

1

Some Basic Concepts of Chemistry

Mole Concept

- **One Mole** Avogadro's Number (N_A) = 6.023×10^{23} . It is the number of atoms present in exactly 12 g of (C^{12}) isotope.

- **Atomic Weight (A)** Atomic weight is the relative weight of one atom of an element with respect to a standard weight.

$$A = \frac{\text{Weight of one atom of an element}}{\frac{1}{12} \text{ th part by weight of an atom of } (C^{12}) \text{ isotope}}$$

- **amu (atomic mass unit) Weight**

$$\begin{aligned} 1 \text{ amu} &= \frac{1}{12} \text{ th part by weight of an atom of } (C^{12}) \text{ isotope} \\ &= \frac{1}{N_A} \text{ g} = 1.66 \times 10^{-24} \text{ g} \end{aligned}$$

Atomic weight (A) \times amu = Absolute atomic weight.

NOTE

- Atomic weight is a relative weight that indicates the relative heaviness of one atom of an element with respect to amu weight.
- Atomic weight has no unit because it is the ratio of weights.
- One mole of an amu = 1.00 g.
- **Change of Scale for Atomic Weight** If an amu is defined differently as $(1/x)$ th part by weight of an atom of (C^{12}) isotope rather $(1/12)$ th part then the atomic weight (A') can be derived as :

$$A' = A \left(\frac{x}{12} \right)$$

Where, A = conventional atomic weight

Molecular Weight (MW) Like atomic weight, it is the relative weight of a molecule or a compound with respect to amu weight.

Molecular weight

$$= \frac{\text{Weight of one molecule of a compound}}{\frac{1}{12} \text{ th part by weight of an atom of } C^{12} \text{ isotope}}$$

Gram Atomic, Gram Molecular Weight (M) It is the weight of 1.0 mole (Avogadro's numbers) of atoms, molecules or ions in gram unit.

$$M = A \text{ amu} \times \text{Avogadro number} = A \text{ gram}$$

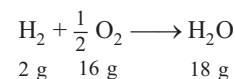
Hence, gram molecular weight (M) is numerically equal to the atomic weight or (molecular weight) in gram unit because

1.0 mole of amu is 1.0 g.

Empirical and Molecular Formula Empirical formula is the simplest formula of a compound with the elements in the simple whole number ratio, and a **molecular formula** is same or a multiple of the empirical formula.
e.g.

Molecular formula	Empirical formula
C_6H_6 (benzene)	CH
$C_6H_{12}O_6$ (glucose)	CH_2O
H_2O_2	HO
$H_2S_2O_8$ (persulphuric acid)	HSO_4

- **Laws of Chemical Combination** Elements combine in a fixed mass ratio, irrespective of their supplied mass ratio, e.g.



Here, H_2 and O_2 combines in a fixed mass ratio of 1 : 8.

No matter in what ratio we mixed hydrogen and oxygen, they will always combine in 1:8 mass ratio (stoichiometric mass ratio).

- **Limiting Reactant** It is the reactant that is consumed completely during a chemical reaction. If the supplied mass ratio of reactants are not stoichiometric ratio, one of the reactant is consumed completely leaving parts of others unreacted. One that is consumed completely is known as limiting reactant.

'Limiting reactant determine the amount of product in a given chemical reaction'

2 Some Basic Concepts of Chemistry

Concentration Units

- **Normality (N)** It is the number of gram equivalent of solute present in one litre of solution :

$$N = \frac{\text{Eq}}{V \text{ (in litres)}}$$

- (i) **Molarity (M)** It is the moles of solute dissolve in one litre of solution.

$$M = \frac{n}{V} : n = \text{Number of moles of solute}$$

($\therefore V =$ Volume of solution in litre)

$$\Rightarrow \text{Molarity } (M) \times \text{Volume } (V) = n \text{ (moles of solute)}$$

If volume is in mL; $MV =$ millimoles

If d (g/cc) is density of a solution and it contains $x\%$ of solute of molar mass M , its molarity can be worked out as

$$\text{Molarity} = \frac{1000 dx}{100 M} = \frac{10dx}{M}$$

- (ii) **Molality (m)** It is the number of moles of solute present in 1.0 kg of solvent.

$$m = \frac{\text{Moles of solute } (n)}{\text{Weight of solvent in gram}} \times 1000$$

NOTE

Molality is a true concentration unit, independent of temperature while molarity depends on temperature.

- (iii) **Normality (N)** It is the number of gram equivalents of solute in one litre of solution.

$$N = \frac{\text{Gram equivalents of solute (Eq)}}{\text{Volume of solution in litre}}$$

- (iv) **Mole Fraction (χ_i)** It is the fraction of moles of a particular component in a mixture as

$$\chi_i = \frac{n_i}{\sum_{i=1}^n n_i}$$

- (v) **ppm (parts per million) Strength** It is defined as parts of solute present in (10^6 part) of solution.

- **Dilution Formula** If a concentrated solution is diluted, following formula work

$$M_1 V_1 = M_2 V_2$$

(M_1 and V_1 are the molarity and volumes before dilution and M_2 and V_2 are molarity and volumes after dilution)

- **Mixing of two or more solutions of different molarities** If two or more solutions of molarities (M_1, M_2, M_3, \dots) are mixed together, molarity of the resulting solution can be worked out as :

$$M = \frac{M_1 V_1 + M_2 V_2 + M_3 V_3 \dots}{V_1 + V_2 + V_3 \dots}$$

Equivalent Concept, Neutralisation and Redox Titration

- **Equivalent Weight** Equivalent weight of an element is that part by weight which combines with 1.0 g of hydrogen or 8.0 g of oxygen or 35.5 g of chlorine.

- (i) Equivalent weight of a salt (EW)

$$= \frac{\text{Molar mass}}{\text{Net positive (or negative) valency}}$$

e.g. Equivalent weight

$$\text{CaCl}_2 = \frac{M}{2}, \text{AlCl}_3 = \frac{M}{3}, \text{Al}_2(\text{SO}_4)_3 = \frac{M}{6}$$

- (ii) Equivalent weight of acids = $\frac{\text{Molar mass}}{\text{Basicity}}$

e.g. Equivalent weight

$$\text{HCl} = M \text{ (basicity} = 1); \text{H}_2\text{SO}_4 = \frac{M}{2} \text{ (basicity} = 2)$$

$$\text{H}_3\text{PO}_4 = \frac{M}{3} \text{ (basicity} = 3)$$

- (iii) Equivalent weight of bases = $\frac{\text{Molar mass}}{\text{Acidity}}$

e.g. Equivalent weight

$$\text{NaOH} = M, \text{Ca(OH)}_2 = \frac{M}{2}, \text{Al(OH)}_3 = \frac{M}{3}$$

- **The number of gram-equivalents (Eq)**

$$\text{Equivalent} = \frac{\text{Weight of compound}}{\text{Equivalent weight}} = \frac{w}{\text{Equivalent weight}}$$

- **Mole Equivalent Relationship** In a given weight (w) of sample, number of moles (n) and number of equivalents (eq) are related as

$$n = \frac{w}{M} \text{ and } \text{Eq} = \frac{w}{\text{Equivalent weight}}$$

\therefore

$$\frac{\text{Eq}}{n} = \frac{M}{\text{Equivalent weight}} = n\text{-factor}$$

- **n -factor** For salt, it is valency, for acid it is basicity, for base it is acidity.

- **Normality/Molarity Relationship**

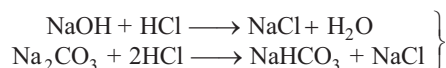
$$N = \frac{\text{Eq}}{V} \text{ and } M = \frac{n}{V} \Rightarrow \frac{N}{M} = \frac{\text{Eq}}{n} = \frac{\text{MW}}{\text{EW}} = n\text{-factor}$$

- **Acid-Base Titration** In acid-base titration, at the 'End Point'.

$$\text{Gram equivalent of acid} = \text{Gram equivalent of base}$$

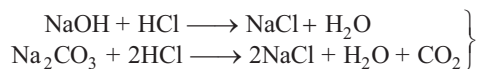
- **Titration of a Mixture of NaOH/ Na_2CO_3** The mixture is analysed by titrating against a standard acid in presence of phenolphthalein and methyl orange indicators.

Phenolphthalein end point occur when the following neutralisation is complete :



1 millimol of (HCl) = 1 millimol of (NaOH + Na₂CO₃)

Methyl orange end point occur when the following neutralisation is complete :



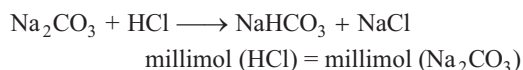
methylorange end point millimol (HCl)

= millimol (NaOH) + 2 millimol of (Na₂CO₃)

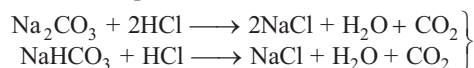
• **Titration of a mixture of NaHCO₃/Na₂CO₃**

The mixture is analysed by titrating against a standard acid in presence of phenolphthalein and methyl orange indicators.

Phenolphthalein end point occur when the following neutralisation is complete :



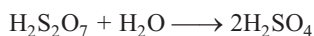
Methyl orange end point occur when the following neutralisation is complete :



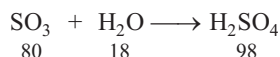
Methyl orange end point millimol (HCl)

= millimol (NaHCO₃) + 2 millimol of (Na₂CO₃)

• **Percentage Strength of Oleum** It is the mass of H₂SO₄ obtained on hydrolysis of 100 g of oleum as :



The net reaction is :

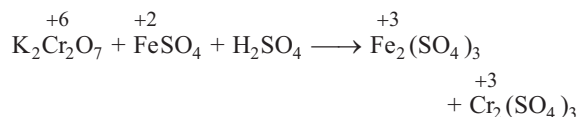


$$\Rightarrow \boxed{\% \text{ of free SO}_3 \text{ in oleum} = \frac{80}{18} (\% \text{ Strength} - 100)}$$

• **Redox Reaction and Redox Titration**

(i) **Oxidation** Loss of electrons or increase in oxidation number is called oxidation.

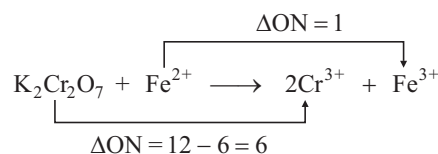
(ii) **Reduction** Gain of electron or decrease in oxidation number is called reduction.



In the above redox reaction, chromium is reduced from (+ 6 to +3) and iron is oxidised from (+ 2 to + 3). Hence, K₂Cr₂O₇ is known as oxidising agent (itself reduced) and FeSO₄ reducing agent (itself oxidised).

Quick Balancing of a Redox Reaction

Cross-multiplication by net change in oxidation number per unit formula of oxidising agent and reducing agent will balance the redox reaction in term of OA and RA as:

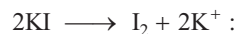
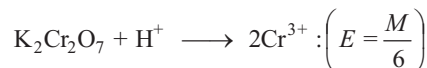
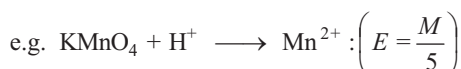


Hence, multiplying Fe²⁺ by 6 and K₂Cr₂O₇ by 1 will balance the reaction in terms of OA and RA.

Disproportionation Reaction It is a special type of redox reaction in which similar species is oxidised as well reduced, e.g. Br₂ + NaOH → NaBr + NaBrO₃. In this reaction, bromine is reduced to bromide ion and the same is oxidised to bromate ion, hence bromine is undergoing disproportionation reaction.

Equivalent Weight of OA / RA

Equivalent weight of OA/RA $= \frac{\text{Molar mass}}{\text{Change in ON per formula unit}}$
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[E = M (ΔON per I⁻ = 1)]



[E = M (ΔON per Na₂S₂O₃ = 1)]

• **n-Factor and Normality/Molarity Relationship**

$$N = \frac{\text{Eq}}{V}$$

and

$$M = \frac{n}{V}$$

⇒

$$\begin{aligned} \frac{N}{M} &= \frac{\text{Eq}}{n} \\ &= \frac{\text{MW}}{\text{EW}} = n\text{-factor} \end{aligned}$$

(n-factor = Change in oxidation number per formula unit).

• **Redox Titration** At the end point:

Gram equivalents of OA = Gram equivalent of RA.

4 Some Basic Concepts of Chemistry

Topic 1 Mole Concept

Objective Questions I (Only one correct option)

- The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (molecular weight = 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resin? (2015 JEE Main)
(a) $\frac{1}{103}$ (b) $\frac{1}{206}$ (c) $\frac{2}{309}$ (d) $\frac{1}{412}$
- 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is (2015 JEE Main)
(a) 18 mg (b) 36 mg (c) 42 mg (d) 54 mg
- The ratio mass of oxygen and nitrogen of a particular gaseous mixture is 1 : 4. The ratio of number of their molecule is (2014 Main)
(a) 1 : 4 (b) 7 : 32 (c) 1 : 8 (d) 3 : 16
- The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2 M HCl will be (2013 Main)
(a) 0.875 M (b) 1.00 M (c) 1.75 M (d) 0.0975M
- Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is (2011)
(a) 1.78 M (b) 2.00 M (c) 2.05 M (d) 2.22 M
- 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 (2009)
(a) 55.85 (b) 55.95 (c) 55.75 (d) 56.05
- Mixture $X = 0.02$ mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 L solution.
1 L of mixture $X +$ excess of $AgNO_3$ solution $\longrightarrow Y$
1 L of mixture $X +$ excess of $BaCl_2$ solution $\longrightarrow Z$
Number of moles of Y and Z are (2003, 1M)
(a) 0.01, 0.01 (b) 0.02, 0.01
(c) 0.01, 0.02 (d) 0.02, 0.02
- Which has maximum number of atoms? (2003, 1M)
(a) 24 g of C (12) (b) 56 g of Fe (56)
(c) 27 g of Al (27) (d) 108 g of Ag (108)
- How many moles of electron weighs 1 kg? (2002, 3M)
(a) 6.023×10^{23} (b) $\frac{1}{9.108} \times 10^{31}$
(c) $\frac{6.023}{9.108} \times 10^{54}$ (d) $\frac{1}{9.108 \times 6.023} \times 10^8$
- The normality of 0.3 M phosphorus acid (H_3PO_3) is (1999, 2M)
(a) 0.1 (b) 0.9 (c) 0.3 (d) 0.6
- In which mode of expression, the concentration of a solution remains independent of temperature? (1988, 1M)
(a) Molarity (b) Normality (c) Formality (d) Molality
- A molal solution is one that contains one mole of solute in (1986, 1M)
(a) 1000 g of solvent (b) 1.0 L of solvent
(c) 1.0 L of solution (d) 22.4 L of solution
- If 0.50 mole of $BaCl_2$ is mixed with 0.20 mole of Na_3PO_4 , the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is (1981, 1M)
(a) 0.70 (b) 0.50 (c) 0.20 (d) 0.10
- 2.76 g of silver carbonate on being strongly heated yields a residue weighing (1979, 1M)
(a) 2.16 g (b) 2.48 g (c) 2.32 g (d) 2.64 g
- When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volumes of hydrogen evolved is (1979, 1M)
(a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 9 : 4
- The largest number of molecules is in (1979, 1M)
(a) 36 g of water (b) 28 g of CO
(c) 46 g of ethyl alcohol (d) 54 g of nitrogen pentoxide (N_2O_5)
- The total number of electrons in one molecule of carbon dioxide is (1979, 1M)
(a) 22 (b) 44 (c) 66 (d) 88
- A gaseous mixture contains oxygen and nitrogen in the ratio of 1:4 by weight. Therefore, the ratio of their number of molecules is (1979, 1M)
(a) 1 : 4 (b) 1 : 8 (c) 7 : 32 (d) 3 : 16

