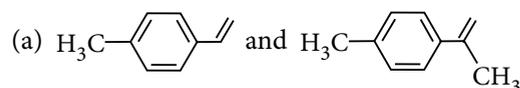
8. The correct statement(s) about surface properties is (are)
- cloud is an emulsion type of colloid in which liquid is dispersed phase and gas is dispersion medium
 - the critical temperatures of ethane and nitrogen are 563 K and 126 K, respectively. The adsorption of ethane will be more than that of nitrogen on same amount of activated charcoal at a given temperature
 - adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system
 - Brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution.

[Surface Chemistry and Colloids]

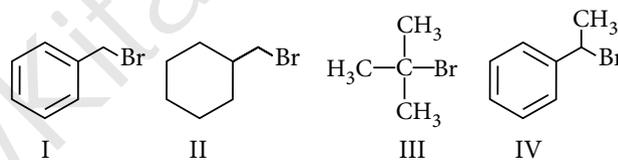
9. Compounds *P* and *R* upon ozonolysis produce *Q* and *S* respectively. The molecular formula of *Q* and *S* is C_8H_8O . *Q* undergoes Cannizzaro reaction but not haloform reaction, whereas *S* undergoes haloform reaction but not Cannizzaro reaction.



The option(s) with suitable combination of *P* and *R*, respectively, is (are)


[Aldehydes and Ketones]

10. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reactions is (are)



- I and II follow S_N2 mechanism
- compound IV undergoes inversion of configuration
- the order of reactivity for I, III, and IV is : IV > I > III
- I and III follow S_N1 mechanism.

[Halogen Derivatives]

11. In a bimolecular reaction, the steric factor *P* was experimentally determined to be 4.5. The correct option(s) among the following is(are)

- experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation
- the value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally
- the activation energy of the reaction is unaffected by the value of the steric factor
- since $P = 4.5$, the reaction will not proceed unless an effective catalyst is used.

[Chemical Kinetics]

12. The option(s) with only amphoteric oxides is(are)

- Cr_2O_3 , BeO, SnO, SnO_2
- ZnO, Al_2O_3 , PbO, PbO_2
- NO, B_2O_3 , PbO, SnO_2
- Cr_2O_3 , CrO, SnO, PbO

[Classification of Elements and Periodicity in Properties]

13. Among the following, the correct statement(s) is(are)
- $\text{Al}(\text{CH}_3)_3$ has the three-centre two-electron bonds in its dimeric structure
 - BH_3 has the three-centre two-electron bonds in its dimeric structure
 - the Lewis acidity of BCl_3 is greater than that of AlCl_3
 - AlCl_3 has the three-centre two-electron bonds in its dimeric structure.

[The p-Block Elements]

14. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by
- with increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
 - with increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases
 - with increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive
 - with increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative.

[Equilibrium]

SECTION 3 (Maximum Marks : 12)

- This section contains TWO paragraphs.
- Based on each paragraph, there are TWO questions.
- Each question has Four options (a), (b), (c) and (d). ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks : +3 If only the bubble corresponding to the correct option is darkened.

Zero Marks : 0 In all other cases.

PARAGRAPH 1

Upon heating KClO_3 in the presence of catalytic amount of MnO_2 , a gas W is formed. Excess amount of W reacts with white phosphorus to give X . The reaction of X with pure HNO_3 gives Y and Z .

15. Y and Z are, respectively
- N_2O_5 and HPO_3
 - N_2O_3 and H_3PO_4
 - N_2O_4 and H_3PO_3
 - N_2O_4 and HPO_3

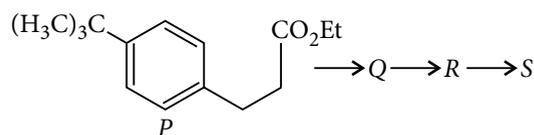
16. W and X are, respectively

- O_2 and P_4O_6
- O_2 and P_4O_{10}
- O_3 and P_4O_6
- O_3 and P_4O_{10}

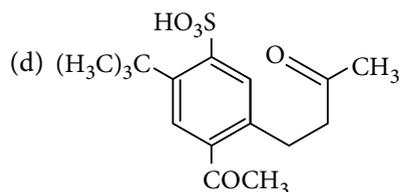
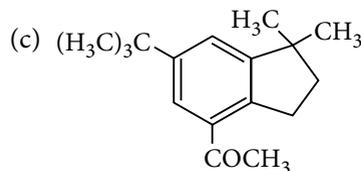
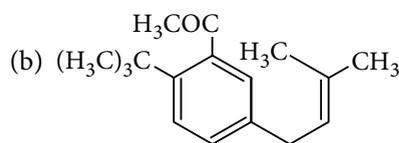
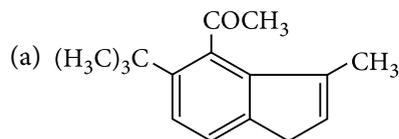
[The p-Block Elements]

PARAGRAPH 2

The reaction of compound P with CH_3MgBr (excess) in $(\text{C}_2\text{H}_5)_2\text{O}$ followed by addition of H_2O gives Q . The compound Q on treatment with H_2SO_4 at 0°C gives R . The reaction of R with CH_3COCl in the presence of anhydrous AlCl_3 in CH_2Cl_2 followed by treatment with H_2O produces compound S . [Et in compound P is ethyl group]



17. The reactions, Q to R and R to S , are
- Friedel-Crafts alkylation and Friedel-Crafts acylation
 - dehydration and Friedel-Crafts acylation
 - Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
 - aromatic sulphonation and Friedel-Crafts acylation.
18. The products S is



[Carboxylic Acids and Their Derivatives]

SOLUTIONS

PAPER-1

1. (b,c) : Energy, $E = \frac{hc}{\lambda}$

The colour of the X_2 molecule of group 17 elements changes gradually from yellow to violet down the group. This is because the amount of energy required for the excitation of the halogen atom decreases down the group from F_2 to I_2 .

HOMO(π^*)-LUMO(σ^*) gap decreases down the group that makes π^* to σ^* excitation easier. Lesser the energy gap, more is the wavelength of light absorbed and hence, lesser is the wavelength of light emitted.

2. (a,b,c) : Magnetic moment, $\mu = \sqrt{n(n+2)}$ B.M.

where, n = No. of unpaired electrons

For X and Z :

$$\sqrt{n(n+2)} = 3.87 \text{ B.M.}$$

$$n^2 + 2n - 15 = 0 \Rightarrow n^2 + 5n - 3n - 15 = 0$$

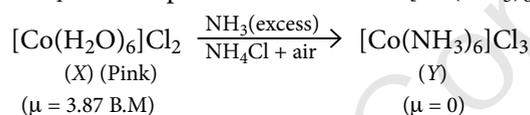
$$\therefore n = 3$$

For complex Y (1 : 3 electrolyte) :

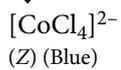
$$\sqrt{n(n+2)} = 0 \Rightarrow n = 0$$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ (X) is pink coloured compound.

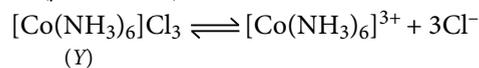
Adding excess of HCl at room temperature, changes (X) into $[\text{CoCl}_4]^{2-}$ (Z) and on adding excess of NH_3 and NH_4Cl in the presence of air forms $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (Y).



↓ HCl (excess)
room temperature



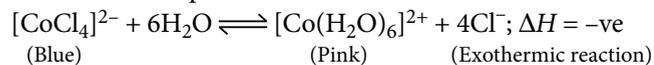
($\mu = 3.87$ B.M.)



Thus, it is a 1 : 3 electrolyte. The hybridisation of Co in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is d^2sp^3 (octahedral).

Adding of AgNO_3 to $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (Y) gives three equivalents of AgCl .

Complex Z $[\text{CoCl}_4]^{2-}$ has sp^3 hybridisation. Thus, it is a tetrahedral complex.



When ice is added to the solution (0°C), the equilibrium shifts towards right hence, pink colour will remain predominant.

3. (a,b,c) : (a) $w = -P_{\text{ext}} \Delta V$

In free expansion, external pressure = 0

$$\therefore w = 0$$

From first law of thermodynamics,

$$\Delta U = q + w$$

$$\therefore \Delta U = q$$

If the expansion is carried out isothermally,

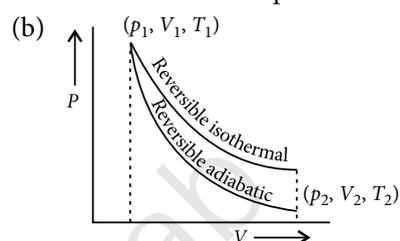
$$q = 0 \quad (\because \Delta U = 0 \text{ for isothermal process})$$

\therefore It is an adiabatic process.

If the expansion is carried out adiabatically,

$$\Delta U = 0 \quad (\because q = 0 \text{ for adiabatic process})$$

\therefore It is an isothermal process.



Thus, area under the curve in reversible adiabatic expansion is lesser than in reversible isothermal expansion.

(c) The work done on the gas is maximum during irreversible compression.

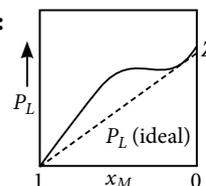
(d) Internal energy change, $\Delta U = nC_v\Delta T$

when gas is expanded reversibly with $T_1 = T_2$, $\Delta U = 0$

When gas is expanded reversibly under adiabatic condition, $T_1 > T_2$.

$$\therefore \Delta U = -ve$$

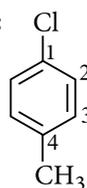
4. (a, d) :



As at point Z, the mole fraction of M is zero, then 'Z' represents the vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \rightarrow 1$.

The solution formed by mixing two liquids L and M exhibiting positive deviation from Raoult's law. Thus, intermolecular forces of attraction between L-L in pure liquid L and M-M in pure liquid M are stronger than that between L-M in the solution.

5. (a, b) :

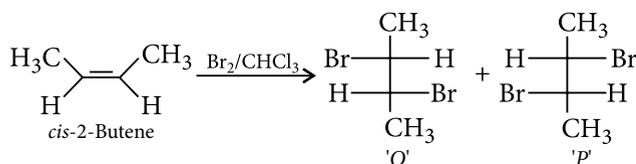
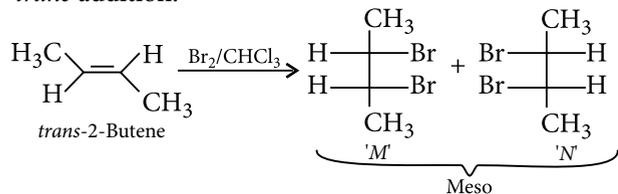


When benzene is taken as a parent chain,

IUPAC Name : 1-chloro-4-methylbenzene

When toluene is taken as a parent molecule,
IUPAC name : 4-chlorotoluene

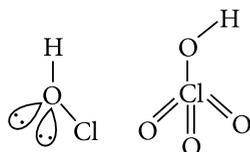
6. (b,d): Bromination of alkenes always proceeds via *trans* addition.



'O' and 'P' are enantiomers.

(M and O) and (N and P) are two pairs of diastereomers.

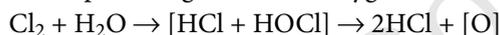
7. (a,b,d) : Structures of HClO and HClO₄ are :



(a) HClO₄ is a stronger acid than H₃O⁺. Therefore, conjugate base of HClO₄, i.e., ClO₄⁻, is weaker base than H₂O.

(b) The hybridisation of central atom in both HClO and HClO₄ is sp³.

(c) Reaction of Cl₂ with water forms HOCl which decomposes to give nascent oxygen.

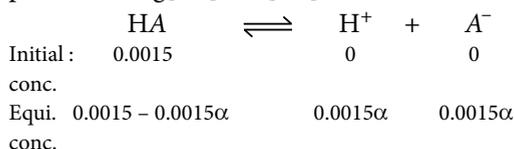


(d) HClO₄ is more acidic than HClO as ClO₄⁻ is more stable than ClO⁻ due to resonance.

8. (6): $\kappa = G \times \frac{l}{a} = 5 \times 10^{-7} \times \frac{120}{1} = 6 \times 10^{-5} \text{ S cm}^{-1}$

$$\Lambda_m^c = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{6 \times 10^{-5} \times 1000}{0.0015} = 40 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{pH} = 4 = -\log[\text{H}^+] \therefore [\text{H}^+] = 10^{-4} \text{ M}$$



$$\text{Thus, } [\text{H}^+] = 0.0015 \alpha = 10^{-4} \Rightarrow \alpha = \frac{10^{-4}}{0.0015}$$

$$\text{Also, } \alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} \therefore \frac{10^{-4}}{0.0015} = \frac{40}{\Lambda_m^\circ}$$

$$\Lambda_m^\circ = \frac{40 \times 0.0015}{10^{-4}} = 600 = 6 \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$$

On comparing it with $Z \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$, we get
 $Z = 6$.

9. (6): According to VSEPR theory,

Total no. of electron pairs around the central atom

$$= \frac{1}{2} (\text{No. of valence electrons of central atom} + \text{No. of atoms linked to central atom by single bonds}$$

- Charge on the cation if the given species is a

polyatomic cation

+ Charge on the anion if the given species is a polyatomic anion)

No. of lone pairs = Total no. of electron pairs

- No. of shared pairs of electrons

Compounds	No. of lone pairs
[TeBr ₆] ²⁻	$\frac{1}{2}(6+6+2)-6=1$
[BrF ₂] ⁺	$\frac{1}{2}(7+2-1)-2=2$
SNF ₃	0
[XeF ₃] ⁻	$\frac{1}{2}(8+3+1)-3=3$

Sum of number of lone pairs = 1 + 2 + 0 + 3 = 6

10. (5): Aromatic compounds follow Huckle's rule of aromaticity, i.e.,

(i) The compound should be planar and has delocalised π-electrons above and below the plane of the molecule.

(ii) The compound should contain (4n + 2)π electrons.