Fill in the Blanks

- The weight of 1×10^{22} molecules of $CuSO_4 \cdot 5H_2O$ is (1991, 1M)
- 3.0 g of a salt of molecular weight 30 is dissolved in 250 g water. The molarity of the solution is (1983, 1M)
- The total number of electrons present in 18 mL of water is (1980, 1M)
- The modern atomic mass unit is based on the mass of (1980, 1M)

Integer Answer Type Questions

23. 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 Adv.)
24. 29.2% (w/W) HCl stock solution has density of 1.25 g mL^{-1} . The molecular weight of HCl is 36.5 g mol^{-1} . The volume (mL) of stock solution required to prepare a 200 mL solution 0.4 M HCl is (2012)

Subjective Questions

25. 20% surface sites have adsorbed N_2 . On heating N_2 gas evolved from sites and were collected at 0.001 atm and 298 K in a container of volume is 2.46 cm^3 . Density of surface sites is $6.023 \times 10^{14} / \text{cm}^2$ and surface area is 1000 cm^2 , find out the number of surface sites occupied per molecule of N_2 . (2005, 3M)
26. In a solution of 100 mL 0.5 M acetic acid, one gram of active charcoal is added, which adsorbs acetic acid. It is found that the concentration of acetic acid becomes 0.49 M. If surface area of charcoal is $3.01 \times 10^2 \text{ m}^2$, calculate the area occupied by single acetic acid molecule on surface of charcoal. (2003)
27. Find the molarity of water. Given: $\rho = 1000 \text{ kg/m}^3$ (2003)
28. 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 $0.75 \text{ cm}^3/\text{g}$. If the virus is considered to be a single particle, find its molar mass. (1999, 3M)
29. $8.0575 \times 10^{-2} \text{ kg}$ of Glauber's salt is dissolved in water to obtain 1 dm^3 of solution of density 1077.2 kg m^{-3} . Calculate the molality, molarity and mole fraction of Na_2SO_4 in solution. (1994, 3M)
30. A is a binary compound of a univalent metal. 1.422 g of A reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid B , that forms a hydrated double salt, C with $Al_2(SO_4)_3$. Identify A , B and C . (1994, 2M)
31. Upon mixing 45.0 mL 0.25 M lead nitrate solution with 25.0 mL of a 0.10 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentrations of species left behind in the final solution. Assume that lead sulphate is completely insoluble. (1993, 3M)
32. Calculate the molality of 1.0 L solution of 93% H_2SO_4 , (weight/volume). The density of the solution is 1.84 g/mL . (1990, 1M)
33. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the weight of the residue was constant. If the loss in weight is 28.0 per cent, find the amount of lead nitrate and sodium nitrate in the mixture. (1990, 4M)
34. n -butane is produced by monobromination of ethane followed by Wurtz's reaction. Calculate volume of ethane at NTP required to produce 55 g n -butane, if the bromination takes place with 90% yield and the Wurtz's reaction with 85% yield. (1989, 3M)
35. A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate (i) molal concentration and (ii) mole fraction of sugar in syrup. (1988, 2M)
36. An unknown compound of carbon, hydrogen and oxygen contains 69.77% C and 11.63% H and has a molecular weight of 86. It does not reduce Fehling's solution but forms a bisulphate addition compound and gives a positive iodoform test. What is the possible structure(s) of unknown compound? (1987, 3M)
37. The density of a 3 M sodium thiosulphate solution ($Na_2S_2O_3$) 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 $S_2O_3^{2-}$ ions. (1983, 5M)
38. (a) 1.0 L 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 L. The volumes are measured under the same conditions. Find the composition of mixture by volume.
(b) A compound contains 28 per cent of nitrogen and 72 per cent of a metal by weight. 3 atoms of metal combine with 2 atoms of nitrogen. Find the atomic weight of metal. (1980, 5M)
39. 5.00 mL of a gas containing only carbon and hydrogen were mixed with an excess of oxygen (30 mL) and the mixture exploded by means of electric spark. After explosion, the volume of the mixed gases remaining was 25 mL. On adding a concentrated solution of KOH, the volume further diminished to 15 mL, the residual gas being pure oxygen. All volumes have been reduced to NTP. Calculate the molecular formula of the hydrocarbon gas. (1979, 3M)
40. In the analysis of 0.5 g sample of feldspar, a mixture of chlorides of sodium and potassium is obtained, which weighs 0.1180 g. Subsequent treatment of the mixed chlorides with silver nitrate gives 0.2451 g of silver chloride. What is the percentage of sodium oxide and potassium oxide in the sample? (1979, 5M)
41. The vapour density (hydrogen = 1) of a mixture consisting of NO_2 and N_2O_4 is 38.3 at 26.7°C . Calculate the number of moles of NO_2 in 100 g of the mixture. (1979, 5M)
42. Accounts for the following. Limit your answer to two sentences, "Atomic weights of most of the elements are fractional". (1979, 1M)
43. Naturally occurring boron consists of two isotopes whose atomic weights are 10.01 and 11.01. The atomic weight of natural boron is 10.81. Calculate the percentage of each isotope in natural boron. (1978, 2M)

6 Some Basic Concepts of Chemistry

Topic 2 Equivalent Concept, Neutralisation and Redox Titration

Objective Questions I (Only one correct option)

- From the following statements regarding H_2O_2 choose the incorrect statement. (2015 Main)
(a) It can act only as an oxidising agent
(b) It decomposed on exposure to light
(c) It has to be stored in plastic or wax lined glass bottles in dark
(d) It has to be kept away from dust
- Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is (2007, 3M)
(a) 3 (b) 4 (c) 5 (d) 6
- In the standardisation of $\text{Na}_2\text{S}_2\text{O}_3$ using $\text{K}_2\text{Cr}_2\text{O}_7$ by iodometry, the equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ is (2001, 1M)
(a) (molecular weight)/2
(b) (molecular weight)/6
(c) (molecular weight)/3
(d) same as molecular weight
- The reaction, $3\text{ClO}^-(aq) \longrightarrow \text{ClO}_3^-(aq) + 2\text{Cl}^-(aq)$ is an example of (2001)
(a) oxidation reaction
(b) reduction reaction
(c) disproportionation reaction
(d) decomposition reaction
- An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is (2001, 1M)
(a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL
- Among the following, the species in which the oxidation number of an element is +6 (2000)
(a) MnO_4^- (b) $\text{Cr}(\text{CN})_6^{3-}$
(c) NiF_6^{2-} (d) CrO_2Cl_2
- The oxidation number of sulphur in S_8 , S_2F_2 , H_2S respectively, are (1999)
(a) 0, +1 and -2 (b) +2, +1 and -2
(c) 0, +1 and +2 (d) -2, +1 and -2
- The number of moles of KMnO_4 that will be needed to react completely with one mole of ferrous oxalate in acidic medium is (1997)
(a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) 1
- The number of moles of KMnO_4 that will be needed to react with one mole of sulphite ion in acidic solution is (1997)
(a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) 1

- For the redox reaction



The correct coefficients of the reactants for the balanced reaction are

- | | | | | |
|-----|------------------|-----------------------------|--------------|--------|
| | MnO_4^- | $\text{C}_2\text{O}_4^{2-}$ | H^+ | (1992) |
| (a) | 2 | 5 | 16 | |
| (b) | 16 | 5 | 2 | |
| (c) | 5 | 16 | 2 | |
| (d) | 2 | 16 | 5 | |

- The volume strength of 1.5 N H_2O_2 is (1990, 1M)
(a) 4.8 (b) 8.4 (c) 3.0 (d) 8.0
- The oxidation number of phosphorus in $\text{Ba}(\text{H}_2\text{PO}_2)_2$ is (1988)
(a) +3 (b) +2 (c) +1 (d) -1
- The equivalent weight of MnSO_4 is half of its molecular weight, when it converts to (1988, 1M)
(a) Mn_2O_3 (b) MnO_2 (c) MnO_4^- (d) MnO_4^{2-}

Objective Question II (More than one correct option)

- For the reaction, $\text{I}^- + \text{ClO}_3^- + \text{H}_2\text{SO}_4 \longrightarrow \text{Cl}^- + \text{HSO}_4^- + \text{I}_2$ the correct statement(s) in the balanced equation is/are
(a) stoichiometric coefficient of HSO_4^- is 6 (2014 Adv)
(b) iodide is oxidised
(c) sulphur is reduced
(d) H_2O is one of the products

Assertion and Reason

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

- (a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.
- Statement I** 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 II Two moles of HCl are required for the complete neutralisation of one mole of Na_2CO_3 . (1991, 2M)

Fill in the Blanks

- The compound $\text{YBa}_2\text{Cu}_3\text{O}_7$, which shows super conductivity, has copper in oxidation state Assume that the rare earth element yttrium is in its usual +3 oxidation state. (1994, 1M)

Integer Answer Type Questions

17. 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)
18. 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)
19. A student performs a titration with different burettes and finds titrate values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titrate value is (2010)

Subjective Questions

20. Calculate the amount of calcium oxide required when it reacts with 852 g of P_4O_{10} . (2005, 2M)
21. 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)
22. How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper (II) carbonate? (1999, 3M)
23. 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 decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution. (1998, 5M)
24. To a 25 mL H_2O_2 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 H_2O_2 solution. (1997, 5M)
25. 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 dilute solution, after complete extraction of the iodine required 12.80 mL of 0.25 M KMnO_4 solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+} . Calculate the percentage of Fe_2O_3 and Fe_3O_4 in the original sample. (1996, 5M)
26. 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, 4M)
27. A 5.0 cm³ solution of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP. (1995, 3M)
28. 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 $\text{KIO}_3 + 2\text{KI} + 6\text{HCl} \longrightarrow 3\text{ICl} + 3\text{KCl} + 3\text{H}_2\text{O}$ (1992, 4M)
29. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is gently heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123.9 mL. A 1.5 g of the same sample requires 150 mL of (M/10) HCl for complete neutralisation. Calculate the percentage composition of the components of the mixture. (1992, 5M)
30. A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100.0 mL. An aliquot of 25.0 mL of this solution requires for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. (1991, 4M)
31. A solution of 0.2 g of a compound containing Cu^{2+} and $\text{C}_2\text{O}_4^{2-}$ ions on titration with 0.02 M KMnO_4 in presence of H_2SO_4 consumes 22.6 mL of the oxidant. The resultant solution is neutralised with Na_2CO_3 , acidified with dilute acetic acid and treated with excess KI. The liberated iodine requires 11.3 mL of 0.05 M $\text{Na}_2\text{S}_2\text{O}_3$ solution for complete reduction. Find out the mole ratio of Cu^{2+} to $\text{C}_2\text{O}_4^{2-}$ in the compound. Write down the balanced redox reactions involved in the above titrations. (1991, 5M)
32. A mixture of $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) and NaHC_2O_4 weighing 2.02 g was dissolved in water and the solution made up to one litre. Ten millilitres of the solution required 3.0 mL of 0.1 N sodium hydroxide solution for complete neutralisation. In another experiment, 10.0 mL of the same solution, in hot dilute sulphuric acid medium, required 4.0 mL of 0.1 N potassium permanganate solution for complete reaction. Calculate the amount of $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 in the mixture. (1990, 5M)
33. An organic compound X on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures Y and Z. Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound while Z on similar treatment gives ethanal. Find out the molecular formula of X and gives the structure of Y and Z. (1989, 5M)

8 Some Basic Concepts of Chemistry

- 34.** An equal volume of a reducing agent is titrated separately with 1 M KMnO_4 in acid, neutral and alkaline medium. The volumes of KMnO_4 required are 20 mL in acid, 33.3 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of manganese in each reduction product. Give the balanced equations for all the three half reaction. 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, 5M)
- 35.** 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 $4\text{Fe}^{3+} + \text{N}_2\text{H}_4 \longrightarrow \text{N}_2 + 4\text{Fe}^{2+} + 4\text{H}^+$
 $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$ (1988, 3M)
- 36.** 5 mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made up to 2 L. 30 mL of this acid mixture exactly neutralise 42.9 mL of sodium carbonate solution containing one gram of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in 100 mL of water. Calculate the amount in gram of the sulphate ions in solution. (1985, 4M)
- 37.** 2.68×10^{-3} moles of a solution containing an ion A^{n+} require 1.61×10^{-3} moles of MnO_4^- for the oxidation of A^{n+} to $A\text{O}_3^-$ in acidic medium. What is the value of n ? (1984, 2M)
- 38.** 4.08 g of a mixture of BaO and 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 neutralisation. Identify the metal M . (1983, 4M)

Topic 1

- | | | | |
|--------------------------------|------------------|--------------|-----------|
| 1. (d) | 2. (d) | 3. (b) | 4. (a) |
| 5. (c) | 6. (b) | 7. (a) | 8. (a) |
| 9. (d) | 10. (d) | 11. (d) | 12. (a) |
| 13. (d) | 14. (a) | 15. (a) | 16. (a) |
| 17. (a) | 18. (c) | 19. (4.14 g) | 20. (0.4) |
| 21. (6.023×10^{24}) | 22. C-12 isotope | 23. (8) | |
| 24. (8) | | | |

Topic 2

- | | | | |
|---------|---------------|---------|-----------|
| 1. (a) | 2. (d) | 3. (b) | 4. (c) |
| 5. (a) | 6. (d) | 7. (a) | 8. (b) |
| 9. (a) | 10. (a) | 11. (b) | 12. (c) |
| 13. (b) | 14. (a, b, d) | 15. (b) | 16. 7 / 3 |
| 17. (5) | 18. (2) | 19. (3) | |

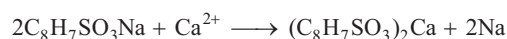
Topic 1 Mole Concept

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

we have to find, mole per gram of resin.

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

Now, reaction looks like



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

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

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

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

2. Given, initial strength of acetic acid = 0.06 N
 Final strength = 0.042 N; Volume given = 50 mL
 \therefore Initial millimoles of $\text{CH}_3\text{COOH} = 0.06 \times 50 = 3$
 Final millimoles of $\text{CH}_3\text{COOH} = 0.042 \times 50 = 2.1$
 \therefore Millimoles of CH_3COOH adsorbed = $3 - 2.1 = 0.9$ mmol
 $= 0.9 \times 60 \text{ mg} = 54 \text{ mg}$

$$3. \frac{n_{\text{O}_2}}{n_{\text{N}_2}} = \frac{\frac{m_{\text{O}_2}}{M_{\text{O}_2}}}{\frac{m_{\text{N}_2}}{M_{\text{N}_2}}}$$

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

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

4. From the formula, $M_f = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$

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

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

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

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

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

Weight of solution = Weight of solvent + Weight of solute
 = $1000 + 120 = 1120 \text{ g}$

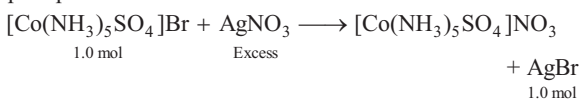
$$\Rightarrow \text{Volume} = \frac{1120 \text{ g}}{1.15 \text{ g/mL}} \times \frac{1}{1000 \text{ mL/L}} = 0.973 \text{ L}$$

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

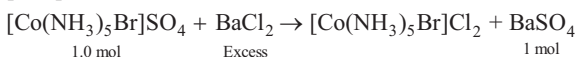
6. From the given relative abundance, the average weight of Fe can be calculated as

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

7. 1.0 L of mixture X contain 0.01 mole of each $[(\text{Co}(\text{NH}_3)_5\text{SO}_4)]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$. Also, with AgNO_3 , only $[(\text{Co}(\text{NH}_3)_5\text{SO}_4)]\text{Br}$ reacts to give AgBr precipitate as



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



Hence, moles of Y and Z are 0.01 each.