8πe⁻s, non-planar (Non-aromatic)



4πe⁻s, planar (Anti-aromatic)



2πe⁻s, planar, conjugated (Aromatic)



4πe⁻s (Non-aromatic)



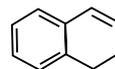
6πe⁻s, conjugated, planar (Aromatic)



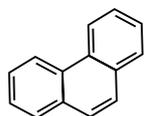
4πe⁻s, conjugated, planar (Anti-aromatic)



6πe⁻s, planar, conjugated (Aromatic)



6πe⁻s, planar, conjugated (Aromatic)



14πe⁻s, planar, conjugated (Aromatic)

$$11. (2): d = \frac{Z \times M}{a^3 \times N_A}$$

For fcc lattice,

Number of atoms per unit cell, Z = 4

Substituting values in equation, we get

$$8 = \frac{4 \times M}{(400 \times 10^{-10})^3 \times 6.023 \times 10^{23}}$$

$$M = \frac{8 \times (400 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{4}$$

$$\therefore M = 77.0944 \text{ g mol}^{-1}$$

77.0944 g of solid has 6.023 × 10²³ atoms

∴ 256 g of solid will have

$$= \frac{6.023 \times 10^{23}}{77.0944} \times 256 \text{ atoms} = 20 \times 10^{23} = 2 \times 10^{24}$$

Comparing it with N × 10²⁴, we get N = 2

12. (6): Molecular orbital electronic configurations of given species :

H₂ : σ1s² (Diamagnetic)

He₂⁺ : σ1s², σ*1s¹ (Paramagnetic)

Li₂ : σ1s², σ*1s², σ2s² (Diamagnetic)

Be₂ : KK, σ2s², σ*2s² (Diamagnetic)

B₂ : KK, σ2s², σ*2s², π2p_x¹ = π2p_y¹ (Paramagnetic)

C₂ : KK, σ2s², σ*2s², π2p_x² = π2p_y² (Diamagnetic)

N₂ : KK, σ2s², σ*2s², π2p_x² = π2p_y², σ2p_z² (Diamagnetic)

O₂⁻ : KK, σ2s², σ*2s², σ2p_z², π2p_x² = π2p_y², π*2p_x² = π*2p_y² (Paramagnetic)

F₂ : KK, σ2s², σ*2s², σ2p_z², π2p_x² = π2p_y², π*2p_x² = π*2p_y² (Diamagnetic)

No. of diamagnetic species is 6 and no. of paramagnetic species is 3.

13. (d): For 1s orbital :

$$\Psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-(Zr/a_0)}$$

Probability density is maximum at nucleus for 1s orbital.

For 2s orbital :

$$\Psi_{2s} = \frac{1}{4\sqrt{2}\pi} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-(Zr/2a_0)}$$

For 2p orbital :

$$\Psi_{2p} = \frac{1}{4\sqrt{2}\pi} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-(Zr/2a_0)} \cos \theta$$

For 3d_{z²} orbital :

$$\Psi_{3d_{z^2}} = \frac{1}{81\sqrt{6}\pi} \left(\frac{Z}{a_0} \right)^{1/2} \frac{Z^2 r^2}{a_0^2} e^{-(Zr/3a_0)} (3 \cos^2 \theta - 1)$$

For He⁺ ion :

E.C. of He⁺ : 1s¹

No. of radial nodes = n - l - 1 = 1 - 0 - 1 = 0

s-orbital is non-directional.

14. (d): For 2s orbital :

No. of radial nodes = 2 - 0 - 1 = 1

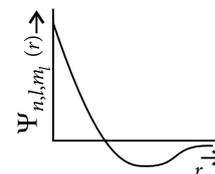
For 1s orbital of hydrogen like species :

$$E \propto -\frac{1}{n^2}$$

$$\text{Then, } E_4 - E_2 = \left(\frac{1}{2} \right)^2 - \left(\frac{1}{4} \right)^2 = \frac{3}{16}$$

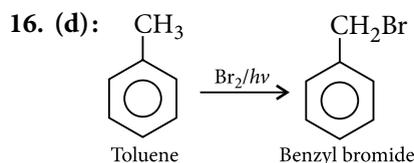
$$E_6 - E_2 = \left(\frac{1}{2} \right)^2 - \left(\frac{1}{6} \right)^2 = \frac{8}{36}$$

$$\therefore (E_4 - E_2) = \frac{27}{32} \times (E_6 - E_2)$$



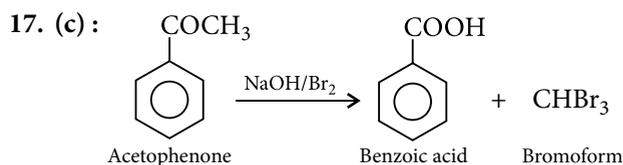
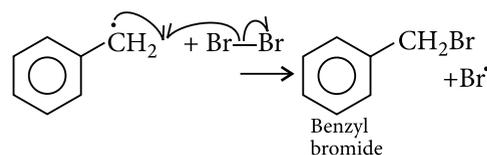
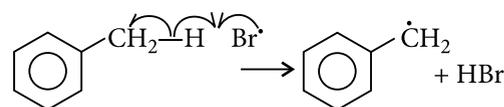
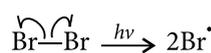
15. (d): E.C. of H : 1s¹ ; for 1s orbital

$$\Psi_{n,l,m_l} \propto \left(\frac{Z}{a_0} \right)^{3/2} e^{-(Zr/a_0)}$$



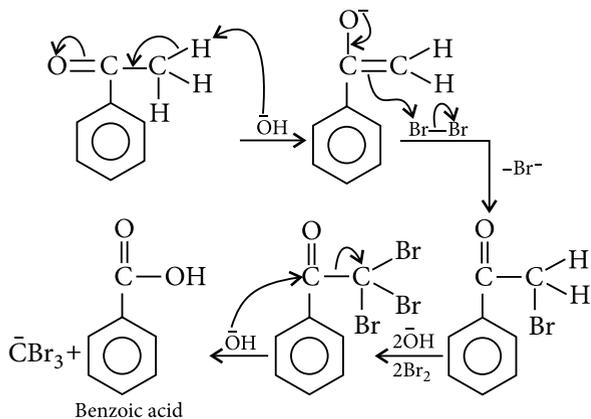
This proceeds via free radical substitution.

Mechanism :

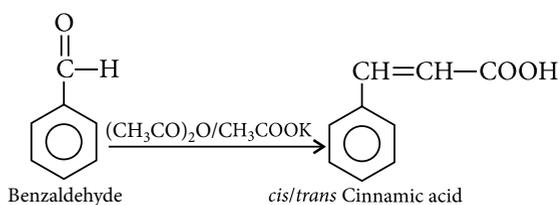


This is haloform reaction.

Mechanism :

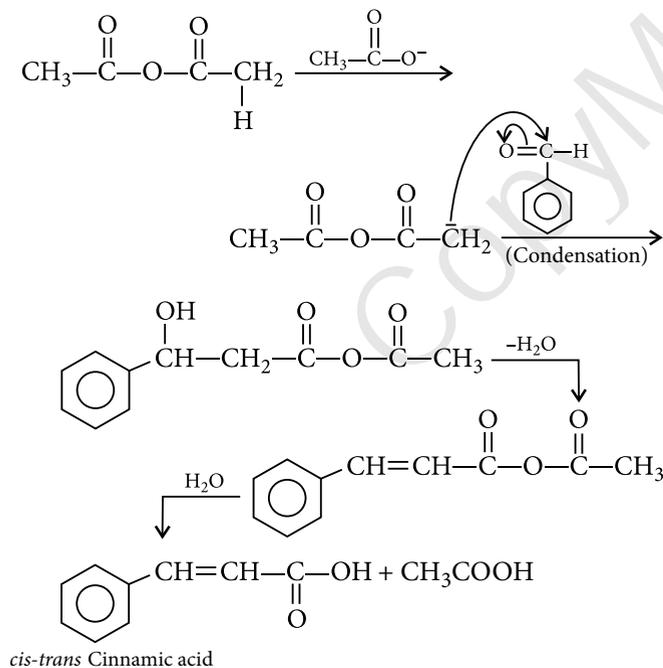


18. (c) :



This is Perkin reaction.

Mechanism :



PAPER-2

1. (c) : $C_{(\text{graphite})} \longrightarrow C_{(\text{diamond})}$ (Isothermally)

$$\Delta_r G^\circ = \Delta G^\circ_{(\text{diamond})} - \Delta G^\circ_{(\text{graphite})}$$

$$= 2.9 - 0 = 2.9 \text{ kJ mol}^{-1}$$

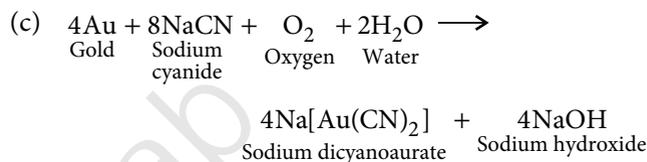
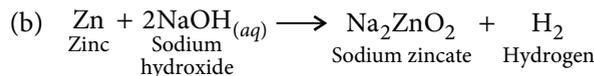
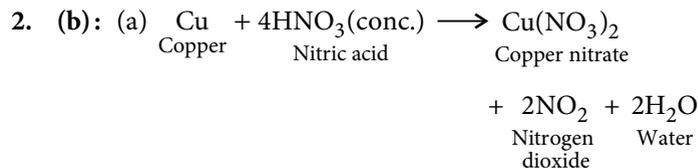
Gibbs free energy is the maximum useful work, then

$$-\Delta G = w_{\text{max}} = P\Delta V$$

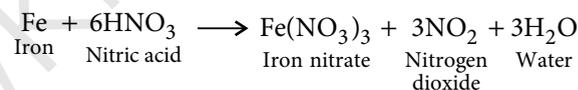
$$-2.9 \times 10^3 = -P \times 2 \times 10^{-6}$$

$$P = \frac{2.9 \times 10^3}{2 \times 10^{-6}} = 1.45 \times 10^9 \text{ Pa} = 1.45 \times 10^9 \times 10^{-5} \text{ bar}$$

$$= 1.45 \times 10^4 \text{ bar} = 14500 \text{ bar}$$



(d) Conc. HNO_3 makes iron passive. Cold relatively concentrated HNO_3 will react with Fe.



3. (a) : Given cell is



Cell reaction is



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303 RT}{nF} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

On substituting values, we get

$$E_{\text{cell}} = 1.1 - \frac{2.303 RT}{2F} \log \frac{10[\text{Cu}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 1.1 - \frac{2.303 RT}{2F} \quad [\because \log 10 = 1]$$

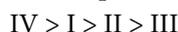
$$\Delta G = -nFE_{\text{cell}}$$

On substituting values, we get

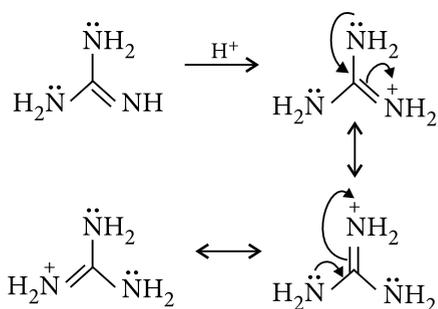
$$\Delta G = -2F \left(1.1 - \frac{2.303 RT}{2F} \right)$$

$$= -2.2 F + 2.303 RT \text{ or } 2.303 RT - 2.2 F$$

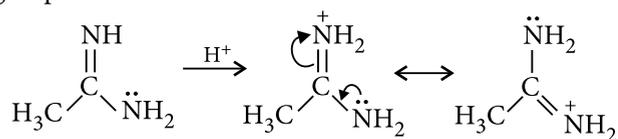
4. (d): Greater the electron density on nitrogen, more basic is the compound. Thus, order of basicity is :



The conjugate acid of IV is stabilised by resonance with lone pairs on both $\ddot{\text{N}}\text{H}_2$ groups.



The conjugate acid of I is stabilised by resonance with lone pair on $-\text{NH}_2$ group and by hyperconjugation of $-\text{CH}_3$ group.



The conjugate acid of II is stabilised by resonance with lone pair on $>\text{NH}$ group.



In compound III, the lone pair of nitrogen is involved in aromaticity. So, it is least basic.

5. (b): Depression in freezing point,

$$\Delta T_f = K_f \cdot m$$

where, K_f = Freezing point depression constant,

m = Molality

$$m = \frac{\text{No. of moles of solute}}{\text{Mass of solvent (in kg)}} = \frac{\frac{34.5}{46}}{\frac{500}{1000}} = 1.5$$

$$\therefore \Delta T_f = 2 \times 1.5 = 3 \text{ K}$$

$$\Delta T_f = T_f^\circ - T_f$$

$$3 = 273 - T_f \quad (\text{Freezing point of H}_2\text{O} = 273 \text{ K})$$

$$T_f = 273 - 3 = 270 \text{ K}$$

Thus, freezing point of solution = 270 K

Also, as temperature increases, the vapour pressure increases. Hence, the curve is as given in option (b).

6. (d): Let oxidation states of phosphorus in H_3PO_2 , H_3PO_4 , H_3PO_3 and $\text{H}_4\text{P}_2\text{O}_6$ be p , q , r and s respectively.

Oxidation state of hydrogen = +1

Oxidation state of oxygen = -2

Thus, in H_3PO_2 :

$$3 \times (+1) + p + 2 \times (-2) = 0 \quad \therefore p = +1$$

In H_3PO_4 :

$$3 \times (+1) + q + 4 \times (-2) = 0 \quad \therefore q = +5$$

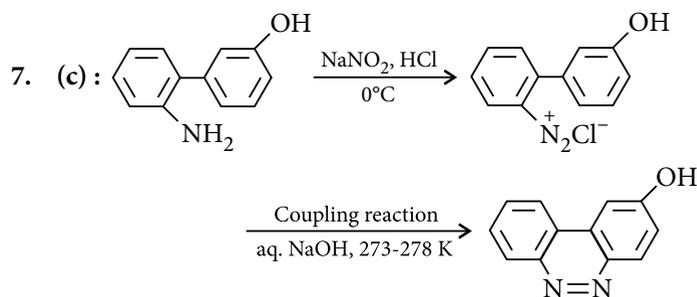
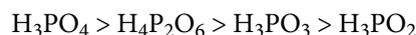
In H_3PO_3 :

$$3 \times (+1) + r + 3 \times (-2) = 0 \quad \therefore r = +3$$

In $\text{H}_4\text{P}_2\text{O}_6$:

$$4 \times (+1) + 2s + 6 \times (-2) = 0 \quad \therefore s = +4$$

Thus, the order of oxidation state is:



8. (b, c):

(a) Cloud is an aerosol in which liquid is dispersed phase and gas is dispersion medium. Whereas, emulsion is liquid in liquid colloidal system.

(b) Higher the critical temperature of a gas, greater the amount of gas adsorbed. Thus, ethane will be adsorbed to a greater extent than nitrogen.