8. Number of atoms = Number of moles

\times Avogadro's number (N_A)

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

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

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

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

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

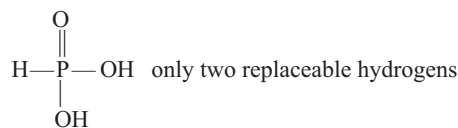
9. Mass of an electron = $9.108 \times 10^{-31} \text{ kg}$

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

$$\therefore 1 \text{ kg} = \frac{1}{9.108 \times 10^{-31}} \text{ electrons} = \frac{10^{31}}{9.108} \times \frac{1}{6.023 \times 10^{23}}$$

$$= \frac{1}{9.108 \times 6.023} \times 10^8 \text{ mole of electrons}$$

10. Phosphorus acid is a dibasic acid as :

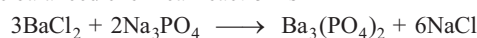


Therefore, normality = molarity \times basicity = $0.3 \times 2 = 0.60$

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

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

13. The balanced chemical reaction is



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

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

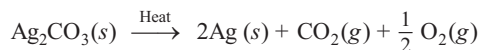
Since, available Na_3PO_4 (0.2 mole) is less than required mole (0.33), it is the limiting reactant and would determine the amount of product $\text{Ba}_3(\text{PO}_4)_2$.

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

\therefore 0.2 mole of Na_3PO_4 would give $\frac{1}{2} \times 0.2$

$$= 0.1 \text{ mole } \text{Ba}_3(\text{PO}_4)_2$$

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

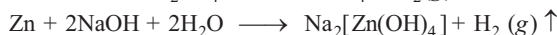
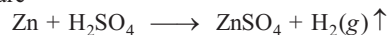


MW = 276 g $2 \times 108 = 216 \text{ g}$

Hence, 2.76 g of Ag_2CO_3 on heating will give

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

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



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

16. Number of molecules present in 36 g of water = $\frac{36}{18} \times N_A = 2N_A$

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

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

Number of molecules present in 54 g of N_2O_5 = $\frac{54}{108} \times N_A = 0.5 N_A$

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

10 Some Basic Concepts of Chemistry

17. In a neutral atom, atomic number represents the number of protons inside the nucleus and equal number of electrons around it. Therefore, the number of total electrons in molecule of CO_2
 = electrons present in one carbon atom
 + 2 × electrons present in one oxygen atom = 6 + 2 × 8 = 22.

18.
$$\frac{\text{Weight of a compound in gram } (w)}{\text{Molar mass } (M)} = \text{Number of moles } (n)$$

$$= \frac{\text{Number of molecules } (N)}{\text{Avogadro number } (N_A)}$$

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

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

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

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

19. Molar mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 = 63.5 + 32 + 4 × 16 + 5 × 18 = 249.5 g

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

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

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

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

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

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

21. Considering density of water to be 1.0 g/mL, 18 mL of water is 18 g (1.0 mol) of water and it contain Avogadro number of molecules. Also one molecule of water contain
 2 × (one from each H-atom) + 8 × (from oxygen atom)
 = 10 electrons.
 \Rightarrow 1.0 mole of H_2O contain = $10 \times 6.023 \times 10^{23}$
 = 6.023×10^{24} electrons.

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

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

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

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

$$\text{Let volume of solution} = 1000 \text{ mL} = \text{Volume of solvent}$$

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

Since, molarity of solution is 3.2 molar

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

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

Hence, correct integer is (8).

24. Mass of HCl in 1.0 mL stock solution

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

Mass of HCl required for 200 mL 0.4 M HCl

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

\therefore 0.365 g of HCl is present in 1.0 mL stock solution.

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

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

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

From ideal gas law : $pV = nRT$

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

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

Now, total surface sites available

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

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

$$= 2 \times 6.023 \times 10^{16}$$

\Rightarrow Sites occupied per molecules

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

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

millimol of CH_3COOH remaining after adsorption

$$= 100 \times 0.49 = 49$$

\Rightarrow millimol of CH_3COOH adsorbed = 50 – 49 = 1

\Rightarrow number of molecules of CH_3COOH adsorbed

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

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

$$= 5 \times 10^{-19} \text{ m}^2$$

27. Mass of 1.0 L water = 1000 g

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

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

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

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

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

\Rightarrow Molar mass of virus

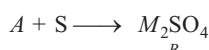
$$= \text{Mass of one virus} \times \text{Avogadro's number}$$

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

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

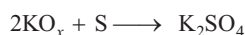
29. Molar mass of Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)
 $= 23 \times 2 + 32 + 64 + 10 \times 18 = 322 \text{ g}$
 \Rightarrow Mole of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in 1.0 L solution $= \frac{80.575}{322} = 0.25$
 \Rightarrow Molarity of solution $= 0.25 \text{ M}$
 Also, weight of 1.0 L solution $= 1077.2 \text{ g}$
 weight of Na_2SO_4 in 1.0 L solution $= 0.25 \times 142 = 35.5 \text{ g}$
 \Rightarrow Weight of water in 1.0 L solution $= 1077.2 - 35.5 = 1041.7 \text{ g}$
 \Rightarrow Molality $= \frac{0.25}{1041.7} \times 1000 = 0.24 \text{ m}$
 Mole fraction of $\text{Na}_2\text{SO}_4 = \frac{\text{Mole of Na}_2\text{SO}_4}{\text{Mole of Na}_2\text{SO}_4 + \text{Mole of water}}$
 $= \frac{0.25}{0.25 + \frac{1041.7}{18}} = 4.3 \times 10^{-3}$.

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



- \therefore 0.321 g sulphur gives 1.743 g of $M_2\text{SO}_4$
 \therefore 32.1 g S (one mole) will give 174.3 g $M_2\text{SO}_4$
 Therefore, molar mass of $M_2\text{SO}_4 = 174.3 \text{ g}$
 $\Rightarrow 174.3 = 2 \times \text{Atomic weight of } M + 32.1 + 64$
 \Rightarrow Atomic weight of $M = 39$, metal is potassium (K)
 K_2SO_4 on treatment with aqueous $\text{Al}_2(\text{SO}_4)_3$ gives potash-alum.
 $\text{K}_2\text{SO}_4 + \text{Al}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

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



- $\Rightarrow x = 2$, i.e. *A* is K_2O .

31. The reaction involved is
 $3\text{Pb}(\text{NO}_3)_2 + \text{Cr}_2(\text{SO}_4)_3 \longrightarrow 3\text{PbSO}_4(s) \downarrow + 2\text{Cr}(\text{NO}_3)_3$
 millimol of $\text{Pb}(\text{NO}_3)_2$ taken $= 45 \times 0.25 = 11.25$
 millimol of $\text{Cr}_2(\text{SO}_4)_3$ taken $= 2.5$
 Here, chromic sulphate is the limiting reagent, it will determine the amount of product.
 \therefore 1 mole $\text{Cr}_2(\text{SO}_4)_3$ produces 3 moles PbSO_4 .
 \therefore 2.5 millimol $\text{Cr}_2(\text{SO}_4)_3$ will produce 7.5 millimol PbSO_4 .
 Hence, mole of PbSO_4 precipitate formed $= 7.5 \times 10^{-3}$
 Also, millimol of $\text{Pb}(\text{NO}_3)_2$ remaining unreacted
 $11.25 - 7.50 = 3.75$
 \Rightarrow Molarity of $\text{Pb}(\text{NO}_3)_2$ in final solution
 $= \frac{\text{millimol of Pb}(\text{NO}_3)_2}{\text{Total volume}} = \frac{3.75}{70} = 0.054 \text{ M}$

Also, millimol of $\text{Cr}(\text{NO}_3)_2$ formed
 $= 2 \times \text{millimol of Cr}_2(\text{SO}_4)_3 \text{ reacted}$
 \Rightarrow Molarity of $\text{Cr}(\text{NO}_3)_2 = \frac{5}{70} = 0.071 \text{ M}$

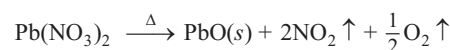
32. 93% H_2SO_4 solution weight by volume indicates that there is 93 g H_2SO_4 in 100 mL of solution.

If we consider 100 mL solution, weight of solution $= 184 \text{ g}$
 Weight of H_2O in 100 mL solution $= 184 - 93 = 91 \text{ g}$

$$\Rightarrow \text{Molality} = \frac{\text{Moles of solute}}{\text{Weight of solvent (g)}} \times 1000$$

$$= \frac{93}{98} \times \frac{1000}{91} = 10.42$$

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



$$\text{MW : } \quad \quad \quad 330 \quad \quad \quad 222$$



$$\text{MW : } \quad \quad \quad 85 \quad \quad \quad 69$$

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

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

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

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

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

Similarly, 85 g NaNO_3 gives 69 g NaNO_2

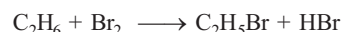
$\Rightarrow (5 - x) \text{ g}$ NaNO_3 will give $\frac{69(5-x)}{85} \text{ g}$ NaNO_2

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

Solving for x gives, $x = 3.3 \text{ g}$ $\text{Pb}(\text{NO}_3)_2$

\Rightarrow $\text{NaNO}_3 = 1.7 \text{ g}$.

34. Reactions involved are



Actual yield of $\text{C}_4\text{H}_{10} = 55 \text{ g}$ which is 85% of theoretical yield.

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

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

$\Rightarrow 64.70 \text{ g}$ of butane would be obtained from

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

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

$$\frac{2.23 \times 100}{90} = 2.48 \text{ moles of } \text{C}_2\text{H}_6 \text{ required.}$$

Therefore, moles of C_2H_6 required $= 2.48$

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

12 Some Basic Concepts of Chemistry

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

Moles of water in syrup = $214.2 - 34.2$
 $= 180 \text{ g}$

Therefore, (i) Molality = $\frac{\text{Moles of solute}}{\text{Weight of Solvent (g)}} \times 1000$
 $= \frac{0.1}{180} \times 1000 = 0.55$

(ii) Mole fraction of sugar = $\frac{\text{Mole of sugar}}{\text{Mole of sugar} + \text{Mole of water}}$
 $= \frac{0.1}{0.1 + 10} = 9.9 \times 10^{-3}$

36. From the given elemental composition, empirical formula can be derived as :

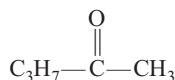
Element	C	H	O
Weight %	69.77	11.63	18.60
Mole %	5.81	11.63	1.1625 (obtained by dividing from M)
Simple ratio	5	10	1

Hence, empirical formula is $\text{C}_5\text{H}_{10}\text{O}$ and empirical formula weight is 86.

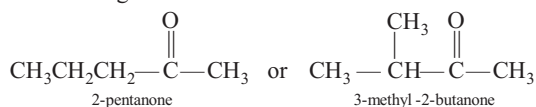
Since, empirical formula weight and molecular weight both are (86), empirical formula is the molecular formula also.

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

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



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



37. (a) Let us consider 1.0 L solution for all the calculation.

(i) Weight of 1 L solution = 1250 g

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

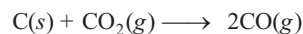
\Rightarrow Weight percentage of $\text{Na}_2\text{S}_2\text{O}_3 = \frac{474}{1250} \times 100 = 37.92$

(ii) Weight of H_2O in 1 L solution = $1250 - 474 = 776 \text{ g}$

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

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

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



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

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

$$\Rightarrow x = 0.6$$

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

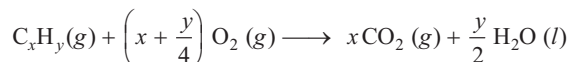
(b) According to the given information, molecular formula of the compound is M_3N_2 . Also, 1.0 mole of compound has 28 g of nitrogen. If X is the molar mass of compound, then :

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

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

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

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



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

\Rightarrow Volume of $\text{CO}_2(g)$ produced = 10 mL (15 mL O_2 remaining)

\because 1 mL C_xH_y produces x mL of CO_2

\therefore 5 mL C_xH_y will produce $5x$ mL of $\text{CO}_2 = 10$ mL

$\Rightarrow x = 2$

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

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

$\Rightarrow 5\left(x + \frac{y}{4}\right) = 15$ (15 mL of O_2 out of 30 mL)

(remaining unreacted)

$\Rightarrow y = 4$, hence hydrocarbon is C_2H_4 .

40. Oxides of sodium and potassium are converted into chlorides according to following reactions :



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

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

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

Now, let the chloride mixture contain x g NaCl.

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

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

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

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

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

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

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

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

41. From the vapour density information

$$\text{Molar mass} = \text{Vapour density} \times 2$$

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

$$= 38.3 \times 2 = 76.6$$

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

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

$$\Rightarrow x = 0.3348$$

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

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

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

43. Average atomic weight

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

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

$$\Rightarrow x = 20\%$$

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

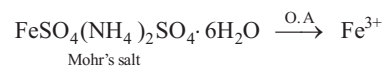
Topic 2 Equivalent Concept, Neutralisation and Redox Titration

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

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

2. n -factor of dichromate is 6.

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



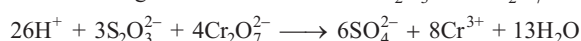
\therefore 1 mole of dichromate = 6 equivalent of dichromate.

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

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

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

3. The following reaction occur between $\text{S}_2\text{O}_3^{2-}$ and $\text{Cr}_2\text{O}_7^{2-}$:



Change in oxidation number of $\text{Cr}_2\text{O}_7^{2-}$ per formula unit is 6 (it is always fixed for $\text{Cr}_2\text{O}_7^{2-}$).

Hence, equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{Molecular weight}}{6}$

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

5. Oxalic acid dihydrate $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$: mw = 126

It is a dibasic acid, hence equivalent weight = 63

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

$$\Rightarrow N_1V_1 = N_2V_2$$

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

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

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

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

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

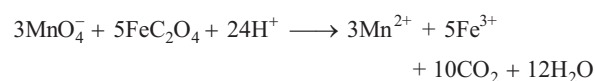
In CrO_2Cl_2 , oxidation state of Cr is +6.

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

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

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

8. The balanced redox reaction is :



\therefore 5 moles of FeC_2O_4 require 3 moles of KMnO_4

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

9. The balanced chemical reaction is :



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

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

14 Some Basic Concepts of Chemistry

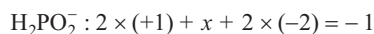
10. The balanced redox reaction is :



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

11. Volume strength of $\text{H}_2\text{O}_2 = \text{Normality} \times 5.6 = 1.5 \times 5.6 = 8.4 \text{ V}$

12. In $\text{Ba}(\text{H}_2\text{PO}_2)_2$, oxidation number of Ba is +2. Therefore,

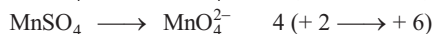
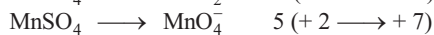
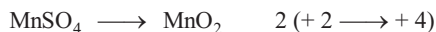
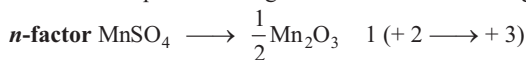


$$\Rightarrow x = +1$$

13. Equivalent weight in redox system is defined as :

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

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



Therefore, MnSO_4 converts to MnO_2 .

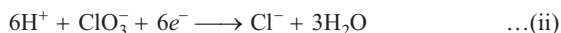
14. **PLAN** This problem includes concept of redox reaction. A redox reaction consists of oxidation half-cell reaction and reduction half-cell reaction. Write both half-cell reactions, i.e. oxidation half-cell reaction and reduction half-cell reaction. Then balance both the equations.

Now determine the correct value of stoichiometry of H_2SO_4 .



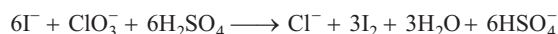
Here, I^- is converted into I_2 . Oxidation number of I is increasing from -1 to 0 hence, this is a type of oxidation reaction.

Reduction half-reaction



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

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



- Stoichiometric coefficient of HSO_4^- is 6.

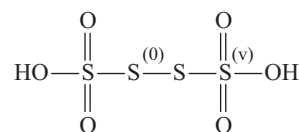
Hence, option (a), (b) and (d) are correct.

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

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

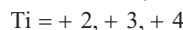
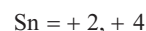
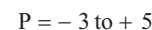
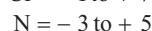
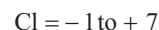
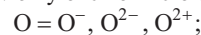
$$3 + 2 \times 2 + 3x + 7 \times (-2) = 0 \Rightarrow x = \frac{7}{3}$$

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



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

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



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

20. The balanced reaction is



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

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

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

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

$$\text{Meq of MnO}_2 \text{ formed} = \text{Meq of oxalate} = 4$$

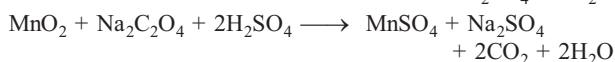
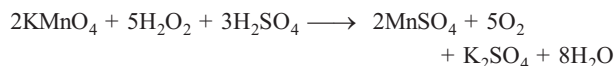
$$\text{Meq of KMnO}_4 \text{ in } 20 \text{ mL} = 4$$

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

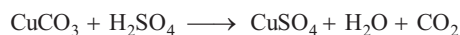
$$\Rightarrow \text{Normality of } \text{H}_2\text{O}_2 = 0.20 \text{ N}$$

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

The balanced reactions are



22. The balanced chemical reaction is



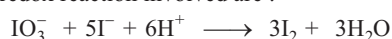
$$\text{millimol of CuCO}_3 = \frac{0.5 \times 1000}{123.5} = 4.048$$

$$\Rightarrow \text{Millimol of } \text{H}_2\text{SO}_4 \text{ required} = 4.048$$

$$\therefore \text{Millimol} = \text{Molarity} \times \text{Volume (in mL)}$$

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

23. The redox reaction involved are :



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

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

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

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

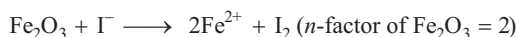
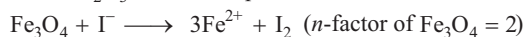
24. Meq of $\text{H}_2\text{O}_2 = \text{Meq of I}_2 = \text{Meq of Na}_2\text{S}_2\text{O}_3$

If N is normality of H_2O_2 , then

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

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

25. Let the original sample contains x millimol of Fe_3O_4 and y millimol of Fe_2O_3 . In the first phase of reaction,



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

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

Now, total millimol of Fe^{2+} formed = $3x + 2y$. In the reaction



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

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

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

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

$$x = 4.5$$

and

$$y = 9.25$$

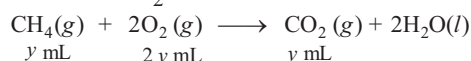
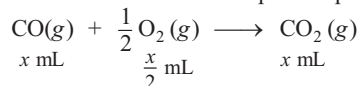
$$\Rightarrow \text{Mass of Fe}_3\text{O}_4 = \frac{4.5}{1000} \times 232 = 1.044 \text{ g}$$

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

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

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

26. The reaction involved in the explosion process is



The first step volume contraction can be calculated as :

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

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

The second volume contraction is due to absorption of CO_2 .

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

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

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

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

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

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

27. The redox reaction involved is :



If M is molarity of H_2O_2 solution, then

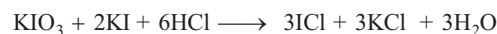
$$5M = \frac{0.508 \times 1000}{254} \quad (\because 1 \text{ mole H}_2\text{O}_2 \equiv 1 \text{ mole I}_2)$$

$$\Rightarrow M = 0.4$$

Also, n -factor of H_2O_2 is 2, therefore normality of H_2O_2 solution is 0.8 N.

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

28. The reaction is



KIO_3 required for 20 mL original KI solution = 3 millimol.

\Rightarrow 7.5 millimol KIO_3 would be required for original 50 mL KI.

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

After AgNO_3 treatment.

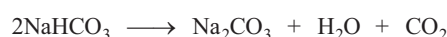
5 millimol of KIO_3 is required, i.e. 10 millimol KI is remaining.

\Rightarrow 5 millimol KI reacted with 5 millimol of AgNO_3 .

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

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

29. CO_2 is evolved due to following reaction :



$$\text{Moles of CO}_2 \text{ produced} = \frac{pV}{RT}$$

$$= \frac{750}{760} \times \frac{123.9}{1000} \times \frac{1}{0.082 \times 298}$$

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

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

\Rightarrow millimol of NaHCO_3 in 1.5 g sample

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

Let the 1.5 g sample contain x millimol Na_2CO_3 , then

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

$$\Rightarrow x = 3.75$$

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

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

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

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

16 Some Basic Concepts of Chemistry

30. Mass of $\text{Fe}_2\text{O}_3 = 0.552 \text{ g}$

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

During treatment with Zn-dust, all Fe^{3+} is reduced to Fe^{2+} , hence

$$\text{millimol of } \text{Fe}^{2+} \text{ (in 100 mL)} = 3.45 \times 2 = 6.90$$

$$\Rightarrow \text{In 25 mL aliquot, } \frac{6.90}{4} = 1.725 \text{ millimol } \text{Fe}^{2+} \text{ ion.}$$

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

$$\begin{aligned} &= 1.725 \times 10^{-3} \times 6.023 \times 10^{23} \\ &= 1.04 \times 10^{21} \end{aligned}$$

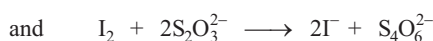
31. With KMnO_4 , oxalate ion is oxidised only as :



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

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

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



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

$$\Rightarrow \text{Meq of } \text{Cu}^{2+} = \text{Meq of } \text{I}_2 = \text{meq of hypo}$$

$$\Rightarrow x = 11.3 \times 0.05 = 0.565$$

$$\Rightarrow \text{Moles of } \text{Cu}^{2+} : \text{moles of } \text{C}_2\text{O}_4^{2-} = 0.565 : 1.13 = 1 : 2$$

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

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

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

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

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

Solving equations (i) and (ii) gives

$$y = 0.1, x = 0.1$$

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

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

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

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

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

Now, the empirical formula can be derived as :

	C	H	Cl
% wt :	24.24	4.04	71.72
Mole :	2	4	2
Simple ratio :	1	2	1

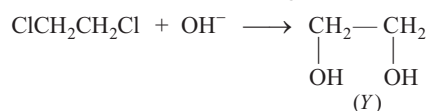
\Rightarrow Empirical formula = CH_2Cl .

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

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



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

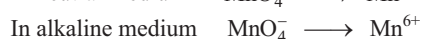
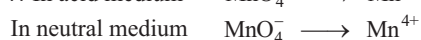
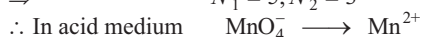


34. Let the n -factor of KMnO_4 in acid, neutral and alkaline media are N_1, N_2 and N_3 respectively. Also, same volumes of reducing agent is used everytime, same number of equivalents of KMnO_4 would be required every time.

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

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

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



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

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

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

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

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

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

Also,

$$\therefore 4 \text{ millimol of } \text{Fe}^{2+} \text{ are formed from 1 millimol } \text{N}_2\text{H}_4$$

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

Therefore, molarity of hydrazine sulphate solution

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

⇒ In 1 L solution $\frac{1}{20}$ mol $\text{N}_2\text{H}_6\text{SO}_4$ is present.

⇒ Amount of $\text{N}_2\text{H}_6\text{SO}_4 = \frac{1}{20} \times 130 = 6.5 \text{ gL}^{-1}$

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

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

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

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

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

Let normality of H_2SO_4 in final solution be N .

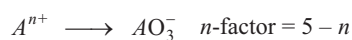
⇒ $(N + 0.02 + 0.012) \times 30 = 0.07 \times 42.9$

⇒ $N = 0.0681$

⇒ Gram equivalent of SO_4^{2-} in 2 L solution = 2×0.0681
= 0.1362

⇒ Mass of SO_4^{2-} in solution = $0.1362 \times \frac{96}{2} = 6.5376 \text{ g}$

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



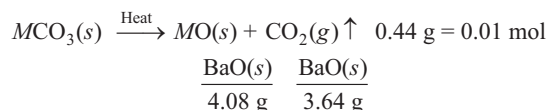
⇒ Gram equivalent of $A^{n+} = 2.68 \times 10^{-3} (5 - n)$

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

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

⇒ $n = +2$

38. During heating MCO_3 is converted into MO liberating CO_2 while BaO is remaining unreacted :



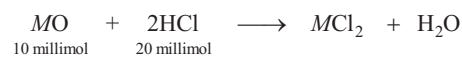
From the decomposition information, it can be deduced that the original mixture contained 0.01 mole of MCO_3 and the solid residue, obtained after heating, contain 0.01 mole (10 millimol) of MO .

Also, millimol of HCl taken initially = 100

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

⇒ millimol of HCl reacted with oxide residue = 60

HCl reacts with oxides as :



$60 - 20 = 40$ millimol

Therefore, the residue contain 20 millimol of BaO .

Also, molar mass of $\text{BaO} = 138 + 16$
= 154

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

⇒ Mass of $\text{MCO}_3 = 4.08 - 3.08 = 1.0 \text{ g}$

∴ 0.01 mole of MCO_3 weight 1.0 g

∴ 1 mole of $\text{MCO}_3 = 100 \text{ g}$

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

⇒ Atomic weight of metal = 40, i.e. Ca

- In the titration of a certain H_2SO_4 solution, 60 mL of 5.0 M NaOH solution was used to completely neutralise 75 mL of the acid. The molarity of the acid solution may be expressed as

(a) $\frac{5 \text{ M} \times 60 \text{ mL}}{2 \times 75 \text{ mL}}$	(b) $\frac{5 \text{ M} \times 75 \text{ mL} \times 2}{60 \text{ mL}}$
(c) $\frac{75 \text{ mL} \times 2}{5.0 \text{ M} \times 60 \text{ mL}}$	(d) $\frac{60 \text{ mL} \times 75 \text{ mL} \times 2}{5.0 \text{ M}}$
- 20 mL of a solution containing equal moles of Na_2CO_3 and NaHCO_3 required 16 mL of a 0.16 M HCl solution to reach the phenolphthalein end point. What volume of a 0.10 M H_2SO_4 solution would have been required had methyl orange been used as indicator?

(a) 38.40 mL	(b) 24.60 mL
(c) 19.20 mL	(d) 0.30 mL
- When aqueous solution of Na_2S is titrated with dilute and acidified KMnO_4 solution, Na_2SO_3 is formed. In this reaction, moles of KMnO_4 reduced per mole of Na_2S is

(a) 0.833	(b) 1.2	(c) 1.50	(d) 1.8
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- For the following metals A, B, C, D react with each other : (NR = No reaction)

$A + B^+ \longrightarrow \text{NR}$	$B + C^+ \longrightarrow \text{NR}$
$B + D^+ \longrightarrow B^+ + D$	$C + D^+ \longrightarrow C^+ + D$
$A^+ + C \longrightarrow C^+ + A$	$D + A^+ \longrightarrow D^+ + A$

 Which is the order of the metals in increasing reducing strength?

(a) $B < D < A < C$	(b) $C < B < D < A$
(c) $A < D < B < C$	(d) $C < A < B$
- 40 mL 0.05 M solution of sodium sesquicarbonate dehydrate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) is titrated against 0.05 M HCl solution, x mL of acid is required to reach the phenolphthalein end point while y mL of same acid were required when methyl orange indicator was used in a separate titration. Which of the following is(are) correct statements?

(a) $y - x = 80 \text{ mL}$
(b) $y + x = 160 \text{ mL}$
(c) If the titration is started with phenolphthalein indicator and methyl orange is added at the end point, 2 x mL of HCl would be required further to reach the end point
(d) If the same volume of same solution is titrated against 0.10 M NaOH, x/2 mL of base would be required
- Which of the following regarding oxalate compound is/are true?

(a) Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) can be estimated by titrating against either KOH or KMnO_4 solution.
(b) KHC_2O_4 can be estimated by titrating against either KOH or K_2CrO_4 and in both analyses equivalent weight of KHC_2O_4 is 64. (MW of $\text{KHC}_2\text{O}_4 = 128$)
(c) $\text{K}_2\text{C}_2\text{O}_4$ can be estimated by titrating against either HCl or KClO_3 and in both analyses equivalent weight of $\text{K}_2\text{C}_2\text{O}_4$ is 83. (MW of $\text{K}_2\text{C}_2\text{O}_4 = 166$)
(d) If 10 mL of a $\text{K}_2\text{C}_2\text{O}_4$ solution required 8.0 mL of a 0.12 M HCl solution, 10 mL of the same $\text{K}_2\text{C}_2\text{O}_4$ solution would require 9.60 mL of a 0.02 M acidified KMnO_4 solution.

Assertion-Reason Type

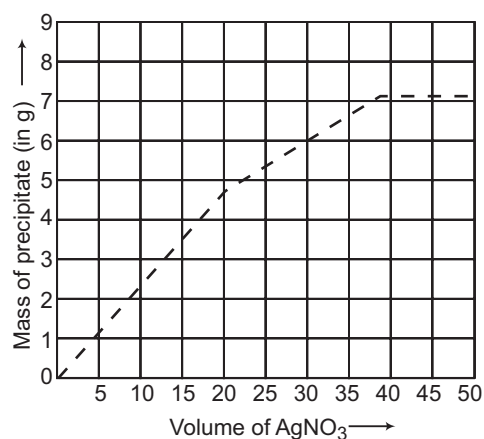
Following two questions have assertion followed by the reason. Answer them according to the following options.