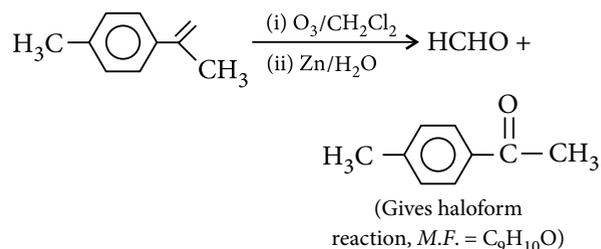
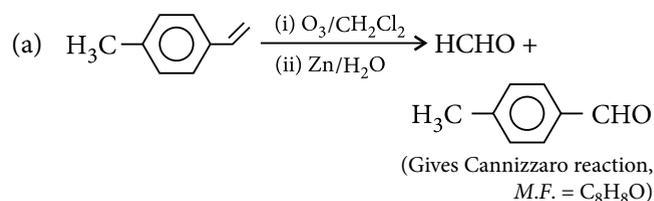
(c) Adsorption is an exothermic process, thus, enthalpy decreases during this process. On adsorption, the randomness of the adsorbate molecules decreases, thus, entropy decreases.

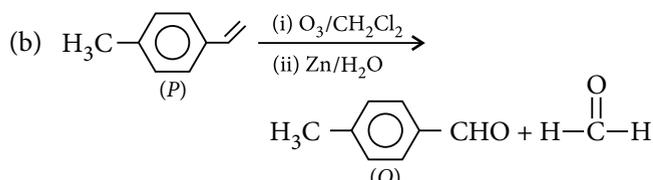
(d) Brownian motion of colloidal particles depends on the size of the particles as well as on viscosity of the solution.

9. (b, c): As 'Q' undergoes Cannizzaro reaction, thus, it is an aldehyde which does not contain α -hydrogen. Also, it does not give haloform reaction. Thus, it does not have CH_3CO - group.

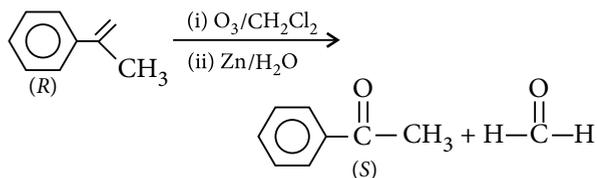
As 'S' undergoes haloform reaction but not Cannizzaro reaction, thus 'S' has CH_3CO - group.

The molecular formula of 'Q' and 'S' is $\text{C}_8\text{H}_8\text{O}$. Thus, both are aromatic.

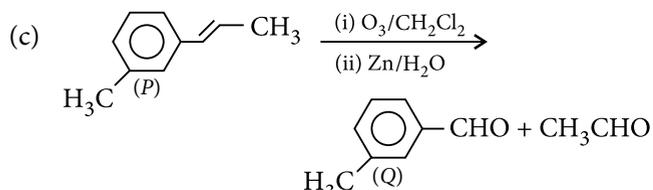




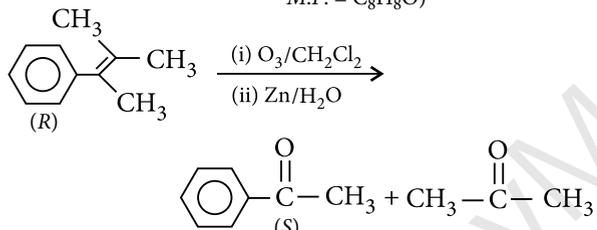
(Gives Cannizzaro reaction,
M.F. = C₈H₈O)



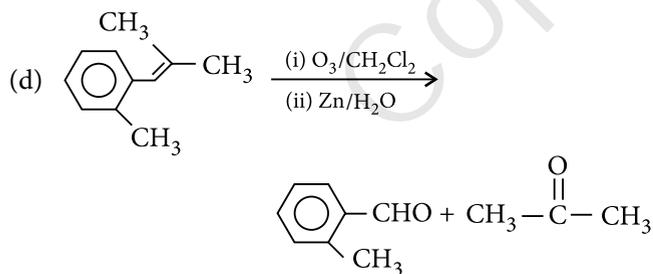
(Gives haloform reaction,
M.F. = C₈H₈O)



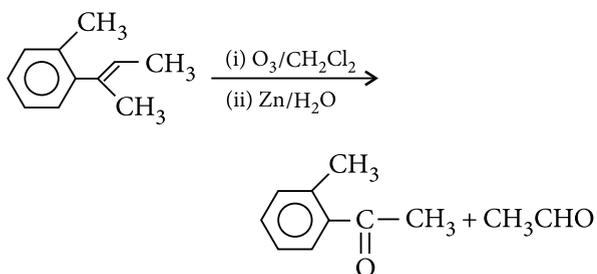
(Gives Cannizzaro reaction,
M.F. = C₈H₈O)



(Gives haloform reaction,
M.F. = C₈H₈O)



(Gives Cannizzaro reaction,
M.F. = C₈H₈O)



(Gives haloform reaction,
M.F. is C₉H₁₀O)

10. (a, b, d) :

- (a) Compounds I and II are 1° alkyl halides, then they undergo S_N2 mechanism.
(b) Compound IV undergoes inversion of configuration due to intimate-ion pair formation, inversion predominates over retention.
(c) Stability of carbocations follows the order :
2° benzylic > 3° alkyl > 1° benzylic
(IV) (III) (I)
(d) I is a benzylic halide, thus, it undergoes S_N1 reaction easily as benzylic carbocation is resonance stabilised. III also follows S_N1 mechanism as it a 3° alkyl halide.

11. (a, c) : Arrhenius equation is

$$k = Ae^{-E_a/RT}$$

where, A = Frequency factor

Taking into account orientation factor,

$$k = PZ_{AB}e^{-E_a/RT}$$

where, P = steric factor, Z_{AB} = collision frequency

The value of steric factor lies between 0 and 1 predicted by Arrhenius equation. Thus, the experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation.

The activation energy of the reaction does not depend upon the value of the steric factor.

If P is very small, then catalyst is required to carry out the reaction at measurable rate.

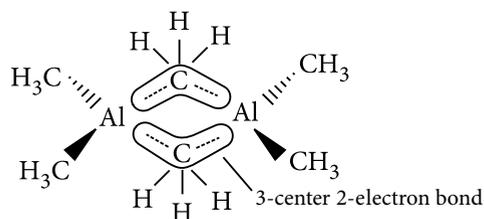
12. (a, b) : Amphoteric oxides are :

Cr₂O₃, BeO, SnO, SnO₂, ZnO, Al₂O₃, PbO and PbO₂

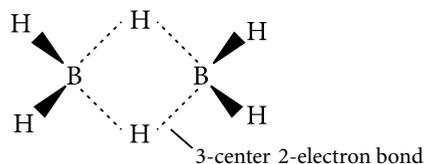
Whereas, NO is a neutral oxide, B₂O₃ is an acidic oxide and CrO is a basic oxide.

13. (a, b, c) :

- (a) Al₂(CH₃)₆ has the three centre-two electron bonds.

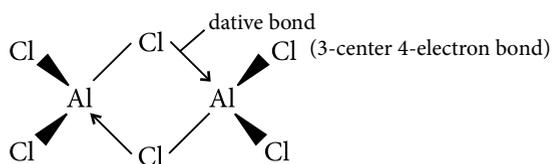


- (b) Dimer of BH₃ has 3-center 2-electron bond.



(c) The size of element increases down the group, thus, Lewis acid character of BCl_3 is greater than that of AlCl_3 .

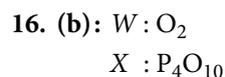
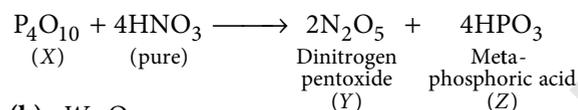
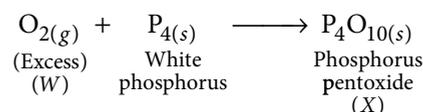
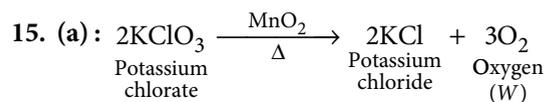
(d) AlCl_3 has dative bond in its dimeric structure.



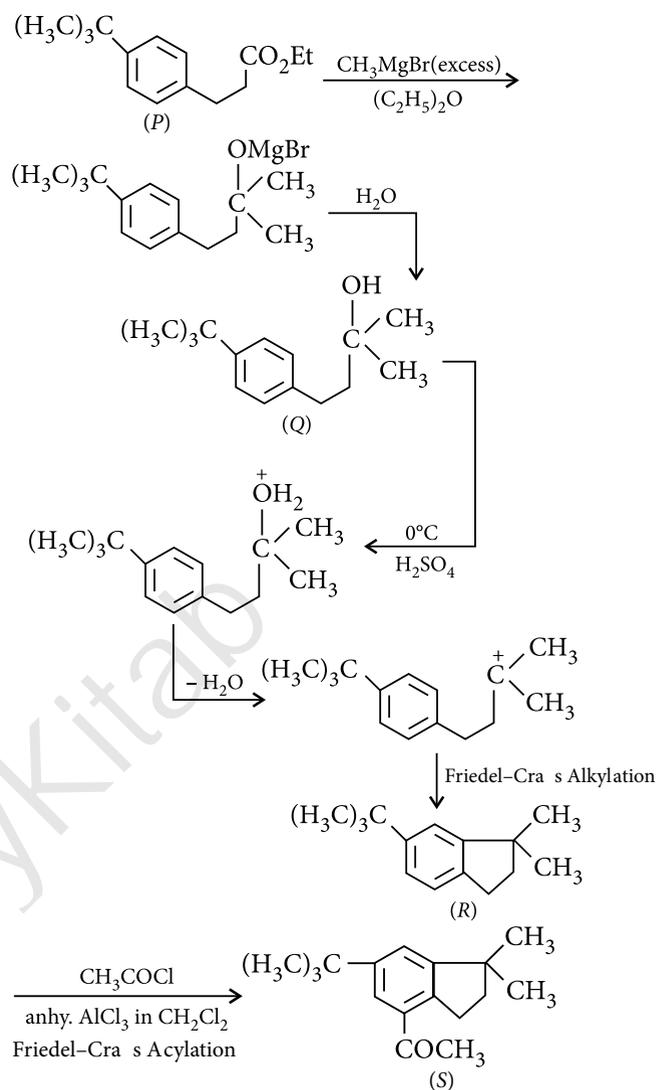
$$14. (a, b): \Delta S_{\text{surr}} = -\frac{\Delta H}{T_{\text{surr}}}$$

For endothermic, if T_{surr} increases, unfavourable change in entropy of the surroundings decreases.

For exothermic, if T_{surr} increases, favourable change in entropy of the surroundings decreases.



17. (a): The reaction Q to R is Friedel–Crafts alkylation reaction whereas, reaction R to S is Friedel–Crafts acylation.



18. (c)



SOLVED PAPER 2018

JEE Advanced ONLINE

PAPER - 1

SECTION 1 (MAXIMUM MARKS : 24)

- This section contains SIX (06) questions.
- Each question has FOUR options for correct answer(s). ONE OR MORE THAN ONE of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.

- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 If only (all) the correct option(s) is (are) chosen.

Partial Marks : +3 If all the four options are correct but ONLY three options are chosen.

Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct options.

Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.

Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered).

Negative Marks : -2 In all other cases.

- For Example: If first, third and fourth are the ONLY three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in -2 marks.

1. The compound(s) which generate(s) N_2 gas upon thermal decomposition below $300^\circ C$ is (are)

- (a) NH_4NO_3 (b) $(NH_4)_2Cr_2O_7$
 (c) $Ba(N_3)_2$ (d) Mg_3N_2

[The p-Block Elements]

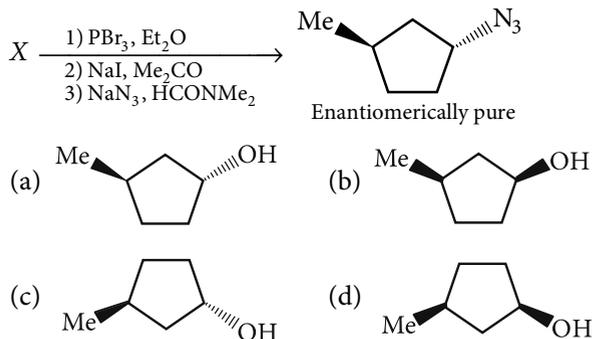
2. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are)
 (Atomic numbers: Fe = 26, Ni = 28)
- (a) total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 16
 (b) these are predominantly low spin in nature
 (c) metal-carbon bond strengthens when the oxidation state of the metal is lowered
 (d) the carbonyl C—O bond weakens when the oxidation state of the metal is increased.

[Coordination Compounds]

3. Based on the compounds of group 15 elements, the correct statement(s) is (are)
- (a) Bi_2O_5 is more basic than N_2O_5
 (b) NF_3 is more covalent than BiF_3
 (c) PH_3 boils at lower temperature than NH_3
 (d) the N—N single bond is stronger than the P—P single bond.

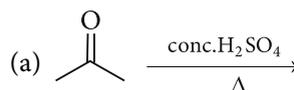
[The p-Block Elements]

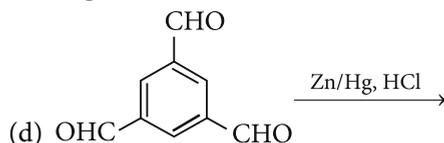
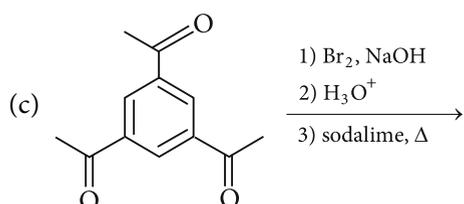
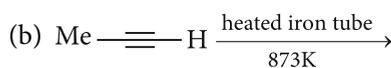
4. In the following reaction sequence, the correct structure(s) of X is (are)



[Alcohols, Phenols and Ethers]

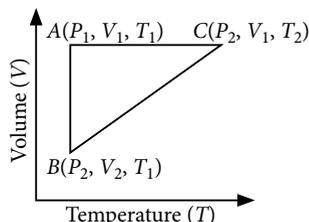
5. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are)





[Hydrocarbons]

6. A reversible cyclic process for an ideal gas is shown below. Here, P , V and T are pressure, volume and temperature, respectively. The thermodynamic parameters q , w , H and U are heat, work, enthalpy and internal energy, respectively.



The correct option(s) is (are)

- (a) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2(V_2 - V_1)$
 (b) $w_{BC} = P_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$
 (c) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$
 (d) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

[Chemical Energetics]

SECTION 2 (MAXIMUM MARKS : 24)

- This section contains EIGHT (08) questions. The answer to each question is a NUMERICAL VALUE.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the second decimal place; e.g. 6.25, 7.00, -0.33, -.30, 30.27, -127.30) using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +3 If ONLY the correct numerical value is entered as answer.

Zero Marks : 0 In all other cases.

7. Among the species given below, the total number of diamagnetic species is ____.

H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapour phase, Mn_3O_4 , $(\text{NH}_4)_2[\text{FeCl}_4]$, $(\text{NH}_4)_2[\text{NiCl}_4]$, K_2MnO_4 , K_2CrO_4

[Chemical Bonding]

8. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ are used in the preparation, the combined weight (in grams) of gypsum and the nickel-ammonia coordination compound thus produced is ____.

(Atomic weights in g mol^{-1} : H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59)

[Coordination Compounds]

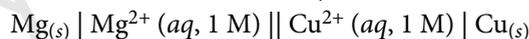
9. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance.

- Remove all the anions (X) except the central one
- Replace all the face centered cations (M) by anions (X)
- Remove all the corner cations (M)
- Replace the central anion (X) with cation (M)

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$ in Z is ____.

[Solid State]

10. For the electrochemical cell,



the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to $x \text{ M}$, the cell potential changes to 2.67 V at 300 K. The value of x is ____.

(Given, $\frac{F}{R} = 11500 \text{ K V}^{-1}$, where F is the Faraday constant

and R is the gas constant, $\ln(10) = 2.30$)

[Redox Reactions and Electrochemistry]

11. A closed tank has two compartments A and B, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Figure 1). If the old partition is replaced by a new partition which can slide and conduct heat but does not allow the gas to leak across (Figure 2), the volume (in m^3) of the compartment A after the system attains equilibrium is ____.

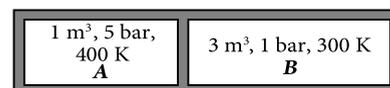


Figure 1

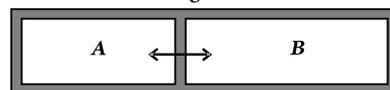


Figure 2

[Gaseous and Liquid States]

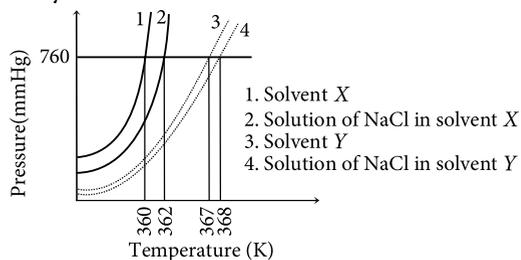
12. Liquids A and B form ideal solution over the entire range of composition. At temperature T , equimolar binary solution of liquids A and B has vapour pressure 45 Torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B , respectively, has vapour pressure of 22.5 Torr. The value of x_A/x_B in the new solution is _____.

(Given that the vapour pressure of pure liquid A is 20 Torr at temperature T .) **[Solutions and Colligative Properties]**

13. The solubility of a salt of weak acid (AB) at pH 3 is $Y \times 10^{-3} \text{ mol L}^{-1}$. The value of Y is _____.

(Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB (K_a) = 1×10^{-8}) **[Equilibrium]**

14. The plot given below shows $P-T$ curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree of dimerization in solvent X is _____.

[Solutions and Colligative Properties]

SECTION 3 (MAXIMUM MARKS : 12)

- This section contains TWO (02) paragraphs. Based on each paragraph, there are TWO (02) questions.
- Each question has FOUR options. ONLY ONE of these four options corresponds to the correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +3 If ONLY the correct option is chosen.

Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered).

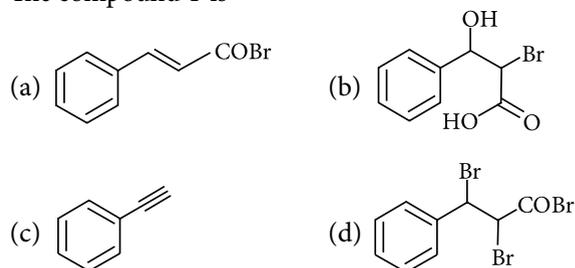
Negative Marks : -1 In all other cases.

PARAGRAPH "X"

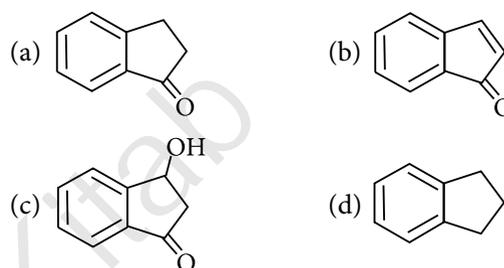
Treatment of benzene with CO/HCl in the presence of anhydrous $\text{AlCl}_3/\text{CuCl}$ followed by reaction with $\text{Ac}_2\text{O}/\text{NaOAc}$ gives compound X as the major product. Compound

X upon reaction with $\text{Br}_2/\text{Na}_2\text{CO}_3$, followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with $\text{H}_2/\text{Pd-C}$, followed by H_3PO_4 treatment gives Z as the major product.

15. The compound Y is



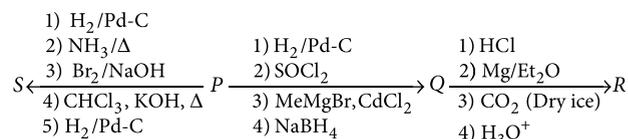
16. The compound Z is



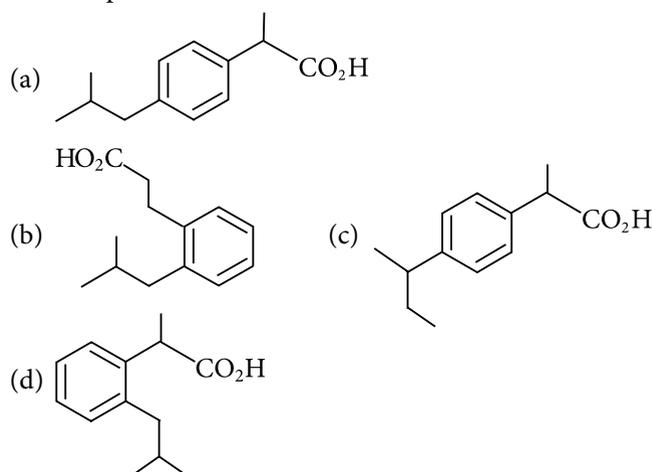
[Aldehydes and Ketones]

PARAGRAPH "A"

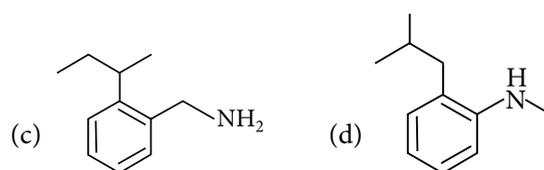
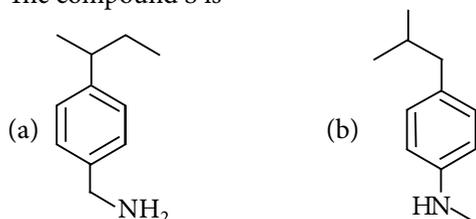
An organic acid P ($\text{C}_{11}\text{H}_{12}\text{O}_2$) can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, P gives an aliphatic ketone as one of the products. P undergoes the following reaction sequences to furnish R via Q. The compound P also undergoes another set of reactions to produce S.



17. The compound R is



18. The compound S is



[Carboxylic Acids and Their Derivatives]

PAPER - 2

SECTION 1 (MAXIMUM MARKS : 24)

- This section contains SIX (06) questions.
- Each question has FOUR options for correct answer(s). ONE OR MORE THAN ONE of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 If only (all) the correct option(s) is (are) chosen.

Partial Marks : +3 If all the four options are correct but ONLY three options are chosen.

Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct options.

Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.

Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered).

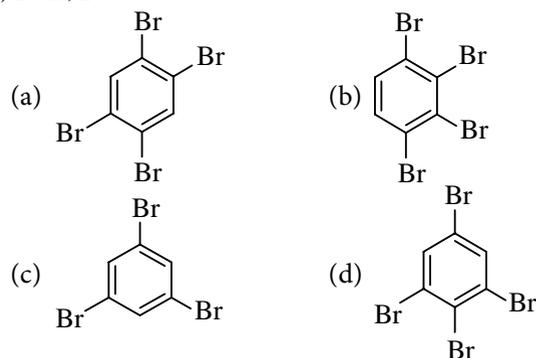
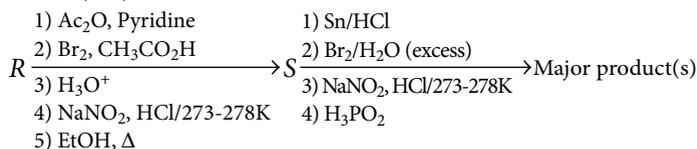
Negative Marks : -2 In all other cases.

- For Example: If first, third and fourth are the ONLY three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in -2 marks.

- The correct option(s) regarding the complex $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ ($\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) is (are)
 - it has two geometrical isomers
 - it will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands
 - it is paramagnetic
 - it absorbs light at longer wavelength as compared to $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$. **[Coordination Compounds]**

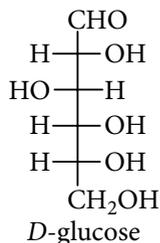
- The correct option(s) to distinguish nitrate salts of Mn^{2+} and Cu^{2+} taken separately is (are)
 - Mn^{2+} shows the characteristic green colour in the flame test
 - only Cu^{2+} shows the formation of precipitate by passing H_2S in acidic medium
 - only Mn^{2+} shows the formation of precipitate by passing H_2S in faintly basic medium
 - Cu^{2+}/Cu has higher reduction potential than Mn^{2+}/Mn (measured under similar conditions). **[The Transition Elements]**

- Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give P (51 %), Q (47%) and R (2%). The major product(s) of the following reaction sequence is (are)

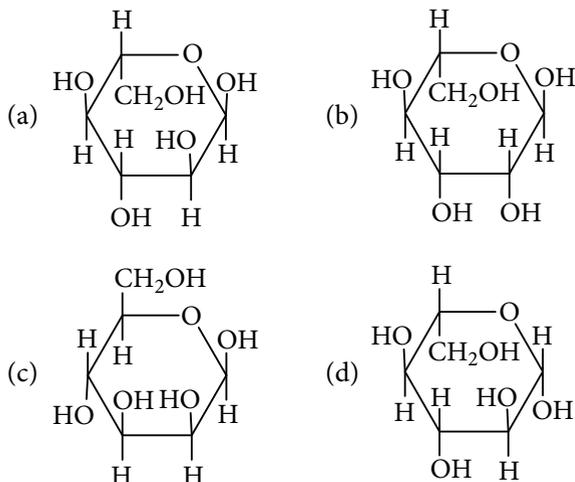


[Compounds Containing Nitrogen]

4. The Fischer presentation of *D*-glucose is given below.

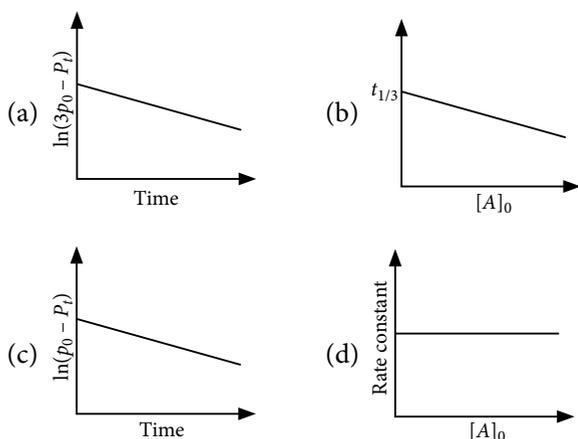


The correct structure(s) of β -*L*-glucopyranose is (are)



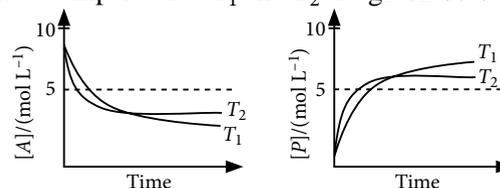
[Biomolecules and Chemistry in Everyday Life]

5. For a first order reaction $A_{(g)} \rightarrow 2B_{(g)} + C_{(g)}$ at constant volume and 300 K, the total pressure at the beginning ($t = 0$) and at time t are P_0 and P_t , respectively. Initially, only *A* is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of *A* to reach $1/3^{\text{rd}}$ of its initial value. The correct option(s) is (are) (Assume that all these gases behave as ideal gases)



[Chemical Kinetics]

6. For a reaction, $A \rightleftharpoons P$, the plots of $[A]$ and $[P]$ with time at temperatures T_1 and T_2 are given below.



If $T_2 > T_1$, the correct statement(s) is (are) (Assume ΔH° and ΔS° are independent of temperature and ratio of $\ln K$ at T_1 to $\ln K$ at T_2 is greater than T_2/T_1 . Here *H*, *S*, *G* and *K* are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

- (a) $\Delta H^\circ < 0, \Delta S^\circ < 0$ (b) $\Delta G^\circ < 0, \Delta H^\circ > 0$
 (c) $\Delta G^\circ < 0, \Delta S^\circ < 0$ (d) $\Delta G^\circ < 0, \Delta S^\circ > 0$

[Equilibrium]

SECTION 2 (MAXIMUM MARKS : 24)

- This section contains EIGHT (08) questions. The answer to each question is a NUMERICAL VALUE.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the second decimal place; e.g. 6.25, 7.00, -0.33, -.30, 30.27, -127.30) using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +3 If ONLY the correct numerical value is entered as answer.

Zero Marks : 0 In all other cases.

7. The total number of compounds having at least one bridging oxo group among the molecules given below is _____.
- $\text{N}_2\text{O}_3, \text{N}_2\text{O}_5, \text{P}_4\text{O}_6, \text{P}_4\text{O}_7, \text{H}_4\text{P}_2\text{O}_5, \text{H}_5\text{P}_3\text{O}_{10}, \text{H}_2\text{S}_2\text{O}_3, \text{H}_2\text{S}_2\text{O}_5$
- [The *p*-Block Elements]**

8. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the contents undergo self-reduction. The weight (in kg) of *Pb* produced per kg of O_2 consumed is _____. (Atomic weights in g mol^{-1} : *O* = 16, *S* = 32, *Pb* = 207)

[Metallurgy]

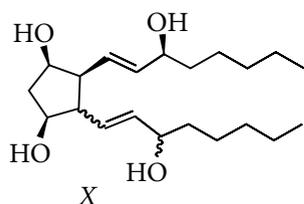
9. To measure the quantity of MnCl_2 dissolved in an aqueous solution, it was completely converted to KMnO_4 using the reaction,
 $\text{MnCl}_2 + \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{HCl}$ (equation not balanced)
 Few drops of concentrated *HCl* were added to this solution and gently warmed. Further, oxalic acid (225 mg) was

added in portions till the colour of the permanganate ion disappeared. The quantity of MnCl_2 (in mg) present in the initial solution is _____.