- | | | | | | | | | | |
|---|--|--------------------------|--------------------------|---------------------------|--|---|--|--|---|
| <p>(a) Both assertion and reason are correct and reason is the correct explanation of the assertion,</p> <p>(b) Both assertion and reason are correct but reason is not the correct explanation of assertion.</p> <p>(c) Assertion is correct but reason is incorrect.</p> <p>(d) Assertion is incorrect but reason is correct.</p> | <p>7. Assertion If certain volume of a basic solution require x mL of HCl, 2x mL of H_2SO_4 of same molarity would be required.</p> <p>Reason HCl is a monobasic acid while H_2SO_4 is a dibasic acid.</p> | | | | | | | | |
| <p>8. Assertion If 10 mL of a H_2O_2 solution required 8.00 mL of 0.02 M acidified KMnO_4 solution for complete oxidation, 12.50 mL of same H_2O_2 will oxidise completely to 5.00 mL of 0.10 M $\text{Na}_2\text{C}_2\text{O}_4$ solution.</p> <p>Reason H_2O_2 act as both oxidising as well as reducing agent.</p> | <p>9. The alkenes are compounds of carbon and hydrogen with the general formula C_nH_{2n}. If 0.561 g of any alkene is burned in excess oxygen, what number of moles of H_2O is formed?</p> <table border="0" style="width: 100%;"> <tr> <td>(a) 0.0400 mol</td> <td>(b) 0.0600 mol</td> </tr> <tr> <td>(c) 0.0800 mol</td> <td>(d) 0.400 mol</td> </tr> </table> | (a) 0.0400 mol | (b) 0.0600 mol | (c) 0.0800 mol | (d) 0.400 mol | | | | |
| (a) 0.0400 mol | (b) 0.0600 mol | | | | | | | | |
| (c) 0.0800 mol | (d) 0.400 mol | | | | | | | | |
| <p>10. What is the density (in g mL^{-1}) of a 3.60 M aqueous sulphuric acid solution that is 29.0% H_2SO_4 by mass?</p> <table border="0" style="width: 100%;"> <tr> <td>(a) 1.22</td> <td>(b) 1.45</td> </tr> <tr> <td>(c) 1.64</td> <td>(d) 1.88</td> </tr> </table> | (a) 1.22 | (b) 1.45 | (c) 1.64 | (d) 1.88 | <p>11. Magnetite, Fe_3O_4, can be converted into metallic iron by heating with carbon monoxide as represented by this equation:</p> $\text{Fe}_3\text{O}_4 (\text{s}) + \text{CO} (\text{g}) \longrightarrow \text{Fe} (\text{s}) + \text{CO}_2 (\text{g})$ <p>The kilograms of Fe_3O_4 which must be processed in this way to obtain 5.00 kg of iron, if the process is 85% efficient is closest to? [$M : \text{Fe} = 56$]</p> <table border="0" style="width: 100%;"> <tr> <td>(a) 6.92 kg</td> <td>(b) 8.15 kg</td> </tr> <tr> <td>(c) 20.8 kg</td> <td>(d) 24.4 kg</td> </tr> </table> | (a) 6.92 kg | (b) 8.15 kg | (c) 20.8 kg | (d) 24.4 kg |
| (a) 1.22 | (b) 1.45 | | | | | | | | |
| (c) 1.64 | (d) 1.88 | | | | | | | | |
| (a) 6.92 kg | (b) 8.15 kg | | | | | | | | |
| (c) 20.8 kg | (d) 24.4 kg | | | | | | | | |
| <p>12. How many H_2O molecules are there in a snowflake that weighs $4.0 \times 10^{-4} \text{ g}$?</p> <table border="0" style="width: 100%;"> <tr> <td>(a) 1.3×10^{19}</td> <td>(b) 2.4×10^{20}</td> </tr> <tr> <td>(c) 2.2×10^{-5}</td> <td>(d) 6.02×10^{23}</td> </tr> </table> | (a) 1.3×10^{19} | (b) 2.4×10^{20} | (c) 2.2×10^{-5} | (d) 6.02×10^{23} | <p>13. Atomic weight of an element X is 120 when one amu is defined as 1/18th part by weight of an element of C^{12}. On the same scale, atomic weight of another element Y is 72. Which of the following statement regarding X and Y is(are) correct?</p> <table border="0" style="width: 100%;"> <tr> <td>(a) On conventional scale, atomic weight of X is 80</td> </tr> <tr> <td>(b) On conventional scale, atomic weight of Y is 108</td> </tr> <tr> <td>(c) On a scale when an amu is defined to be 1/30th of the weight of an atom of C^{12}, atomic weight of X is 200</td> </tr> <tr> <td>(d) On a scale when an amu is defined to be 1/15th of the weight of an atom of C^{12}, atomic weight of Y is 90</td> </tr> </table> | (a) On conventional scale, atomic weight of X is 80 | (b) On conventional scale, atomic weight of Y is 108 | (c) On a scale when an amu is defined to be 1/30th of the weight of an atom of C^{12} , atomic weight of X is 200 | (d) On a scale when an amu is defined to be 1/15th of the weight of an atom of C^{12} , atomic weight of Y is 90 |
| (a) 1.3×10^{19} | (b) 2.4×10^{20} | | | | | | | | |
| (c) 2.2×10^{-5} | (d) 6.02×10^{23} | | | | | | | | |
| (a) On conventional scale, atomic weight of X is 80 | | | | | | | | | |
| (b) On conventional scale, atomic weight of Y is 108 | | | | | | | | | |
| (c) On a scale when an amu is defined to be 1/30th of the weight of an atom of C^{12} , atomic weight of X is 200 | | | | | | | | | |
| (d) On a scale when an amu is defined to be 1/15th of the weight of an atom of C^{12} , atomic weight of Y is 90 | | | | | | | | | |

14. Which of the following statement regarding Avogadro number is(are) correct?
- It is 6.023×10^{23}
 - It is the number of atoms present in exactly 12 g of C-12 isotope
 - It is the number of atoms present in 1.0 mole of any substance
 - It is the number of atoms of deuterium present in its 2.0 g

Comprehension for Q. Nos. 15 to 17

4.0 g of a mixture of NaCl and an unknown metal iodide MI_2 was dissolved in water to form its aqueous solution. To this aqueous solution, aqueous solution of $AgNO_3$ was added gradually so that silver halides are precipitated. The precipitates were weighed at regular interval and following curve for the mass of precipitate versus volume of $AgNO_3$ added was obtained. With the knowledge of the fact that halides are precipitated successively, i.e. when less soluble halide is precipitating, the other halide remain in the solution, answer the following questions: (Molar mass of Ag = 108, I = 127, Na = 23).



15. What is the approximate mass percentage of MI_2 ?
- 25
 - 40
 - 60
 - 75
16. What is the approximate molarity of $AgNO_3$ solution?
- 0.1
 - 0.5
 - 1.0
 - 1.5

17. What is the approximate molar mass of unknown metal M ?
- 20
 - 40
 - 56
 - 60

Assertion-Reason Type

Following two questions have assertion followed by the reason. Answer them according to the following options.

- Both assertion and reason are correct and reason is the correct explanation of the assertion.
 - Both assertion and reason are correct but reason is not the correct explanation of assertion.
 - Assertion is correct but reason is incorrect.
 - Assertion is incorrect but reason is correct.
18. **Assertion** The average mass of an atom of Mg is 24.305 u, which is not the actual mass of an atom of Mg.
Reason This is the average mass determined considering different isotopes of Mg present in natural Mg.
19. **Assertion** A 8.0 g N_2H_4 ($M = 32$) has more atoms than 6.0 g H_2O .
Reason N_2H_4 has more atoms per molecule than water.

20. Match the statements of Column I with values of Column II.

	Column I	Column II
A.	Different number of atoms	p. 4.25 g NH_3 and 4.5 g of H_2O
B.	Same number of molecules	q. 2.20 g CO_2 and 0.90 g H_2O
C.	Same numbers of atoms as well as molecules	r. 4.0 g CH_3Cl and 5.0 g NH_3
D.	Different numbers of atoms as well as molecules	s. 4.80 g O_2 and 2.80 g CO

21. On a conventional scale, atomic weight of sulphur is 32. If on a new scale, an amu is defined as one-third by weight of an atom of C-12 isotope, what would be the atomic weight of sulphur on this new scale?
22. If equal volumes of 3.5 M $CaCl_2$ and 3.0 M $NaCl$ are mixed, what would be the molarity of chloride ion in the final solution?

Answers

1. (a) 2. (c) 3. (b) 4. (c) 5. (a, b, c, d) 6. (a, c, d) 7. (d) 8. (b) 9. (a) 10. (a)
 11. (b) 12. (a) 13. (b, c) 14. (a, b, d) 15. (d) 16. (c) 17. (b) 18. (a) 19. (b)
 20. A → s; B → p; C → q; D → r 21. (8) 22. (5)

2

Atomic Structure

Preliminary Developments and Bohr's Model

• Terms Related to Atom

Atomic number (Z)	Equals to the number of protons (or electrons) in a neutral atom.
Mass number (A)	Number of protons (Z) + number of neutrons (N)
Isotopes	Atoms of same element having different mass number, e.g. ${}_6\text{C}^{12}$, ${}_6\text{C}^{14}$.
Isobars	Atoms of different elements having same mass number, e.g. ${}_6\text{C}^{14}$, ${}_7\text{N}^{14}$.
Isotones	Atoms of different elements having same number of neutrons, e.g. ${}_{19}\text{K}^{39}$, ${}_{20}\text{Ca}^{40}$, ${}_{16}\text{S}^{36}$.
Isoelectronic	Species having same number of electrons, e.g. K^+ , Ca^{2+} , Ar , Cl^- .
Isodiaphers	Different atoms having same neutron to proton difference (neutron excess), e.g. ${}_{92}\text{U}^{238}$ and ${}_{90}\text{Th}^{234}$ both have ($N - Z$) equals to 54.
Isosters	Species having same number of atoms and electrons are isosters, e.g. N_2 , CO .

• The Details About Some of the Important Subatomic Particles are given in the Table Below:

Particles and symbol	Absolute charge (C)	Relative charge	Mass (gram)	Mass (MeV/c^2)	Discoverer
Electron (e)	-1.602×10^{-19}	-1	9.1×10^{-28}	0.511	JJ Thomson
Proton (p)	$+1.602 \times 10^{-19}$	+1	1.6726×10^{-24}	938.5	Rutherford
Neutron (n)	0	0	1.6749×10^{-24}	940	Chadwick
Positron (B^+ / e^+) (anti-electron)	$+1.602 \times 10^{-19}$	+1	9.1×10^{-28}	0.511	D Anderson
Anti-proton (\bar{p})	-1.602×10^{-19}	-1	1.6726×10^{-24}	938.5	Emilio Segra and Owen chamberlain

• Rutherford's Nuclear Model of Atom

Rutherford performed an alpha particle (He^{2+}) scattering experiment on a thin gold foil and presented that :

- most part of atom is empty.
- every atom possesses a highly dense, positively charged centre called "nucleus".
- entire mass of atom is concentrated inside the nucleus.
- later Rutherford model was abandoned due to its failure to comply with classical theory of electromagnetic radiation. This theory also failed to explain the line spectrum of H-atom.

- **Planck's Equation**

$$E = h\nu = \frac{hc}{\lambda}$$

(where, $h = 6.625 \times 10^{-34}$ Js)

- **Black Body Radiation** Radiation by a black body (an ideal body that emits and absorbs radiations of all frequencies) can be explained by Planck's quantum theory.

- **Photoelectric Effect** When a light of frequency more than threshold frequency (ν_0) strikes a metal surfaces it ejects electron. This phenomenon is called photoelectric effect.

$$\begin{aligned} \text{Hence, } \frac{1}{2}m_e v^2 &= h\nu - h\nu_0 \\ &= h(\nu - \nu_0) \end{aligned}$$

...(i)

where, ν = Frequency of light,
 ν_0 = Threshold frequency
 h = Planck's constant = 6.625×10^{-34} Js

$$\frac{1}{2}m_e v^2 = hc \left(\frac{1}{\lambda} - \frac{1}{\lambda_0} \right)$$

...(ii)

- **Bohr's Model** Bohr proposed an idea of stationary orbits in which electron revolves. According to Bohr's model, electron does not lose energy as long as it stays in an stationary orbit. When an electron jumps to lower stationary orbit, energy is lost in the form of electromagnetic radiation. Conversely when energy is supplied, electron jumps to higher stationary orbit. According to Bohr's model,

(i) Angular momentum of an electron is quantised :

$$\text{Angular momentum } (mvr) = \frac{nh}{2\pi}$$

...(i)

where, $n = 1, 2, 3, \dots, \infty$
 (orbit number)

(ii) Centrifugal force of orbiting electron is exactly balanced by the electrostatic attraction between nucleus and electron.

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \quad \dots(ii)$$

- **Bohr's Radius** Using the above relationships (i and ii), radius of a stationary orbit is

$$r_n = a_0 \left(\frac{n^2}{Z} \right),$$

where, $a_0 = 0.529 \text{ \AA}$ (First Bohr

radius)

- **Energy of Stationary Orbit (E_n)**

$$E_n = \frac{-kZ^2}{n^2}, \quad (\because k = 13.6 \text{ eV} = 2.18 \times 10^{-18} \text{ J})$$

- **Potential Energy**

$$E_p = \frac{-Ze^2}{4\pi\epsilon_0 r} = -\frac{2kZ^2}{n^2}$$

- **Speed of Electron in nth Bohr Orbit**

$$\frac{2.18 \times 10^6 Z}{n} \text{ ms}^{-1}.$$

Number of revolutions made by an electron in n th Bohr's orbit is

$$\text{Revolution/second} = \frac{v_n}{2\pi r_n}; \quad (v_n = \text{Speed in } n\text{th orbit})$$

Advanced Concept (Quantum Mechanical Theory) Electronic Configuration and Quantum Number

- **Emission Spectrum of H-atom** The frequency, wavelengths or wave-number of a spectral line in any of the series in the emission spectrum of hydrogen atom can be calculated using the following Rydberg's equation :

$$\frac{1}{\lambda} = \bar{\nu} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]; \quad R_H = 1.09678 \times 10^7 \text{ m}^{-1}$$

- (i) For Lyman series : $n_1 = 1, n_2 = 2, 3 \dots$
(occur in UV region)
- (ii) For Balmer series : $n_1 = 2, n_2 = 3, 4 \dots$
(occur in visible region)
- (iii) For Paschen series : $n_1 = 3, n_2 = 4, 5 \dots$
(occur in IR region)
- (iv) For Brackett series : $n_1 = 4, n_2 = 5, 6 \dots$
(occur in IR region)
- (v) For Pfund series : $n_1 = 5, n_2 = 6, 7 \dots$
(occur in IR region)

- **Wave-Particle Duality** (de-Broglie Relationship)

$$\lambda = \frac{h}{p}; \quad (p = \text{momentum } (mv))$$

- **Bohr's de-Broglie Relationship** $[2\pi r = n\lambda]$, i.e. in a given stationary orbit, the number of de-Broglie wavelengths is equal to orbit number. If an electron at rest is accelerated by a potential difference of V volt, then de-Broglie wavelength is :

$$\lambda = \frac{h}{\sqrt{2meV}}$$

- **Heisenberg's Uncertainty Principle** According to this principle, simultaneous and accurate measurement of both position and momentum of an electron in an atom is impossible.