(Atomic weights in g mol^{-1} : $\text{Mn} = 55$, $\text{Cl} = 35.5$)

[Basic Concepts of Chemistry]

10. For the given compound X, the total number of optically active stereoisomers is _____.

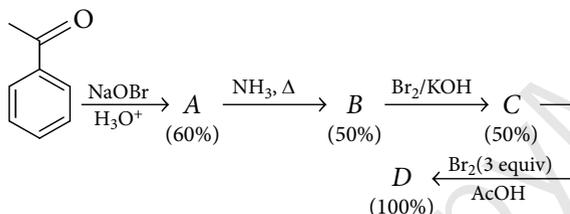


— This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed.

~~~~ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is NOT fixed.

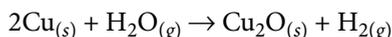
### [General Organic Chemistry]

11. In the following reaction sequence, the amount of D (in g) formed from 10 moles of acetophenone is \_\_\_\_\_.
- (Atomic weights in  $\text{g mol}^{-1}$ :  $\text{H} = 1$ ,  $\text{C} = 12$ ,  $\text{N} = 14$ ,  $\text{O} = 16$ ,  $\text{Br} = 80$ . The yield (%) corresponding to the product in each step is given in the parenthesis.)



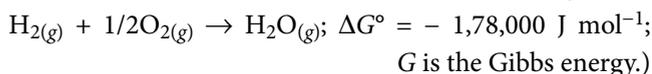
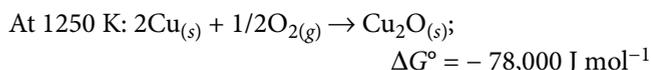
### [Aldehydes and Ketones]

12. The surface of copper gets tarnished by the formation of copper oxide.  $\text{N}_2$  gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the  $\text{N}_2$  gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below :



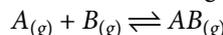
$p_{\text{H}_2}$  is the minimum partial pressure of  $\text{H}_2$  (in bar) needed to prevent the oxidation at 1250 K. The value of  $\ln(p_{\text{H}_2})$  is \_\_\_\_\_.

(Given: total pressure = 1 bar,  $R$  (universal gas constant) =  $8 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\ln(10) = 2.3$ ,  $\text{Cu}_{(s)}$  and  $\text{Cu}_2\text{O}_{(s)}$  are mutually immiscible.



### [Chemical Energetics]

13. Consider the following reversible reaction,



The activation energy of the backward reaction exceeds that of the forward reaction by  $2RT$  (in  $\text{J mol}^{-1}$ ). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of  $\Delta G^\circ$  (in  $\text{J mol}^{-1}$ ) for the reaction at 300 K is \_\_\_\_\_.

(Given :  $\ln(2) = 0.7$ ,  $RT = 2500 \text{ J mol}^{-1}$  at 300 K and  $G$  is the Gibbs energy)

### [Chemical Kinetics]

14. Consider an electrochemical cell :

$A_{(s)} | A^{n+}(\text{aq}, 2 \text{ M}) || B^{2n+}(\text{aq}, 1 \text{ M}) | B_{(s)}$ . The value of  $\Delta H^\circ$  for the cell reaction is twice that of  $\Delta G^\circ$  at 300 K. If the emf of the cell is zero, the  $\Delta S^\circ$  (in  $\text{J K}^{-1} \text{ mol}^{-1}$ ) of the cell reaction per mole of B formed at 300 K is \_\_\_\_\_.

(Given:  $\ln(2) = 0.7$ ,  $R$  (universal gas constant) =  $8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ .  $H$ ,  $S$  and  $G$  are enthalpy, entropy and Gibbs energy, respectively).

### [Redox Reactions and Electrochemistry]

#### SECTION 3 (MAXIMUM MARKS : 12)

- This section contains FOUR (04) questions.
- Each question has TWO (02) matching lists: LIST-I and LIST-II.
- FOUR options are given representing matching of elements from LIST-I and LIST-II. ONLY ONE of these four options corresponds to a correct matching.
- For each question, choose the option corresponding to the correct matching.
- For each question, marks will be awarded according to the following marking scheme:

Full Marks : +3 If ONLY the option corresponding to the correct matching is chosen.

Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered).

Negative Marks : -1 In all other cases.

15. Match each set of hybrid orbitals from List-I with complex(es) given in List-II.

#### List-I

- P.  $dsp^2$   
Q.  $sp^3$   
R.  $sp^3d^2$   
S.  $d^2sp^3$

#### List-II

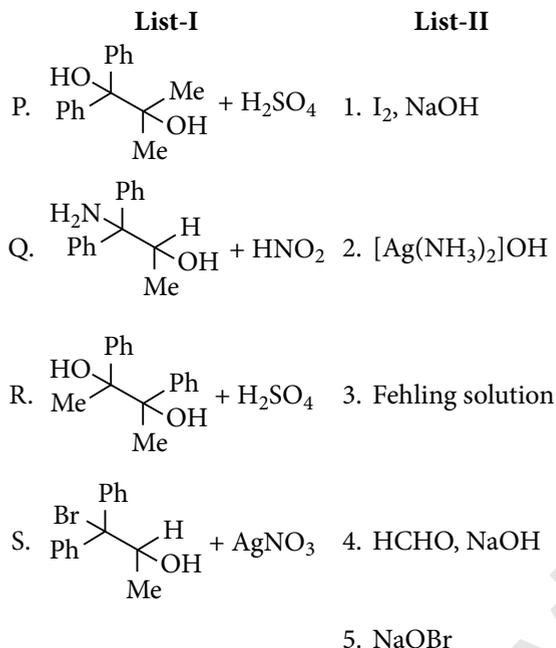
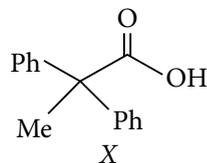
1.  $[\text{FeF}_6]^{4-}$   
2.  $[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$   
3.  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
4.  $[\text{FeCl}_4]^{2-}$   
5.  $\text{Ni}(\text{CO})_4$   
6.  $[\text{Ni}(\text{CN})_4]^{2-}$

The correct option is

- (a)  $P \rightarrow 5$ ;  $Q \rightarrow 4,6$ ;  $R \rightarrow 2, 3$ ;  $S \rightarrow 1$   
(b)  $P \rightarrow 5,6$ ;  $Q \rightarrow 4$ ;  $R \rightarrow 3$ ;  $S \rightarrow 1, 2$   
(c)  $P \rightarrow 6$ ;  $Q \rightarrow 4, 5$ ;  $R \rightarrow 1$ ;  $S \rightarrow 2,3$   
(d)  $P \rightarrow 4, 6$ ;  $Q \rightarrow 5, 6$ ;  $R \rightarrow 1, 2$ ;  $S \rightarrow 3$

### [Coordination Compounds]

16. The desired product X can be prepared by reacting the major product of the reactions in List-I with one or more appropriate reagents in List-II. (given, order of migratory aptitude: aryl > alkyl > hydrogen)

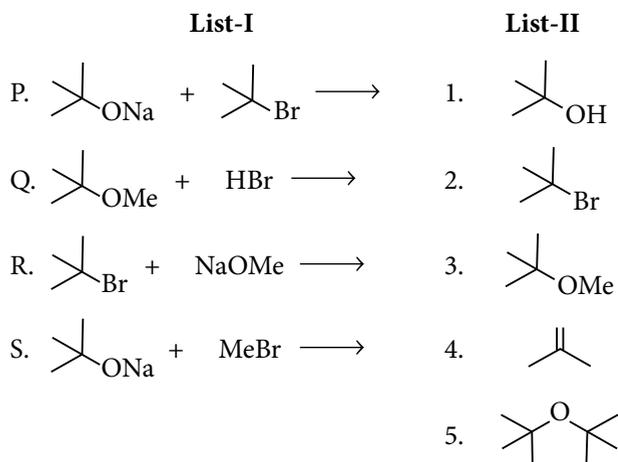


The correct option is

- (a) P → 1; Q → 2, 3; R → 1, 4; S → 2, 4  
 (b) P → 1, 5; Q → 3, 4; R → 4, 5; S → 3  
 (c) P → 1, 5; Q → 3, 4; R → 5; S → 2, 4  
 (d) P → 1, 5; Q → 2, 3; R → 1, 5; S → 2, 3

**[Alcohols, Phenols and Ethers]**

17. List-I contains reactions and List-II contains major products.



Match each reaction in List-I with one or more products in List-II and choose the correct option.

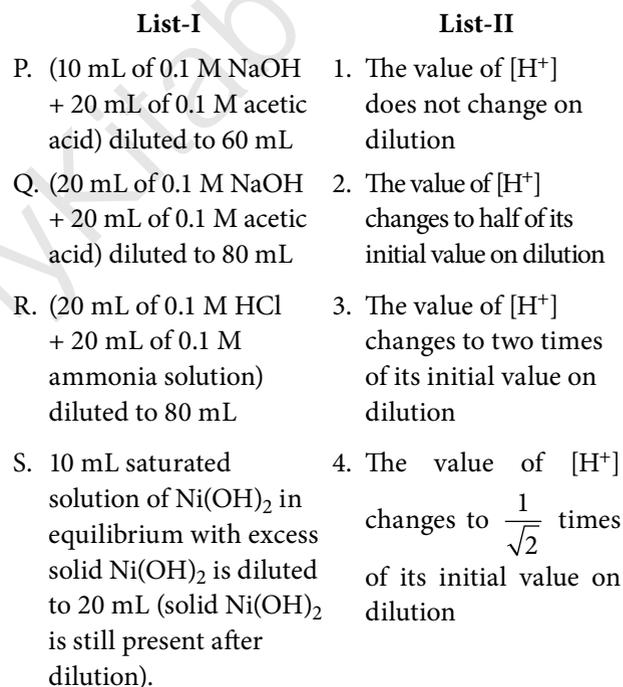
The correct option is

- (a) P → 1, 5; Q → 2; R → 3; S → 4  
 (b) P → 1, 4; Q → 2; R → 4; S → 3  
 (c) P → 1, 4; Q → 1, 2; R → 3, 4; S → 4  
 (d) P → 4, 5; Q → 4; R → 4; S → 3, 4

**[General Organic Chemistry]**

18. Dilution processes of different aqueous solutions, with water, are given in List-I. The effects of dilution of the solutions on [H<sup>+</sup>] are given in List-II.

(Note: Degree of dissociation ( $\alpha$ ) of weak acid and weak base is  $\ll 1$ ; degree of hydrolysis of salt  $\ll 1$ ; [H<sup>+</sup>] represents the concentration of H<sup>+</sup> ions)



Match each process given in List-I with one or more effect(s) in List-II.

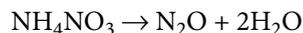
The correct option is

- (a) P → 4; Q → 2; R → 3; S → 1  
 (b) P → 4; Q → 3; R → 2; S → 3  
 (c) P → 1; Q → 4; R → 5; S → 3  
 (d) P → 1; Q → 5; R → 4; S → 1

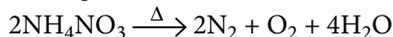
**[Equilibrium]**

**SOLUTIONS**
**PAPER-1**

1. (b, c) : Ammonium nitrate decomposes below 300°C to produce N<sub>2</sub>O and H<sub>2</sub>O.



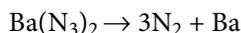
On further heating *i.e.*, above 300°C,



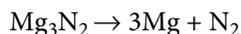
Ammonium dichromate on heating below 300°C decomposes to give N<sub>2</sub> and Cr(III) oxide.