\Rightarrow

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Here, (Δx is uncertainty in position and Δp is uncertainty in momentum.)

22 Atomic Structure

- **Quantum Numbers** To describe an electron completely inside the atom, four sets of quantum numbers are required. They are as :

(i) **Principal Quantum Number (n)** This specifies **position** and **energy** of an electron in the atom. Possible values of ' n ' are 0, 1, 2, 3, ..., ∞ .

(ii) **Angular Momentum (Azimuthal or Subsidiary) Quantum Number (l)** This is used to specify subshell (orbital). Possible values of ' l ' are 0, 1, 2, ... ($n - 1$). Orbitals with different values of l are denoted as :

- $l = 0$, for s -orbital — spherical
- $l = 1$, for p -orbital — dumb-bell shape
- $l = 2$, for d -orbital — double dumb-bell shape
- $l = 3$, for f -orbital etc.

The value of ' l ' also determines shape of orbital as mentioned above.

The value of ' l ' determines orbital angular momentum (L) as :

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

The value of ' l ' also determines the magnitude of magnetic moment as :

$$\mu_L = \frac{eh}{4\pi mC} \sqrt{l(l+1)} \quad \text{where, } \frac{eh}{4\pi mC} = 9.27 \times 10^{-14} \text{ J}$$

(iii) **Magnetic Quantum Number (m)** It determines the preferred orientation of orbitals in three dimensional space. Its possible values are :

$$m = -l, \dots, 0, \dots, +l$$

e.g. for $l = 2$, $m = -2, -1, 0, +1, +2$.

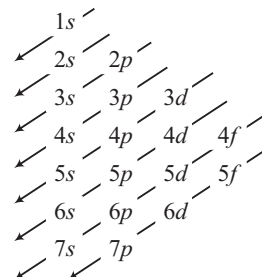
- Total values of m for a given value of $l = (2l + 1) =$ total number of orbitals in a given orbital.
- Splitting of spectral lines occurs when placed in a magnetic field (Zeeman effect) or in an electric field (Stark effect). Total lines from a single line in the normal spectrum = $(2l + 1)$.
- Total number of orbitals in n th orbit = n^2
- Total number of electrons in n th orbit = $2n^2$

(iv) **Spin Quantum Number (s)** Electrons spin on its own axis like a top, in clockwise and anti-clockwise directions. The two directions of spinning are denoted by spin quantum number as :

$$s = +\left(\frac{1}{2}\right) \text{ and } -\left(\frac{1}{2}\right)$$

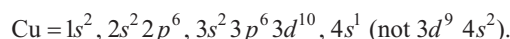
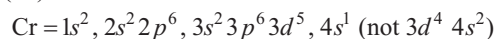
The spin quantum numbers are also denoted by **up-half arrow (\uparrow)** and **down-half arrow (\downarrow)** but neither the $+1/2$ and $-1/2$ or the \uparrow or \downarrow are specific for any direction, they just represent the two opposite directions of spinning of electrons.

- **Electronic Configuration** Electrons are filled in atomic orbitals in increasing order of their energy according to Aufbau principle :



- During filling up of electrons in atomic orbitals, **Pauli's exclusion principle** must be obeyed, i.e. no two electrons in an atom can have all four sets of quantum numbers same. This limits the number of electrons in an orbital to two.

- **Hund's rule** of maximum multiplicity is obeyed, i.e. orbitals of same energies (degenerate atomic orbitals) are first singly occupied, then pairing starts. Exception occurs in case of Cr (24) and Cu (29).



- **Quantum Mechanical Model** (The Schrodinger's Equation)

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

ψ = Wave function, represents an orbital

E = Total energy of an electron

V = Potential energy associated with electron

Solution of the second order differential equation (Schrodinger equation) gives the normalised wave functions (ψ). Normalised wave-function for some of the orbitals are :

$$\text{for } s\text{-orbital } \psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

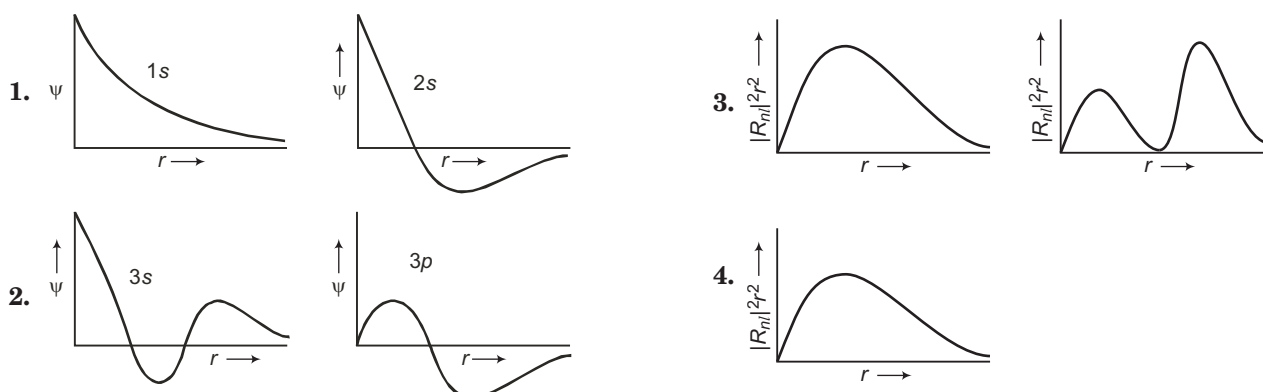
$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}$$

$$\text{for } p_x\text{-orbital } \psi_{2p_x} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^4 r \sin \theta \cos \phi e^{-r/2a_0}$$

Radial Wave Functions and Number of Nodes As ψ is plotted against distance from nucleus (r), $(n - l - 1)$ radial nodes are obtained. At nodes, ψ changes its sign.

Probability density (ψ^2) and radial distribution function $|R_{n,l}|^2 r^2$. For an orbital, probability density, ψ^2 is maximum at nucleus but, $|R_{n,l}|^2 r^2$ is minimum at nucleus. Also, when any of these two functions are plotted against r , $(n - l - 1)$ nodes are obtained.

Some plots of ψ and $|R_{n,l}|^2 r^2$



Topic 1 Preliminary Developments and Bohr's Model

Objective Questions I (Only one correct option)

- Rutherford's experiment, which established the nuclear model of the atom, used a beam of (2002, 3M)
 - β -particles, which impinged on a metal foil and got absorbed
 - γ -rays, which impinged on a metal foil and got scattered
 - helium atoms, which impinged on a metal foil and got scattered
 - helium nuclei, which impinged on a metal foil and got scattered
- Rutherford's alpha particle scattering experiment eventually led to the conclusion that (1986, 1M)
 - mass and energy are related
 - electrons occupy space around the nucleus
 - neutrons are buried deep in the nucleus
 - the point of impact with matter can be precisely determined
- The radius of an atomic nucleus is of the order of (1985, 1M)
 - 10^{-10} cm
 - 10^{-13} cm
 - 10^{-15} cm
 - 10^{-8} cm
- Bohr's model can explain (1985, 1M)
 - the spectrum of hydrogen atom only
 - spectrum of an atom or ion containing one electron only
 - the spectrum of hydrogen molecule
 - the solar spectrum
- The increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle (α) is (1984, 1M)
 - e, p, n, α
 - n, p, e, α
 - n, p, α, e
 - n, α, p, e
- Rutherford's scattering experiment is related to the size of the (1983, 1M)
 - nucleus
 - atom
 - electron
 - neutron
- Rutherford's experiment on scattering of α -particles showed for the first time that the atom has (1981, 1M)
 - electrons
 - protons
 - nucleus
 - neutrons

Objective Questions II

(One or more than one correct option)

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

24 Atomic Structure

Match the Columns

13. According to Bohr's theory,
 E_n = Total energy K_n = Kinetic energy
 V_n = Potential energy r^n = Radius of n th orbit
 Match the following : (2006, 6M)

	Column I	Column II	
A.	$V_n/K_n = ?$	p.	0
B.	If radius of n th orbit $\propto E_n^x, x = ?$	q.	-1
C.	Angular momentum in lowest orbital	r.	-2
D.	$\frac{1}{r^n} \propto Z^y, y = ?$	s.	1

Fill in the Blanks

14. The light radiations with discrete quantities of energy are called (1993, 1M)
 15. The mass of a hydrogen is kg. (1982, 1M)
 16. Isotopes of an element differ in the number of in their nuclei. (1982, 1M)
 17. Elements of the same mass number but of different atomic numbers are known as (1983, 1M)

Subjective Questions

18. With what velocity should an α -particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{-13} m from the nucleus of the copper atom? (1997 (C), 3M)

Topic 2 Advanced Concept (Quantum Mechanical Theory) Electronic Configuration and Quantum Number

Objective Questions I (Only one correct option)

1. Which of the following is the energy of a possible excited state of hydrogen? (2015 Main)
 (a) +13.6 eV (b) -6.8 eV
 (c) -3.4 eV (d) +6.8 eV

2. The correct set of four quantum numbers for the valence electrons of rubidium atom ($Z = 37$) is (2013 Main)
 (a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$
 (c) $5, 1, 1, +\frac{1}{2}$ (d) $5, 0, 1, +\frac{1}{2}$

3. Energy of an electron is given by

$$E = -2.178 \times 10^{-18} \text{ J} \left(\frac{Z^2}{n^2} \right) \quad (2013 \text{ Main})$$

Wavelength of light required to excite an electron in an hydrogen atom from level $n = 1$ to $n = 2$ will be

$$(h = 6.62 \times 10^{-34} \text{ Js and } c = 3.0 \times 10^8 \text{ ms}^{-1})$$

- (a) $1.214 \times 10^{-7} \text{ m}$ (b) $2.816 \times 10^{-7} \text{ m}$
 (c) $6.500 \times 10^{-7} \text{ m}$ (d) $8.500 \times 10^{-7} \text{ m}$
4. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [a_0 is Bohr radius] (2012)
 (a) $\frac{h^2}{4\pi^2 m a_0^2}$ (b) $\frac{h^2}{16\pi^2 m a_0^2}$
 (c) $\frac{h^2}{32\pi^2 m a_0^2}$ (d) $\frac{h^2}{64\pi^2 m a_0^2}$

5. The number of radial nodes in $3s$ and $2p$ respectively are (2005, 1M)
 (a) 2 and 0 (b) 0 and 2
 (c) 1 and 2 (d) 2 and 1





6. Which hydrogen like species will have same radius as that of Bohr orbit of hydrogen atom? (2004, 1M)
 (a) $n = 2, \text{Li}^{2+}$ (b) $n = 2, \text{Be}^{3+}$
 (c) $n = 2, \text{He}^+$ (d) $n = 3, \text{Li}^{2+}$

7. If the nitrogen atom had electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$, because the electrons would be closer to the nucleus, yet $1s^7$ is not observed, because it violates (2002, 3M)
 (a) Heisenberg uncertainty principle
 (b) Hund's rule
 (c) Pauli exclusion principle
 (d) Bohr postulate of stationary orbits

8. The quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ for the electron spin represent (2001, 1M)
 (a) rotation of the electron in clockwise and anti-clockwise direction respectively
 (b) rotation of the electron in anti-clockwise and clockwise direction respectively
 (c) magnetic moment of the electron pointing up and down respectively
 (d) two quantum mechanical spin states which have no classical analogue

9. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order (2001, 1M)
 (a) 10^{-10} m (b) 10^{-20} m (c) 10^{-30} m (d) 10^{-40} m

10. The number of nodal planes in a p_x orbital is (2001, 1M)
 (a) one (b) two
 (c) three (d) zero

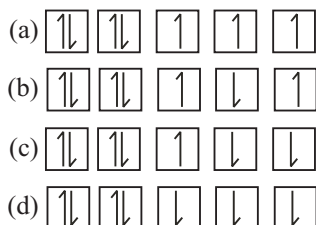
11. The electronic configuration of an element is $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$. This represents its (2000, 1M)
 (a) excited state (b) ground state
 (c) cationic form (d) anionic form
12. The electrons, identified by quantum numbers n and l ,
 (i) $n = 4, l = 1$, (ii) $n = 4, l = 0$, (iii) $n = 3, l = 2$, (iv) $n = 3, l = 1$
 can be placed in order of increasing energy, from the lowest to highest, as (1999, 2M)
 (a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)
 (c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii)
13. The energy of an electron in the first Bohr orbit of H-atom is -13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are) (1998, 2M)
 (a) -3.4 eV (b) -4.2 eV (c) -6.8 eV (d) $+6.8$ eV
14. For a d -electron, the orbital angular momentum is (1997, 1M)
 (a) $\sqrt{6} \left(\frac{h}{2\pi}\right)$ (b) $\sqrt{2} \left(\frac{h}{2\pi}\right)$ (c) $\left(\frac{h}{2\pi}\right)$ (d) $2 \left(\frac{h}{2\pi}\right)$
15. The first use of quantum theory to explain the structure of atom was made by (1997, 1M)
 (a) Heisenberg (b) Bohr
 (c) Planck (d) Einstein
16. Which of the following has the maximum number of unpaired electrons? (1996, 1M)
 (a) Mg^{2+} (b) Ti^{3+} (c) V^{3+} (d) Fe^{2+}
17. The orbital angular momentum of an electron in $2s$ -orbital is (1996, 1M)
 (a) $+\frac{1}{2} \cdot \frac{h}{2\pi}$ (b) zero (c) $\frac{h}{2\pi}$ (d) $\sqrt{2} \cdot \frac{h}{2\pi}$
18. Which of the following relates to photons both as wave motion and as a stream of particles? (1992, 1M)
 (a) Interference (b) $E = mc^2$
 (c) Diffraction (d) $E = h\nu$
19. Which of the following does not characterise X-rays? (1992, 1M)
 (a) The radiation can ionise gases
 (b) It causes ZnS to fluoresce
 (c) Deflected by electric and magnetic fields
 (d) Have wavelengths shorter than ultraviolet rays
20. The correct set of quantum numbers for the unpaired electron of chlorine atom is (1989, 1M)
- | n | l | m | n | l | m |
|-------|-----|-----|-------|-----|-----|
| (a) 2 | 1 | 0 | (b) 2 | 1 | 1 |
| (c) 3 | 1 | 1 | (d) 3 | 0 | 0 |
21. The correct ground state electronic configuration of chromium atom is (1989, 1M)
 (a) $[Ar] 3d^5 4s^1$ (b) $[Ar] 3d^4 4s^2$
 (c) $[Ar] 3d^6 4s^0$ (d) $[Ar] 4d^5 4s^1$
22. The outermost electronic configuration of the most electronegative element is (1988, 90, 1M)
 (a) $ns^2 np^3$ (b) $ns^2 np^4$ (c) $ns^2 np^5$ (d) $ns^2 np^6$
23. The orbital diagram in which the Aufbau principle is violated (1988, 1M)
- (a) 
- (b) 
- (c) 
- (d) 
24. The wavelength of a spectral line for an electronic transition is inversely related to (1988, 1M)
 (a) the number of electrons undergoing the transition
 (b) the nuclear charge of the atom
 (c) the difference in the energy of the energy levels involved in the transition
 (d) the velocity of the electron undergoing the transition
25. The ratio of the energy of a photon of 200 \AA wavelength radiation to that of 4000 \AA radiation is (1986, 1M)
 (a) $\frac{1}{4}$ (b) 4 (c) $\frac{1}{2}$ (d) 2
26. Which one of the following sets of quantum numbers represents an impossible arrangement? (1986, 1M)
- | n | l | m | s |
|-------|-----|-----|----------------|
| (a) 3 | 2 | -2 | 1/2 |
| (b) 4 | 0 | 0 | 1/2 |
| (c) 3 | 2 | -3 | $\frac{1}{2}$ |
| (d) 5 | 3 | 0 | $-\frac{1}{2}$ |
27. Electromagnetic radiation with maximum wavelength is (1985, 1M)
 (a) ultraviolet (b) radio wave
 (c) X-ray (d) infrared
28. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon? (1984, 1M)
 (a) $3s$ (b) $2p$ (c) $2s$ (d) $1s$
29. Correct set of four quantum numbers for the valence (outermost) electron of rubidium ($Z = 37$) is (1984, 1M)
 (a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$
 (c) $5, 1, 1, +\frac{1}{2}$ (d) $6, 0, 0, +\frac{1}{2}$
30. The principal quantum number of an atom is related to the (1983, 1M)
 (a) size of the orbital
 (b) spin angular momentum
 (c) orientation of the orbital in space
 (d) orbital angular momentum
31. Any p -orbital can accommodate upto (1983, 1M)
 (a) four electrons
 (b) six electrons
 (c) two electrons with parallel spins
 (d) two electrons with opposite spins

26 Atomic Structure

Objective Questions II

(One or more than one correct option)

32. The ground state electronic configuration of nitrogen atom can be represented by (1999, 3M)



33. Which of the following statement (s) is (are) correct ?

(1998, 2M)

- (a) The electronic configuration of Cr is $[\text{Ar}] 3d^5 4s^1$ (atomic number of Cr = 24)
 (b) The magnetic quantum number may have a negative value
 (c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (atomic number of Ag = 47)
 (d) The oxidation state of nitrogen in HN_3 is -3

34. An isotone of ${}^{76}_{32}\text{Ge}$ is

(1984, 1M)



Assertion and Reason

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

- (a) Both Statement I and Statement II are correct; Statement II is the correct explanation of Statement I
 (b) Both Statement I and Statement II are correct; Statement II is not the correct explanation of Statement I
 (c) Statement I is correct; Statement II is incorrect
 (d) Statement I is incorrect; Statement II is correct

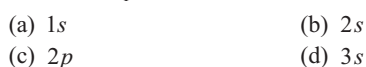
35. **Statement I** The first ionisation energy of Be is greater than that of B.

Statement II $2p$ -orbital is lower in energy than $2s$. (2000)

Passage Based Problems

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.

36. The state S_1 is (2010)



37. Energy of the state S_1 in units of the hydrogen atom ground state energy is (2010)



38. The orbital angular momentum quantum number of the state S_2 is (2010)



Match the Columns

39. Match the entries in Column I with the correctly related quantum number(s) in Column II. (2008, 6M)

Column I	Column II
A. Orbital angular momentum of the electron in a hydrogen-like atomic orbital.	p. Principal quantum number
B. A hydrogen-like one-electron wave function obeying Pauli's principle.	q. Azimuthal quantum number
C. Shape, size and orientation of hydrogen-like atomic orbitals.	r. Magnetic quantum number
D. Probability density of electron at the nucleus in hydrogen-like atom.	s. Electron spin quantum number

Fill in the Blanks

40. The outermost electronic configuration of Cr is (1994, 1M)
 41. 8 g each of oxygen and hydrogen at 27°C will have the total kinetic energy in the ratio of (1989, 1M)
 42. The uncertainty principle and the concept of wave nature of matter were proposed by and respectively. (1988, 1M)
 43. Wave functions of electrons in atoms and molecules are called (1993, 1M)
 44. The $2p_x$, $2p_y$ and $2p_z$ orbitals of atom have identical shapes but differ in their (1993, 1M)
 45. When there are two electrons in the same orbital, they have spins. (1983, 1M)

True/False

46. In a given electric field, β -particles are deflected more than α -particles in spite of α -particles having larger charge. (1993, 1M)
 47. The electron density in the XY -plane in $3d_{x^2-y^2}$ orbital is zero. (1986, 1M)
 48. The energy of the electron in the $3d$ -orbital is less than that in the $4s$ -orbital in the hydrogen atom. (1983, 1M)
 49. Gamma rays are electromagnetic radiations of wavelengths of 10^{-6} to 10^{-5} cm. (1983, 1M)
 50. The outer electronic configuration of the ground state chromium atom is $3d^4 4s^2$. (1982, 1M)

Integer Answer Type Questions

51. In an atom, the total number of electrons having quantum numbers (2014 Adv.)

$$n = 4, |m_l| = 1 \quad \text{and} \quad m_s = -\frac{1}{2} \text{ is}$$

52. The atomic masses of He and Ne are 4 and 20 amu, respectively. The value of the de-Broglie wavelength of He gas at -73°C is ' M ' times that of the de-Broglie wavelength of Ne at 727°C . M is (2013 Adv.)
53. The work function (ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is (2011)

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

54. The maximum number of electrons that can have principal quantum number, $n = 3$ and spin quantum number, $m_s = -1/2$, is (2011)

Subjective Questions

55. (a) Calculate velocity of electron in first Bohr orbit of hydrogen atom (Given, $r = a_0$).
 (b) Find de-Broglie wavelength of the electron in first Bohr orbit.
 (c) Find the orbital angular momentum of $2p$ -orbital in terms of $h/2\pi$ units. (2005, 2M)
56. (a) The Schrodinger wave equation for hydrogen atom is

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

where, a_0 is Bohr's radius. Let the radial node in $2s$ be at r_0 . Then, find r in terms of a_0 .

- (b) A base ball having mass 100 g moves with velocity 100 m/s. Find out the value of wavelength of base ball. (2004, 2M)
57. The wavelength corresponding to maximum energy for hydrogen is 91.2 nm. Find the corresponding wavelength for He^+ ion. (2003, 2M)
58. Calculate the energy required to excite 1 L of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bond is 436 kJ mol^{-1} . (2000)
59. 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 (C), 2M)
60. Consider the hydrogen atom to be proton embedded in a cavity of radius a_0 (Bohr's radius) whose charge is neutralised by the addition of an electron to the cavity in vacuum, infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralisation process. Also, if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy. (1996, 2M)

61. Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. (1996, 1M)
62. Iodine molecule dissociates into atoms after absorbing light to 4500 \AA . If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (Bond energy of $\text{I}_2 = 240 \text{ kJ mol}^{-1}$) (1995, 2M)
63. Find out the number of waves made by a Bohr's electron in one complete revolution in its 3rd orbit. (1994, 3M)
64. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum? (1993, 3M)
65. Estimate the difference in energy between 1st and 2nd Bohr's orbit for a hydrogen atom. At what minimum atomic number, a transition from $n = 2$ to $n = 1$ energy level would result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8} \text{ m}$? Which hydrogen atom-like species does this atomic number correspond to? (1993, 5M)
66. According to Bohr's theory, the electronic energy of hydrogen atom in the n th Bohr's orbit is given by :

$$E_n = \frac{-21.7 \times 10^{-19}}{n^2} \text{ J}$$

Calculate the longest wavelength of electron from the third Bohr's orbit of the He^+ ion. (1990, 3M)

67. What is the maximum number of electrons that may be present in all the atomic orbitals with principal quantum number 3 and azimuthal quantum number 2? (1985, 2M)
68. Give reason why the ground state outermost electronic configuration of silicon is (1985, 2M)
- $$\begin{array}{|c|} \hline 3s \\ \hline \uparrow\downarrow \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline 3p \\ \hline \uparrow \quad \uparrow \quad \square \\ \hline \end{array} \quad \text{and not} \quad \begin{array}{|c|} \hline 3s \\ \hline \uparrow\downarrow \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline 3p \\ \hline \uparrow \quad \downarrow \quad \square \\ \hline \end{array}$$
69. The electron energy in hydrogen atom is given by $E_n = -\frac{21.7 \times 10^{-12}}{n^2} \text{ erg}$. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition? (1984, 3M)
70. Calculate the wavelength in Angstroms of the photon that is emitted when an electron in the Bohr's orbit, $n = 2$ returns to the orbit, $n = 1$ in the hydrogen atom. The ionisation potential of the ground state hydrogen atom is $2.17 \times 10^{-11} \text{ erg per atom}$. (1982, 4M)
71. The energy of the electron in the second and third Bohr's orbits of the hydrogen atom is $-5.42 \times 10^{-12} \text{ erg}$ and $-2.41 \times 10^{-12} \text{ erg}$ respectively. Calculate the wavelength of the emitted light when the electron drops from the third to the second orbit. (1981, 3M)

28 Atomic Structure

Topic 1

1. (d) 2. (b) 3. (b) 4. (b)
 5. (d) 6. (a) 7. (c) 8. (a)
 9. (a,b) 10. (d) 11. (a,c) 12. (a,c)
 13. $A \rightarrow r; B \rightarrow q; C \rightarrow p, D \rightarrow s$ 14. (photons)
 15. $(1.66 \times 10^{-27} \text{ kg})$ 16. (neutrons) 17. (isobars)

Topic 2

1. (c) 2. (a) 3. (a) 4. (c)
 5. (a) 6. (b) 7. (c) 8. (d)
 9. (c) 10. (a) 11. (b) 12. (a)
 13. (a) 14. (a) 15. (b) 16. (d)
 17. (b) 18. (d) 19. (c) 20. (c)

21. (a) 22. (c) 23. (b) 24. (c)
 25. (d) 26. (c) 27. (b) 28. (d)
 29. (a) 30. (a) 31. (d) 32. (a,d)
 33. (a,b,c) 34. (b,d) 35. (c) 36. (b)
 37. (c) 38. (b)
 39. $A \rightarrow q; B \rightarrow p, q, r, s; C \rightarrow p, q, r; D \rightarrow p, q, r$
 40. $\text{Cr} = [\text{Ar}] 3d^5, 4s^1$ 41. 1 : 16
 42. Heisenberg, de-Broglie. 43. orbital
 44. Orientation in space 45. opposite
 46. True 47. False
 48. True 49. False 50. False 51. (6)
 52. (5) 53. (4) 54. (9)

Topic 1 Preliminary Developments and Bohr's Model

- Rutherford used α -particle (He^{2+} nuclei) in his experiment.
- According to Rutherford's model, there is a heavily positively charged nucleus and negatively charged electrons occupies space around it in order to maintain electro-neutrality.
- Radius of a nucleus is in the order of 10^{-13} cm, a fact.
- Bohr's model is applicable to one-electron system only.
- Neutron has no charge, hence e/m is zero for neutron. Next, α -particle (He^{2+}) has very high mass compared to proton and electron, therefore very small e/m ratio. Proton and electron have same charge (magnitude) but former is heavier, hence has smaller value of e/m .

$$\frac{e}{m} : n < \alpha < p < e$$

- The negligibly small size of nucleus compared to the size of atom was first established in Rutherford's experiment.
- The most important findings of Rutherford's experiment is discovery of nucleus.
- Energy of electron in H-atom is determined by the expression:

$$E_n = -\frac{13.6}{n^2} \text{ eV} \quad \text{where, } n = 1, 2, 3, \dots$$

$$\text{In excited states, } E_2 = -\frac{13.6}{4} = -3.4 \text{ eV}$$

$$E_3 = -\frac{13.6}{9} = -1.51 \text{ eV etc.}$$

- Nucleus is composed of neutrons and protons.

- The isotopes of hydrogen are ${}_1\text{H}^2$ and ${}_1\text{H}^3$.
- Alpha particles passes mostly undeflected when sent through thin metal foil mainly, because
 - it is much heavier than electrons.
 - most part of atom is empty space.
- Many elements have several isotopes. For such elements, atomic mass is average of the atomic masses of different isotopes, which is usually non-integral.
- A. $V_n = -\frac{1}{4\pi\epsilon_0} \left(\frac{Ze^2}{r} \right)$

$$K_n = \frac{1}{8\pi\epsilon_0} \left(\frac{Ze^2}{r} \right) \Rightarrow \frac{V_n}{K_n} = -2 \text{ --- (r)}$$

B. $E_n = -\frac{Ze^2}{8\pi\epsilon_0 r} \propto r^{-1} \Rightarrow x = -1 \text{ --- (q)}$

C. Angular momentum = $\sqrt{l(l+1)} \frac{h}{2\pi} = 0$ in 1s-orbital --- (p).

D. $r_n = \frac{a_0 n^2}{Z} \Rightarrow \frac{1}{r_n} \propto Z \text{ --- (s)}$
- Photons have quantised energy.
- Mass of one H-atom = $\frac{10^{-3}}{6.023 \times 10^{23}} \text{ kg} = 1.66 \times 10^{-27} \text{ kg}$
- Isotopes have different number of neutrons.
- Isobars have same mass number but different atomic numbers.
- When α -particle stop at 10^{-13} m from nucleus, kinetic energy is zero, i.e. whole of its kinetic energy at the starting point is now converted into potential energy.

Potential energy of this α -particle can be determined as

$$\text{PE} = -\frac{Z_1 \times Z_2 e^2}{(4\pi\epsilon_0) r}$$

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}, r = 10^{-13} \text{ m}$$

$$\Rightarrow |\text{PE}| = \frac{2 \times 29 \times (1.6 \times 10^{-19})^2}{4 \times 3.14 \times 8.85 \times 10^{-12} \times 10^{-13}} \text{ J}$$

$$= 1.33 \times 10^{-13} \text{ J}$$

= kinetic energy of α -particle at $t = 0$

$$\Rightarrow \text{KE} = \frac{1}{2} mv^2 = 1.33 \times 10^{-13}$$

$$\Rightarrow v = \sqrt{\frac{2 \times 1.33 \times 10^{-13}}{4 \times 1.66 \times 10^{-27}}} = 6.3 \times 10^6 \text{ ms}^{-1}$$

Topic 2 Advanced Concept (Quantum Mechanical Theory) Electronic Configuration and Quantum Number

1. $\therefore E_n = -\frac{13.6}{n^2} \text{ eV}$ where, $n = 1, 2, 3 \dots$

In excited states, $E_2 = -\frac{13.6}{4} = -3.4 \text{ eV}$

2. Given, atomic number of Rb, $Z = 37$

Thus, its electronic configuration is $[\text{Kr}]5s^1$. Since, the last electron or valence electron enter in $5s$ subshell.

So, the quantum numbers are $n = 5, l = 0$, (for s -orbital) $m = 0$ ($\because m = +l$ to $-l$), $s = +1/2$ or $-1/2$.