Barium azide on heating around 180°C decomposes to give N<sub>2</sub> gas and Ba.

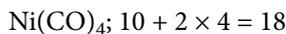
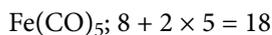


Magnesium nitride decomposes above 700°C to give Mg and N<sub>2</sub> gas.



So, on heating below 300°C only (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and Ba(N<sub>3</sub>)<sub>2</sub> produce N<sub>2</sub> gas.

2. (b, c) : (a) Total number of valence shell electrons in central metal atom are



(b) Due to the presence of strong field ligand (CO) both complexes are low spin in nature.

(c) In lower oxidation state, number of electrons in *d*-subshell are higher, so due to  $\pi$ -backbonding, electrons from filled *t*<sub>2g</sub> of metal are transferred to vacant  $\pi^*$  of CO which strengthens the M—C bond in complexes.

(d) In higher oxidation number, metal may have less number of electrons in *d*-orbitals, which decreases the extent of synergic bonding. So, in this case M—C bond is weaker while C—O bond is stronger.

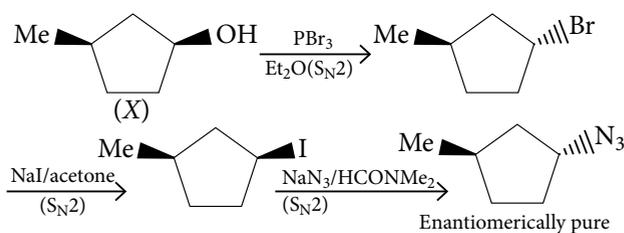
3. (a, b, c) : (a) Basic character of oxide increases as we move down the group. Therefore, Bi<sub>2</sub>O<sub>5</sub> is more basic than N<sub>2</sub>O<sub>5</sub>.

(b) Covalent nature depends on the electronegativity difference between the bonded atoms. Therefore, NF<sub>3</sub> is more covalent than BiF<sub>3</sub>.

(c) Due to H-bonding, boiling point of NH<sub>3</sub> is more than PH<sub>3</sub>.

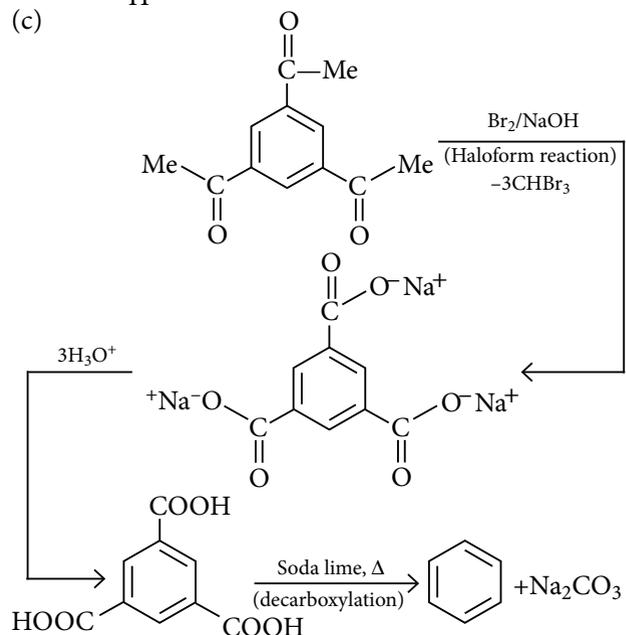
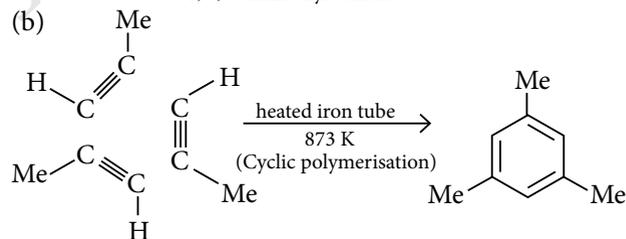
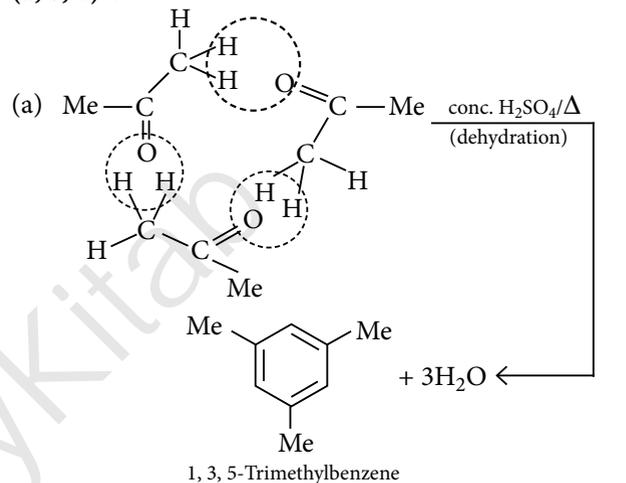
(d) Due to small size of N-atom, *l.p-l.p.* repulsion will be more in N—N single bond than in P—P single bond. Therefore, N—N single bond is weaker than P—P single bond.

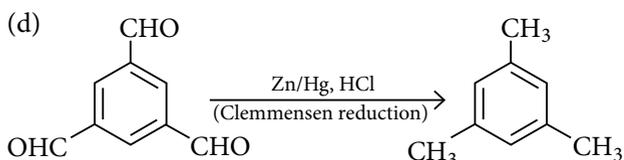
4. (b): The correct structure of X is :



Enantiomerically pure product after several substitution reactions, is only possible when each reaction is stereospecific in nature which confirms the pathway used is S<sub>N</sub>2 in nature.

5. (a, b, d) :





6. (b, c) : A - C (Isochoric process)  $\Rightarrow w_{AC} = 0$  and

$$\Delta U_{AC} = q_{AC}$$

B - C (Isobaric process)

$$\Rightarrow \Delta U_{BC} = q_{BC} + w_{BC}$$

$$w_{BC} = -P_2(V_1 - V_2) = P_2(V_2 - V_1)$$

$$\Rightarrow q_{BC} = \Delta H_{BC}$$

$$\therefore (\Delta T)_{A-C} = (\Delta T)_{B-C}$$

$$\therefore \Delta U_{BC} = \Delta U_{AC} = q_{AC}$$

$$\Delta H_{BC} = \Delta H_{AC} = q_{BC}$$

$$(\because T_2 > T_1)$$

$\Delta H_{CA}$  and  $\Delta U_{CA}$  are negative.

$$\Delta H_{CA} = \Delta U_{CA} + V\Delta P$$

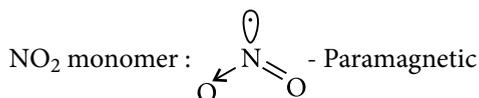
$$\therefore \Delta H_{CA} < \Delta U_{CA}$$

A - B (Isothermal process)

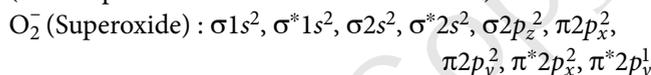
$$\Delta U_{AB} = \Delta H_{AB} = 0$$

$$w_{AB} = -nRT_1 \ln \frac{V_2}{V_1}$$

7. (1) : H atom :  $\uparrow$  - Paramagnetic  
 $1s^1$



(Due to presence of one unshared electron)



One unpaired electron is present in either  $\pi^* 2p_x$  or  $\pi^* 2p_y$ , hence, it is paramagnetic in nature.

Dimeric sulphur in vapour phase : It is similar as O<sub>2</sub> in vapour phase. Hence, it is paramagnetic in nature.

Mn<sub>3</sub>O<sub>4</sub> : It is combined form of MnO and Mn<sub>2</sub>O<sub>3</sub>.

Mn<sup>2+</sup> has 5 unpaired electrons and Mn<sup>3+</sup> has 4 unpaired electrons. Hence, it is paramagnetic in nature.

(NH<sub>4</sub>)<sub>2</sub>[FeCl<sub>4</sub>] or [Fe<sup>2+</sup>Cl<sub>4</sub>]<sup>2-</sup> ion

[FeCl<sub>4</sub>]<sup>2-</sup> : It is tetrahedral,  $sp^3$ -hybridized with  $e^3, t^3$  configuration, hence, it is paramagnetic in nature.

(NH<sub>4</sub>)<sub>2</sub>[NiCl<sub>4</sub>] or [Ni<sup>2+</sup>Cl<sub>4</sub>]<sup>2-</sup> ion

[NiCl<sub>4</sub>]<sup>2-</sup> : It is tetrahedral,  $sp^3$ -hybridized with  $e^4, t^2$  configuration, hence, it is paramagnetic in nature.

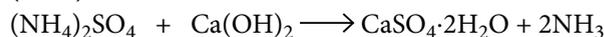
K<sub>2</sub>MnO<sub>4</sub>

Mn<sup>6+</sup> : [Ar]3d<sup>1</sup>

Hence, it is paramagnetic in nature.

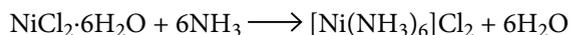
K<sub>2</sub>CrO<sub>4</sub> : Cr<sup>6+</sup> has zero unpaired electron, hence, it is diamagnetic in nature.

8. (2992) :



$$n = \frac{1584}{132} = 12 \text{ mol}$$

Gypsum  
12 mol



$$n = \frac{952}{238} = 4 \text{ mol}$$

4 mol

Combined weight of Gypsum and nickel - ammonia coordination compound

$$= 12 \times M_{CaSO_4 \cdot 2H_2O} + 4M_{[Ni(NH_3)_6]Cl_2}$$

$$= (12 \times 172) + (4 \times 232) = 2992 \text{ g}$$

9. (3.00) : MX has NaCl type structure.

From given instructions, it is clear that in MX ionic solid :  
Cation M<sup>+</sup> - occupies face centres and corners (fcc lattice).  
Anion X<sup>-</sup> - occupies all octahedral voids (body centre + edge centres)

(i) No. of anions left = 1

(ii) No. of anions added = 3

No. of cations left = 1

(iii) No. of cations left = 0

(iv) No. of cations added = 1

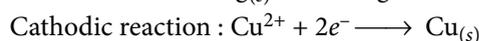
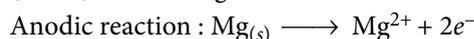
No. of anions left = 3

Final no. of cations in the unit cell of Z = 1.

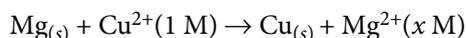
Final no. of anions in the unit cell of Z = 3.

$$\text{The value of } \left( \frac{\text{number of anions}}{\text{number of cations}} \right) = \frac{3}{1} = 3.00$$

10. (10.00) : For the given cell,



and balanced reaction is



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{x}{1}$$

$$\Rightarrow E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{T}{nF} \ln x$$

$$\Rightarrow 2.67 = 2.70 - \frac{300}{2 \times 11500} \ln x$$

$$\Rightarrow 0.03 = \frac{300}{2 \times 11500} \ln x$$

$$\Rightarrow 2.3 = \ln x \quad \therefore x = 10$$

11. (2.22) : From figure 1,

$$n_A = \frac{5 \times 1}{R \times 400} = \frac{5}{400R}$$

$$n_B = \frac{1 \times 3}{R \times 300} = \frac{3}{300R} = \frac{1}{100R}$$

Figure 2 - After the system attains equilibrium,

$$P_A = P_B \text{ and } T_A = T_B = T$$

$$\therefore \frac{n_A RT}{V_A} = \frac{n_B RT}{V_B}$$

$$\Rightarrow \frac{5}{400 RV_A} = \frac{1}{100 RV_B} \Rightarrow \frac{V_A}{V_B} = \frac{5}{4} \Rightarrow V_B = \frac{4}{5} V_A$$

$$\therefore V_A + V_B = 4 \text{ m}^3 \Rightarrow V_A + \frac{4}{5} V_A = 4$$

$$\Rightarrow V_A = \frac{20}{9} = 2.22 \text{ m}^3$$

12. (19.00) :  $p_A^\circ = 20 \text{ Torr}$

For equimolar binary solution :  $x_A = x_B = \frac{1}{2}$

$$\therefore \frac{p_A^\circ + p_B^\circ}{2} = 45 \Rightarrow p_B^\circ = 70 \text{ Torr}$$

If mole fractions are  $x_A$  and  $x_B$  then according to Dalton's law of partial pressures,

$$p_B^\circ + (p_A^\circ - p_B^\circ)x_A = 22.5$$

$$\Rightarrow 70 + (20 - 70)x_A = 22.5$$

$$\Rightarrow x_A = \frac{47.5}{50} \text{ and } x_B = \frac{2.5}{50}$$

$$\frac{x_A}{x_B} = \frac{47.5}{2.5} = 19.00$$

13. (4.47) :  $AB_{(s)} \rightleftharpoons A_{(aq)}^+ + B_{(aq)}^-$

$$B^- + H^+ \rightleftharpoons HB \quad (\text{given, pH} = 3)$$

$$K_a \text{ of HB} = 1 \times 10^{-8}$$

$$K_a = \frac{[H^+][B^-]}{[HB]} = 10^{-8} = \frac{10^{-3} \times (s-x)}{x}$$

$$\frac{s-x}{x} = 10^{-5} \Rightarrow s-x = x \times 10^{-5}$$

$$K_{sp} = [A^+][B^-] \Rightarrow 2 \times 10^{-10} = s(s-x)$$

$$\Rightarrow sx = 2 \times 10^{-10} \text{ and } s^2 - sx = 2 \times 10^{-10}$$

$$s^2 = 2 \times 10^{-10} + 2 \times 10^{-10}$$

$$s^2 = 2 \times 10^{-10} \therefore s = 4.47 \times 10^{-5}$$

14. (0.05) : When NaCl as solute is used

For solvent X; For solvent Y;

$$2 = 2K_b m$$

$$1 = 2 \times K'_b m$$

$$\therefore \frac{K_b}{K'_b} = 2$$

When solute S is used then molality in both the solvents is equal.

For solvent X; For solvent Y;

$$i = 1 - \frac{\alpha}{2}$$

$$i = 1 - \frac{0.7}{2} = 0.65$$

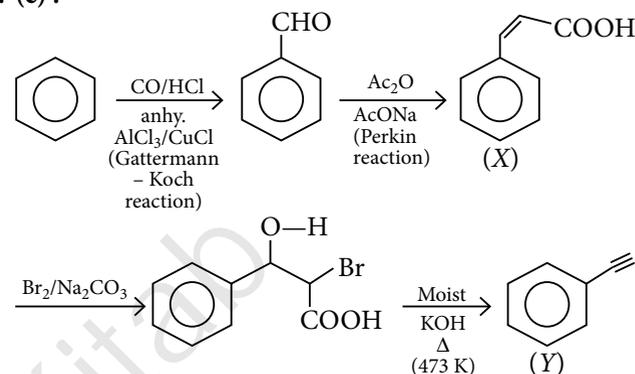
$$\Delta T_b = \left(1 - \frac{\alpha}{2}\right) K_b m \quad \Delta T'_b = (0.65) K'_b m$$

$$3 = \frac{\Delta T_b}{\Delta T'_b} = \frac{\left(1 - \frac{\alpha}{2}\right) \times 2}{0.65}$$

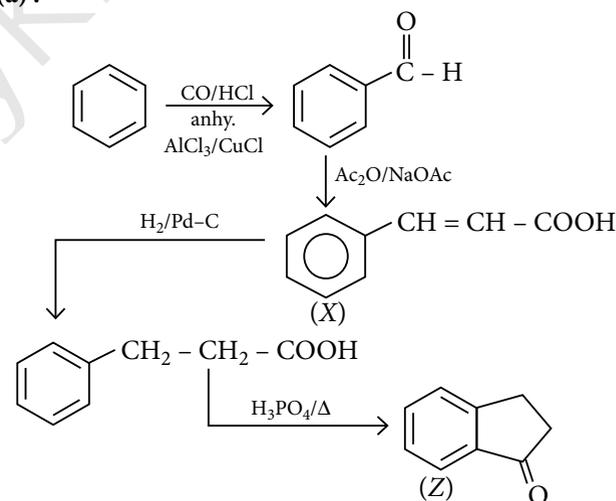
$$1 - \frac{\alpha}{2} = \frac{3}{2} \times 0.65 \Rightarrow \frac{\alpha}{2} = 1 - \frac{3}{2} \times 0.65$$

$$\therefore \alpha = 0.05$$

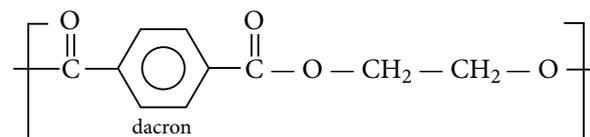
15. (c) :



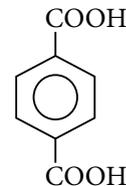
16. (a) :



17. (a) :  $(C_{11}H_{12}O_2) \xrightarrow{\text{oxidation}}$  dibasic acid  $\begin{matrix} \text{CH}_2 - \text{CH}_2 \\ | \quad | \\ \text{OH} \quad \text{OH} \\ \text{H}^+ \end{matrix}$

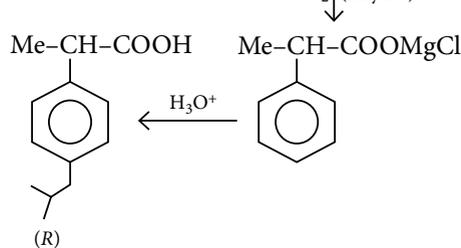
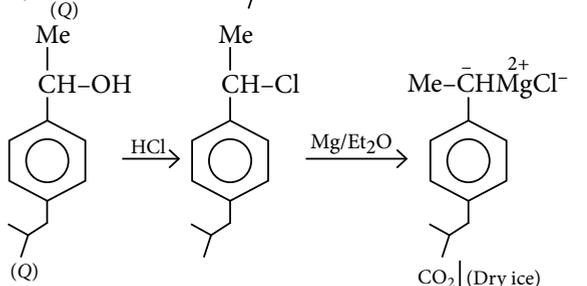
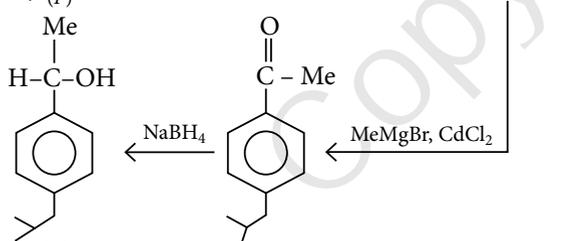
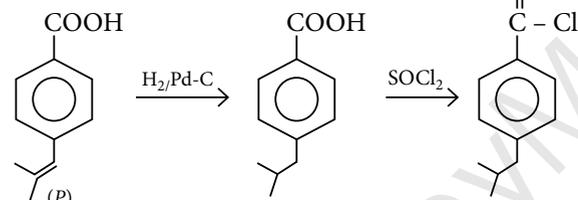
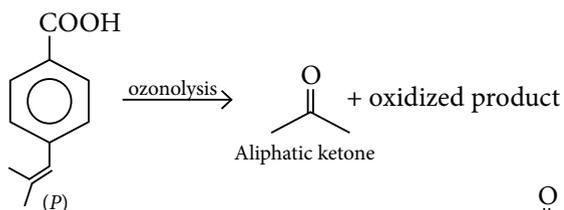
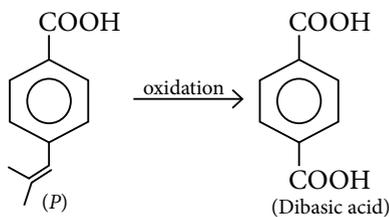
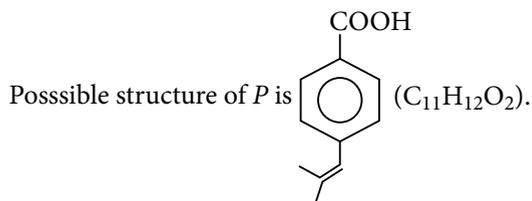


Dibasic acid must be terephthalic acid *i.e.*,

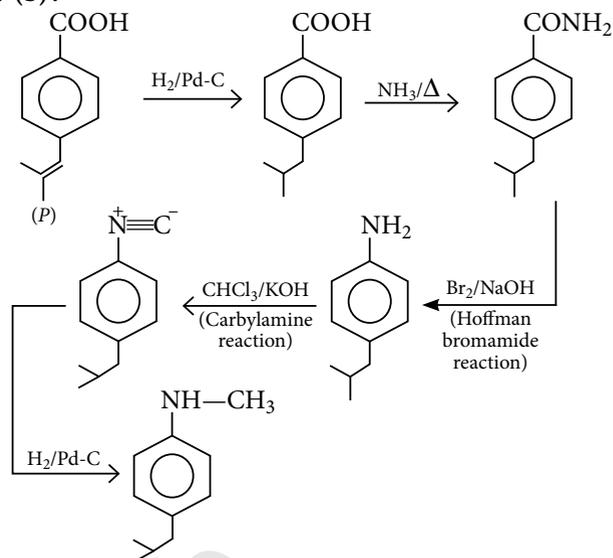


To give dacron, compound *P* must have benzene based structure.

$C_{11}H_{12}O_2 \xrightarrow{\text{Ozonolysis}}$  ketone + oxidized products of benzene.

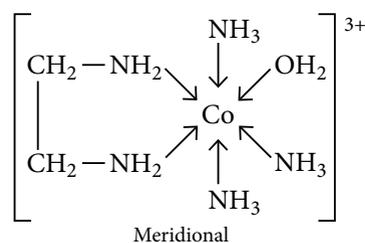
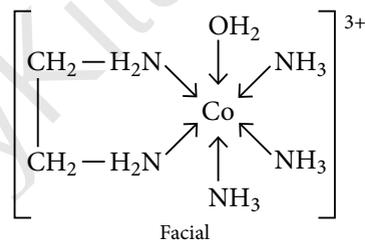


18. (b):

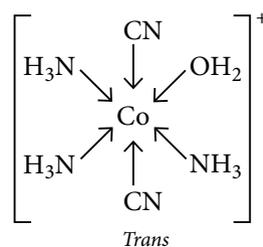
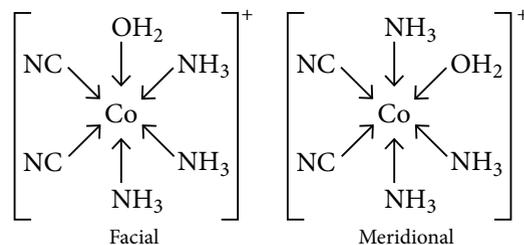


### PAPER-2

1. (a, b, d) : (a)  $[Co(en)(NH_3)_3(H_2O)]^{3+}$

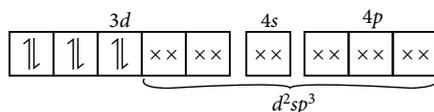


(b)  $[Co(CN)_2(NH_3)_3(H_2O)]^+$



(c)  $\text{Co}^{3+} : [\text{Ar}]3d^6$  in presence of *en* and  $\text{NH}_3$  it forms low spin complex.

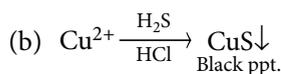
$\text{Co}^{3+}$  in  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$ :



Due to absence of unpaired electron, this complex is diamagnetic in nature.

(d)  $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$  has larger energy gap between  $t_{2g}$  and  $e_g$  than  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  as  $\text{NH}_3$  is stronger ligand than  $\text{H}_2\text{O}$ . So,  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  absorbs longer wavelength than  $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$ .

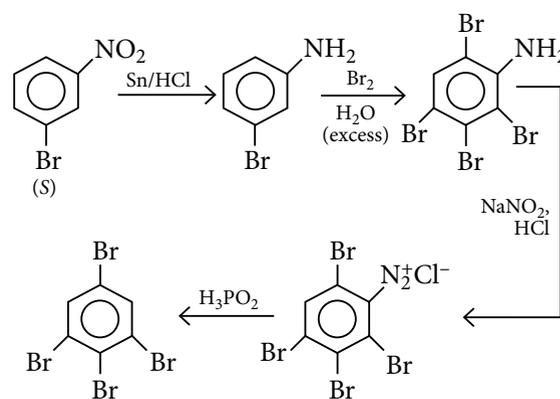
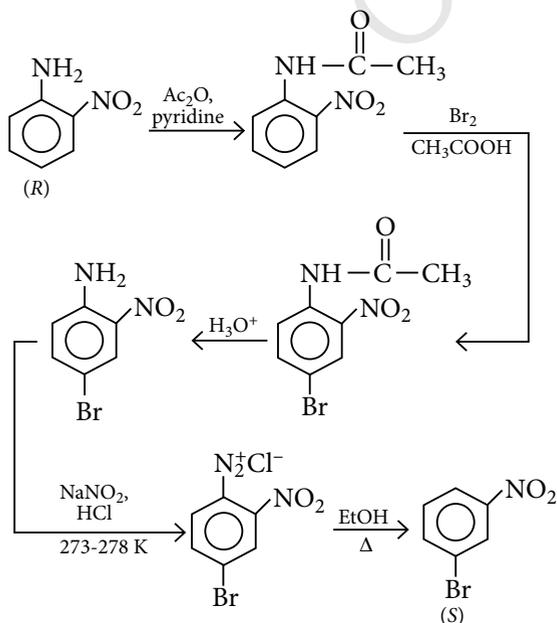
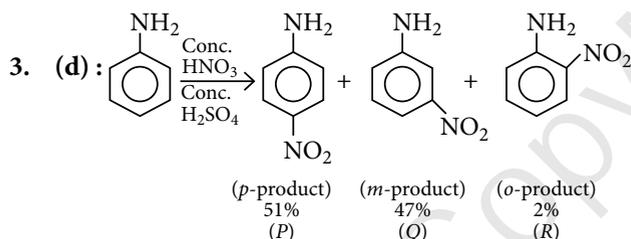
2. (b, d): (a) Manganese show pale purple colour in flame test.



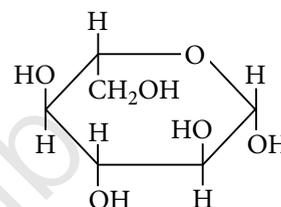
(c) Both  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  form precipitate with  $\text{H}_2\text{S}$  in basic medium.

(d)  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$ ,

$E^\circ_{\text{Mn}^{2+}/\text{Mn}} = -1.18 \text{ V}$



4. (d): Structure of  $\beta$ -L-glucopyranose is



5. (a, d):  $A(g) \xrightarrow{\text{First order}} 2B(g) + C(g); V = \text{constant}$

$T = 300 \text{ K}$

$t = 0$      $P_0$                       0            0

$t = t_{1/3}$      $\left(P_0 - \frac{2P_0}{3}\right) = \frac{P_0}{3}$      $\frac{4P_0}{3}$      $\frac{2P_0}{3}$

$t = t$          $P_0 - x$                      $2x$          $x$

So,  $P_t = P_0 - x + 2x + x = P_0 + 2x$

or  $2x = P_t - P_0$

$t = \frac{1}{k} \ln \frac{P_0}{(P_0 - x)}$

or  $t = \frac{1}{k} \ln \frac{P_0}{P_0 - \frac{(P_t - P_0)}{2}} = \frac{1}{k} \ln \frac{2P_0}{2P_0 - P_t + P_0}$

or  $kt = \ln \frac{2P_0}{3P_0 - P_t}$ ,  $kt = \ln 2P_0 - \ln (3P_0 - P_t)$

or  $\ln (3P_0 - P_t) = -kt + \ln 2P_0$

Comparing the above equation with general straight line equation we get, slope =  $-k$ , intercept =  $\ln 2P_0$

So, (a) is correct option.

Now,  $t_{1/3} = \frac{1}{k} \ln \frac{P_0}{(P_0/3)} = \frac{1}{k} \ln 3$

$\Rightarrow$  It is independent of initial concentration.

So, (b) is wrong option.

For first order reaction, rate constant is independent of initial concentration.

So, graph (d) is correct.

6. (a, c):  $\frac{\ln K_1}{\ln K_2} > \frac{T_2}{T_1}$

On increasing temperature, concentration of product decreases and hence,  $K$  decreases.

Since, reaction is exothermic, therefore,  $\Delta H^\circ < 0$

From the graph,

$$[P]_{\text{eq}} > 5, [A]_{\text{eq}} < 5$$

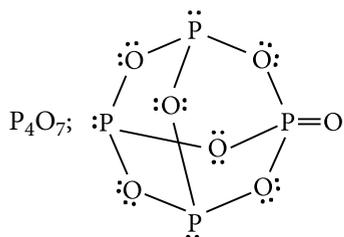
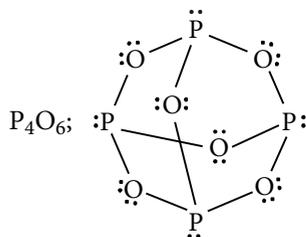
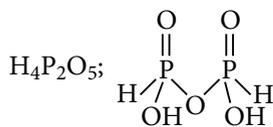
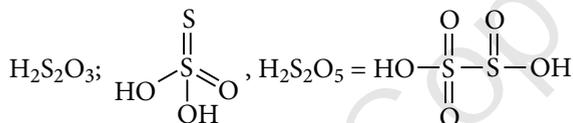
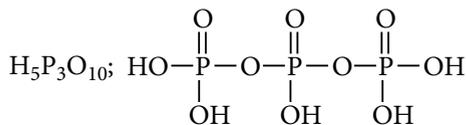
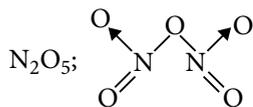
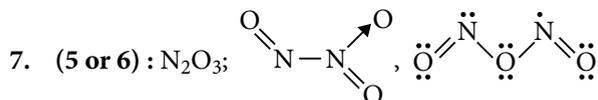
$$K_{\text{eq}} = \frac{[P]}{[A]} > 1$$

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \Rightarrow \Delta G^\circ < 0$$

$$\frac{\ln K_1}{\ln K_2} = \frac{\frac{-\Delta H^\circ}{T_1 R} + \frac{\Delta S^\circ}{R}}{\frac{-\Delta H^\circ}{T_2 R} + \frac{\Delta S^\circ}{R}} > \frac{T_2}{T_1}$$

$$\frac{(-\Delta H^\circ + T_1 \Delta S^\circ) T_2}{(-\Delta H^\circ + T_2 \Delta S^\circ) T_1} > \frac{T_2}{T_1}$$

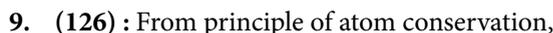
$$-\Delta H^\circ + T_1 \Delta S^\circ > -\Delta H^\circ + T_2 \Delta S^\circ \Rightarrow \Delta S^\circ < 0$$



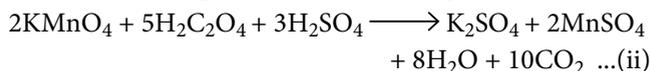
3 moles of  $\text{O}_2$  produce 3 moles of lead.

96 kg of oxygen produce 621 kg of lead.

$$1 \text{ kg of oxygen produce } \frac{621}{96} = 6.468 = 6.47 \text{ kg}$$



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



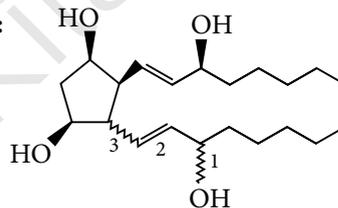
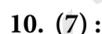
meq of  $\text{KMnO}_4 = \text{meq of oxalic acid}$

$$x \times 5 = \left( \frac{225}{90} \right) \times 2 \Rightarrow x = 1$$

( $\therefore$  mass of oxalic acid added = 225 mg)

$\therefore$  mmoles of  $\text{MnCl}_2 = 1$

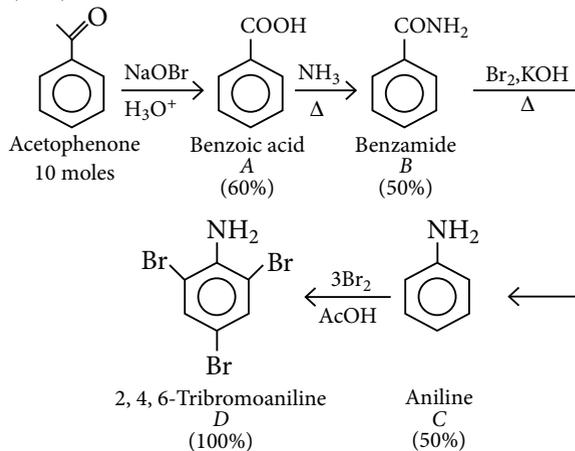
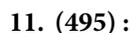
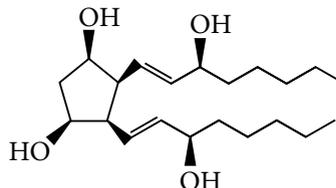
mg of  $\text{MnCl}_2 = (55 + 71) = 126 \text{ mg}$



Stereochemistry around these three centres can vary.

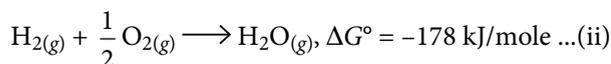
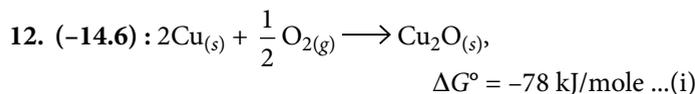
$\therefore$  Total isomers =  $2^3 = 8$

Out of these eight possible isomers, one isomer will be optically inactive.

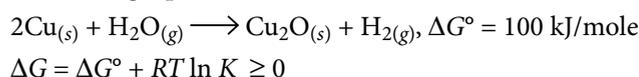


$$\begin{aligned} \text{Yield of } D \text{ in moles} &= 10 \times \frac{60}{100} \times \frac{50}{100} \times \frac{50}{100} \\ &= 1.5 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{Amount of } D &= \text{Number of moles} \times \text{Molecular weight} \\ &= 1.5 \times 330 = 495 \end{aligned}$$



Subtracting eqn. (ii) from (i)



$$\Rightarrow 10^5 + 8 \times 1250 \ln \left( \frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right) \geq 0$$

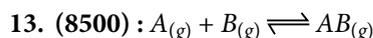
$$10^4 \ln \left( \frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right) + 10^5 \geq 0$$

$$\ln p_{\text{H}_2} - \ln p_{\text{H}_2\text{O}} \geq -10$$

$$\text{Now, } \ln p_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}} \times P_{\text{Total}} = 0.01 \times 1 = 10^{-2}$$

$$\therefore \ln p_{\text{H}_2} + 2 \ln 10 \geq -10$$

$$\ln p_{\text{H}_2} + 4.6 \geq -10 \Rightarrow \ln p_{\text{H}_2} \geq -14.60$$



$$\text{Given, } E_{a_b} - E_{a_f} = 2RT \text{ and } \frac{A_f}{A_b} = 4 \Rightarrow K_{eq} = \frac{K_f}{K_b}$$

$$\text{Also, } K_f = A_f e^{-E_{a_f}/RT} \dots(i)$$

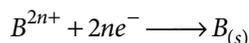
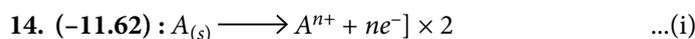
$$K_b = A_b e^{-E_{a_b}/RT} \dots(ii)$$

$$\text{Now, } \frac{K_f}{K_b} = \frac{A_f}{A_b} e^{(E_{a_b} - E_{a_f})/RT}$$

$$\text{or } K_{eq} = 4e^{2RT/RT}; \quad K_{eq} = 4e^2$$

$$\begin{aligned} \Delta G^\circ &= -RT \ln K_{eq} = -RT \ln(4e^2) = -RT(2 + \ln 4) \\ &= -2500(2 + 2 \times 0.7) = -8500 \text{ J mol}^{-1} \end{aligned}$$

$\therefore$  Absolute value of  $\Delta G^\circ$  is 8500.



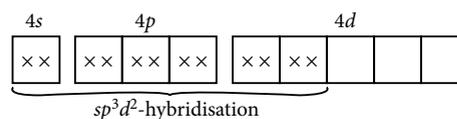
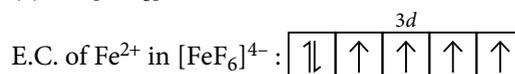
$$\text{Given, } \Delta H^\circ = 2\Delta G^\circ, E_{\text{cell}} = 0$$

$$\text{As, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \therefore \Delta G^\circ = 2\Delta G^\circ - T\Delta S^\circ$$

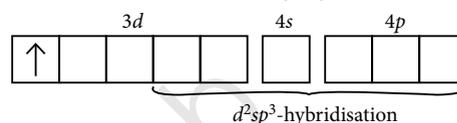
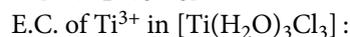
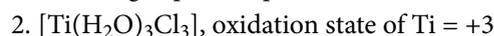
$$\text{or, } \Delta G^\circ = T\Delta S^\circ \text{ or } \Delta S^\circ = \frac{\Delta G^\circ}{T}$$

$$\text{Also, } \Delta S^\circ = \frac{-RT \ln K}{T} = -R \ln \frac{[A^{n+}]^2}{[B^{2n+}]} = -8.3 \times \ln \frac{2^2}{1}$$

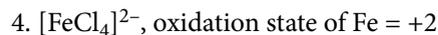
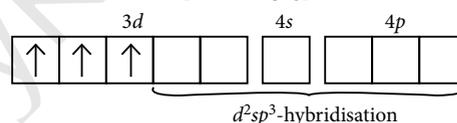
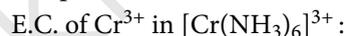
$$\therefore \Delta S^\circ = -11.62 \text{ J K}^{-1} \text{ mol}^{-1}$$



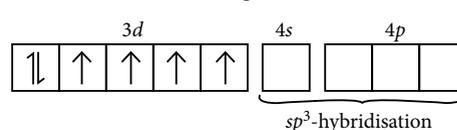
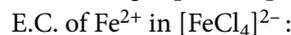
It forms high spin complex because  $\text{F}^-$  is weak field ligand.



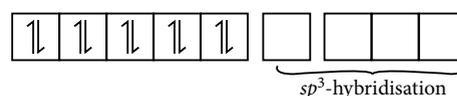
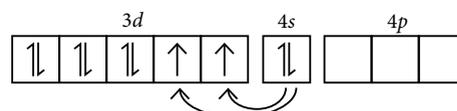
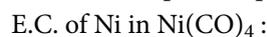
Due to presence of strong field ligand, inner orbital complex is formed.



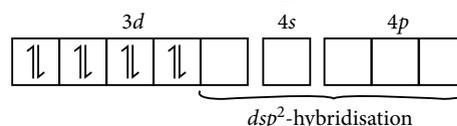
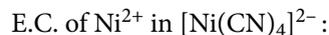
It forms high spin complex as  $\text{Cl}^-$  is weak field ligand.



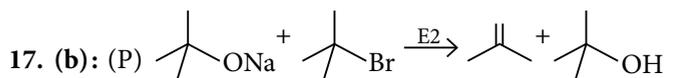
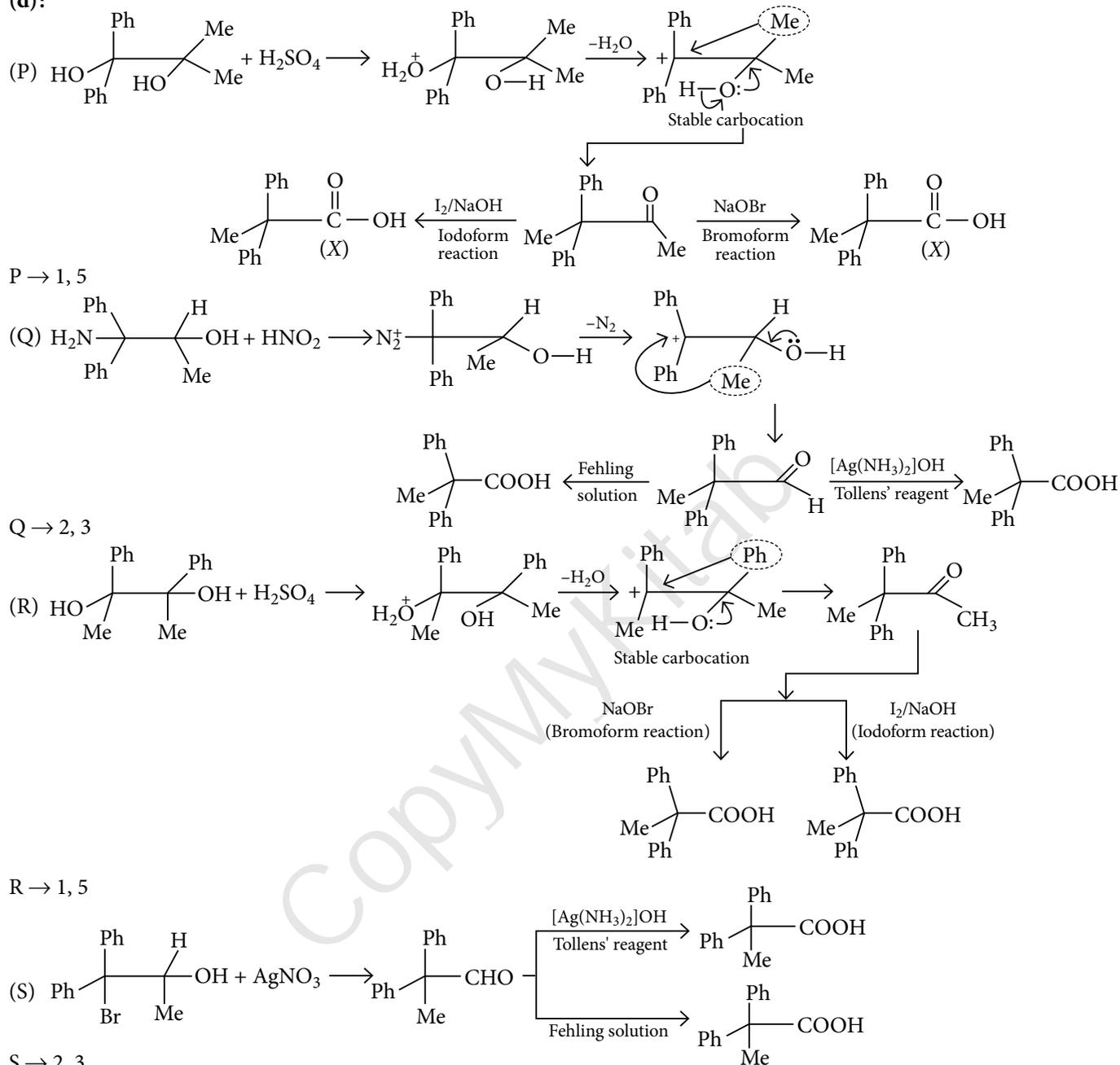
It forms low spin complex as CO is strong field ligand.



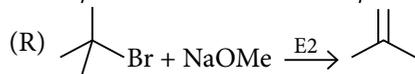
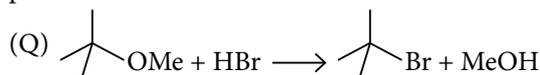
It forms low spin complex as CN is strong field ligand.



16. (d):



With 3° halide and strong base, elimination predominates.



P → 1, 4; Q → 2; R → 4; S → 3

18. (d): (P)  $[\text{CH}_3\text{COOH}]_{\text{old}} = \frac{20 \times 0.1 - 10 \times 0.1}{30} = \frac{1}{30}$

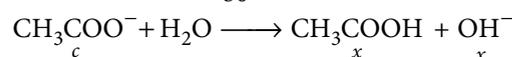
$$[\text{CH}_3\text{COO}^-]_{\text{new}} = \frac{1}{30}$$

Buffer with [Salt] = [Acid]

pH does not change on dilution (P) → (1)

(Q)  $[\text{CH}_3\text{COO}^-]_{\text{old}} = \frac{20 \times 0.1}{40} = \frac{2}{40}$

$$[\text{CH}_3\text{COO}^-]_{\text{new}} = \frac{2}{80}$$



$$K_h = \frac{x^2}{c} = \frac{[\text{OH}^-]_{\text{old}}^2}{2/40} = \frac{[\text{OH}^-]_{\text{new}}^2}{2/80}$$

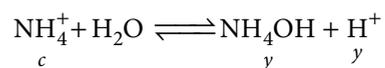
$$\text{or, } [\text{OH}^-]_{\text{new}}^2 = \frac{[\text{OH}^-]_{\text{old}}^2}{2}$$

$$\text{or, } [\text{OH}^-]_{\text{new}} = \frac{[\text{OH}^-]_{\text{old}}}{\sqrt{2}}$$

$$\therefore [\text{H}^+]_{\text{new}} = \sqrt{2}[\text{H}^+]_{\text{old}}$$

(Q)  $\rightarrow$  (5)

$$(R) [\text{NH}_4^+]_{\text{old}} = \frac{20 \times 0.1}{40} = \frac{2}{40}, [\text{NH}_4^+]_{\text{new}} = \frac{2}{80}$$

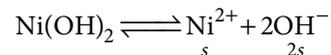


$$K_h = \frac{y^2}{c} = \frac{[\text{H}^+]_{\text{old}}^2}{2/40} = \frac{[\text{H}^+]_{\text{new}}^2}{2/80}$$

$$\text{or } [\text{H}^+]_{\text{new}}^2 = \frac{[\text{H}^+]_{\text{old}}^2}{2} \Rightarrow [\text{H}^+]_{\text{new}} = \frac{[\text{H}^+]_{\text{old}}}{\sqrt{2}}$$

(R)  $\rightarrow$  (4)

(S) For a saturated solution,



$$K_{sp} = s \times (2s)^2 = 4s^3$$

$$s = [\text{OH}^-] = \sqrt[3]{\frac{K_{sp}}{4}}$$

Irrespective of volume of solution,  $[\text{H}^+]$  remains constant.

(S)  $\rightarrow$  (1)