3. Given, in the question $E = -2.178 \times 10^{-18} \text{ J} \left[\frac{Z^2}{n^2} \right]$

For hydrogen $Z = 1$,

So, $E_1 = -2.178 \times 10^{-18} \text{ J} \left[\frac{1}{1^2} \right]$

$$E_2 = -2.178 \times 10^{-18} \text{ J} \left[\frac{1}{2^2} \right]$$

Now, $E_1 - E_2$

i.e. $\Delta E = 2.178 \times 10^{-18} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{hc}{\lambda}$

$$2.178 \times 10^{-18} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{6.62 \times 10^{-34} \times 3.0 \times 10^8}{\lambda}$$

$$\therefore \lambda \approx 1.21 \times 10^{-7} \text{ m}$$

4. According to Bohr's model,

$$mvr = \frac{nh}{2\pi} \Rightarrow (mv)^2 = \frac{n^2 h^2}{4\pi^2 r^2}$$

$$\Rightarrow \text{KE} = \frac{1}{2} mv^2 = \frac{n^2 h^2}{8\pi^2 r^2 m} \dots(i)$$

Also, Bohr's radius for H-atom is, $r = n^2 a_0$

Substituting ' r ' in Eq. (i) gives

$$\text{KE} = \frac{h^2}{8\pi^2 n^2 a_0^2 m} \text{ when } n = 2, \text{ KE} = \frac{h^2}{32\pi^2 a_0^2 m}$$

5. The number of radial nodes is given by expression $(n - l - 1)$.

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

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

6. Expression for Bohr's orbit is, $r_n = \frac{a_0 n^2}{Z} = a_0$

when $n = 2, Z = 4$.

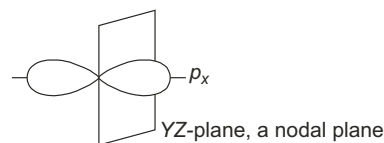
7. $1s^7$ violate Pauli exclusion principle, according to which an orbital cannot have more than two electrons.

8. $+\frac{1}{2}$ and $-\frac{1}{2}$ just represents two quantum mechanical spin states which have no classical analogue.

9. Using the de-Broglie's relationship :

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{0.2 \times \frac{5}{60 \times 60}} = 2.3 \times 10^{-30} \text{ m}$$

10. Nodal plane is an imaginary plane on which probability of finding an electron is minimum. Every p -orbital has one nodal plane :



11. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ is ground state electronic configuration of Cr.

12. (i) $n = 4, l = 1 \Rightarrow 4p$ -orbital

(ii) $n = 4, l = 0 \Rightarrow 4s$ -orbital

(iii) $n = 3, l = 2 \Rightarrow 3d$ -orbital

(iv) $n = 3, l = 1 \Rightarrow 3d$ -orbital

According to Aufbau principle, energies of above mentioned orbitals are in the order of

(iv) $3p < (ii) 4s < (iii) 3d < (i) 4p$

13. The energy of an electron in a Bohr atom is expressed as

$$E_n = -\frac{kZ^2}{n^2} \text{ where, } k = \text{Constant,}$$

$$Z = \text{Atomic number,}$$

$$n = \text{Orbit number}$$

$$= -13.6 \text{ eV for H } (n = 1)$$

$$\text{when } n = 2, E_2 = \frac{-13.6}{2^2} \text{ eV} = -3.40 \text{ eV}$$

(n can have only integral value $1, 2, 3, \dots, \infty$)

14. The orbital angular momentum (L) = $\sqrt{l(l+1)} \frac{h}{2\pi}$

$$= \sqrt{6} \frac{h}{2\pi} \text{ (} l=2 \text{ for } d\text{-orbital)}$$

30 Atomic Structure

15. Bohr first made use of quantum theory to explain the structure of atom and proposed that energy of electron in an atom is quantised.

16. $\text{Mg}^{2+} = 1s^2 2s^2 2p^6$ no unpaired electron

$\text{Ti}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ one unpaired electron

$\text{V}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ two unpaired electrons

$\text{Fe}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ four unpaired electrons

17. Expression for orbital angular momentum (L) is

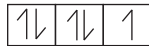
$$L = \sqrt{l(l+1)} \frac{h}{2\pi} = 0 \quad \text{for } 2s\text{-electrons}$$

\therefore For s -orbital, $l=0$.

18. Diffraction is property of wave, $E = mc^2$ determine energy of particle and $E = h\nu$ determine energy of photon. Interference phenomena is exhibited by both matter and waves.

19. X-rays is electrically neutral, not deflected in electric or magnetic fields.

20. $\text{Cl} (17) = 1s^2 2s^2 2p^6 3s^2 3p^5$



The last, unpaired electron has, $n=3, l=1(p)$ and m can have any of the three value $(-1, 0, +1)$.

21. $\text{Cr} (24) = \underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{\text{Ar}} 3d^5 4s^1$

The above configuration is exception to Aufbau's principle.

22. Fluorine, a halogen, is the most electronegative atom, has the electronic configuration $2s^2 2p^5$ (valence shell).

23. Option (b) is wrong representation according to aufbau principle. A high energy atomic orbital ($2p$) cannot be filled unless the low energy orbital ($2s$) is completely occupied.

24. Transition energy (ΔE) $= kZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{hc}{\lambda}$

i.e. $\Delta E \propto \frac{1}{\lambda}$

25. $E = \frac{hc}{\lambda} \Rightarrow \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} = 2$

26.

n	l	m	s
3	2	-3	$\frac{1}{2}$

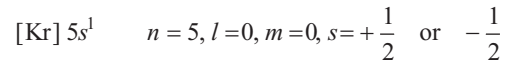
This is the wrong set of quantum number because $|m|$ cannot be greater than l .

27. The wavelength order is

X-ray < ultraviolet < infrared < radio wave

28. When electron jumps to lower orbit photons are emitted while photons are absorbed when electron jumps to higher orbit. $1s$ -orbital is the lower most, electron in this orbital can absorb photons but cannot emit.

29. The valence shell configuration of Rubidium (Rb) is



30. The principal quantum number ' n ' represents orbit number hence, determine the size of orbitals.

31. According to Pauli exclusion principle, an atomic orbital can accommodate at the most, two electrons, with opposite spins.

32. Both (a) and (d) are correct. The three electrons in the $2p$ -orbitals must have same spin, no matter up spin or down spin.

33. (a) $\text{Cr} = [\text{Ar}] 3d^5 4s^1$, an exception to aufbau principle.

(b) For a given value of l, m can have any value from $(-l$ to $+l)$, so can have negative value.

(c) Ag is in copper group with $d^{10}s^1$ configuration, i.e. 46 electrons are spin paired.

34. Isotones have same number of neutrons.

${}_{32}\text{Ge}^{76}, {}_{33}\text{As}^{77}$ and ${}_{34}\text{Se}^{78}$ have same number (44) of neutrons, hence they are isotones.

35. Assertion is correct $\text{Be}(1s^2, 2s^2)$ has stable electronic configuration, removing an electron require more energy than the same for $\text{B}(2p^1)$. Reason is incorrect (Aufbau principle).

36. S_1 is spherically symmetrical state, i.e. it correspond to a s -orbital. Also, it has one radial node.

Number of radial nodes $= n - l - 1$

$$\Rightarrow n - 0 - 1 = 1$$

$$\Rightarrow n = 2 \text{ i.e. } S_1 = 2s\text{-orbital.}$$

37. Ground state energy of electron in H-atom (E_H)

$$E_H = \frac{kZ^2}{n^2} = k \quad (Z=1, n=1)$$

For S_1 state of Li^{2+} ,

$$E = \frac{k(3)^2}{2^2} = \frac{9}{4} k = 2.25 k$$

38. In S_2 state, $E(\text{Li}^{2+}) = K$ (given)

$$K = \frac{qk}{n^2}$$

$$\Rightarrow n = 3$$

Since, S_2 has one radial node.

$$3 - l - 1 = 1$$

$$l = 1$$

39. A. Orbital angular momentum

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

i.e. L depends on azimuthal quantum number only.

B. To describe a one electron wave function, three quantum numbers n, l and m are needed. Further to abide by Pauli exclusion principle, spin quantum number(s) is also needed.

- C. For shape, size and orientation, only n , l and m are needed.
 D. Probability density (ψ^2) can be determined if n , l and m are known.

40. $\text{Cr} = [\text{Ar}] 3d^5 4s^1$
 41. 1 : 16
 42. Heisenberg proposed uncertainty principle and de-Broglie proposed wave nature of electron.
 43. orbital
 44. $2p_x, 2p_y$ and $2p_z$ have different orientation in space.
 45. Two electrons in same orbital must have opposite spin.
 46. Very large mass of alpha particles than beta particles is responsible for less deflection in former case.
 47. $3d_{x^2-y^2}$ orbital lies in XY -plane.
 48. Aufbau principle.
 49. This is the wavelength of infrared radiation.
 50. $\text{Cr} = 3d^5 4s^1$.

51. **PLAN** This problem is based on concept of quantum number. Follow the following steps to solve this problem.
 Write all possible orbitals having combination of same principal, azimuthal, magnetic and spin quantum number.

Then count the all possible electrons having given set of quantum numbers.

For $n = 4$, the total number of possible orbitals are

4s		4p			4d					4f					
0	-1	0	+1	-2	-1	0	+1	+2	-3	-2	-1	0	+1	+2	+3

According to question $|m_l| = 1$, i.e. there are two possible values of m_l , i.e. +1 and -1 and one orbital can contain maximum two electrons one having $s = +\frac{1}{2}$ and other having

$$s = -1/2.$$

So, total number of orbitals having $\{|m_l| = 1\} = 6$

Total number of electrons having

$$\{|m_l| = 1 \text{ and } m_s = -\frac{1}{2}\} = 6$$

52. **PLAN** $\text{KE} = \frac{1}{2}mv^2 = \frac{3}{2}RT$

$$\therefore m^2v^2 = 2m\text{KE} \quad \therefore mv = \sqrt{2m\text{KE}}$$

$$\lambda (\text{wavelength}) = \frac{h}{mv} = \frac{h}{\sqrt{2m\text{KE}}} \propto \frac{h}{\sqrt{2m(T)}}$$

where, $T =$ Temperature in Kelvin

$$\lambda (\text{He at } -73^\circ\text{C} = 200 \text{ K}) = \frac{h}{\sqrt{2 \times 4 \times 200}}$$

$$\lambda (\text{Ne at } 727^\circ\text{C} = 1000 \text{ K}) = \frac{h}{\sqrt{2 \times 20 \times 1000}}$$

$$\therefore \frac{\lambda(\text{He})}{\lambda(\text{Ne})} = M = \sqrt{\frac{2 \times 20 \times 1000}{2 \times 4 \times 200}} = 5$$

Thus,

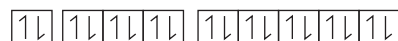
$$M = 5$$

53. Energy of photon

$$= \frac{hc}{\lambda} \text{ J} = \frac{hc}{e\lambda} \text{ eV} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9} \times 1.602 \times 10^{-19}} = 4.14 \text{ eV}$$

For photoelectric effect to occur, energy of incident photons must be greater than work function of metal. Hence, only Li, Na, K and Mg have work functions less than 4.14 V.

54. When $n = 3$, $l = 0, 1, 2$ i.e. there are $3s, 3p$ and $3d$ -orbitals. If all these orbitals are completely occupied as



Total 18 electrons, 9 electrons with $s = +\frac{1}{2}$ and 9 with $s = -\frac{1}{2}$.

Alternatively In any n th orbit, there can be a maximum of $2n^2$ electrons. Hence, when $n = 3$, number of maximum electrons = 18. Out of these 18 electrons, 9 can have spin $-\frac{1}{2}$ and remaining nine with spin $+\frac{1}{2}$.

55. (a) $mvr = \frac{nh}{2\pi}$

$$\Rightarrow v = \frac{nh}{2\pi mr} = \frac{6.625 \times 10^{-34}}{2 \times 3.14 \times 9.1 \times 10^{-31} \times 0.529 \times 10^{-10}} = 2.18 \times 10^6 \text{ ms}^{-1}$$

$$(b) \lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.18 \times 10^6} = 0.33 \times 10^{-9} \text{ m}$$

- (c) Orbital angular momentum

$$(L) = \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{2} \left(\frac{h}{2\pi} \right)$$

[\because For p -orbital, $l = 1$]

56. (a) At radial node, ψ^2 must vanishes, i.e.

$$\psi_{2s}^2 = 0 = \left[\frac{1}{4\sqrt{2}\pi} \right]^2 \left(2 - \frac{r_0}{a_0} \right)^2 e^{-\frac{r_0}{a_0}}$$

$$\Rightarrow 2 - \frac{r_0}{a_0} = 0 \Rightarrow r_0 = 2a_0$$

$$(b) \lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{100 \times 10^{-3} \times 100} = 6.625 \times 10^{-35} \text{ m} = 6.625 \times 10^{-25} \text{ \AA} \text{ (negligibly small)}$$

57. The general Rydberg's equation is

$$\bar{\nu} = \frac{1}{\lambda} = R(Z)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow \frac{1}{\lambda} \propto Z^2$$

$$\Rightarrow \frac{\lambda(\text{He}^+)}{\lambda(\text{H})} = \frac{Z(\text{H})^2}{Z(\text{He}^+)^2} = \frac{1}{4}$$

$$\Rightarrow \lambda(\text{He}^+) = \frac{\lambda(\text{H})}{4} = \frac{91.2}{4} \text{ nm} = 22.8 \text{ nm}$$

32 Atomic Structure

58. Moles of $H_2 = \frac{pV}{RT} = \frac{1 \times 1}{0.082 \times 298} = 0.0409$
 \Rightarrow Bond energy = $0.0409 \times 436 = 17.84$ kJ
 Number of H-atoms produced after dissociation
 $= 2 \times 0.0409 \times 6.023 \times 10^{23} = 4.93 \times 10^{22}$

Transition energy/atom = $2.18 \times 10^{-18} \left(1 - \frac{1}{4}\right)$ J
 $= \frac{3}{4} \times 2.18 \times 10^{-18}$ J

\Rightarrow Total transition energy
 $= \frac{3}{4} \times 2.18 \times 10^{-18} \times 4.93 \times 10^{22}$ J
 $= 80.60 \times 10^3$ J = 80.60 kJ

Therefore, total energy required
 $=$ dissociation energy + transition energy
 $= (17.84 + 80.60)$ kJ = 98.44 kJ

59. If accelerated by potential difference of V volt, then

$$\frac{1}{2} mv^2 = eV$$

$\Rightarrow \frac{p^2}{2m} = eV$, here $p =$ momentum (mv)

Using de-Broglie equation, $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}}$

$\Rightarrow 1.54 \times 10^{-10} = \frac{6.625 \times 10^{-34}}{(2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} V)^{1/2}}$

Solving for V gives : $V = 63.56$ V.

60. The work done in the given neutralisation process is

$$W = - \int_{a_0}^{\infty} F dr$$

and $F = \frac{e^2}{4\pi\epsilon_0 r^2}$

$\Rightarrow W = \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{r} \right]_{a_0}^{\infty} = - \frac{e^2}{4\pi\epsilon_0 r} =$ Total energy (E)

Now, if ' V ' is magnitude of potential energy, then according to given information, kinetic energy (E_k) is $V/2$. Therefore,

$$E = -V + \frac{V}{2} \quad (\text{PE is always negative})$$

$$= -\frac{V}{2}$$

$\Rightarrow V = -2E = \frac{-e^2}{2\pi\epsilon_0 r}$

61. The Rydberg's equation for H-atom is

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

For Balmer series, $n_1 = 2$ and $n_2 = 3, 4, 5, \dots, \infty$

For shortest λ , n_2 has to be maximum, i.e. infinity. Then

$$\bar{\nu} = R_H \left(\frac{1}{4} - \frac{1}{\infty} \right)$$

$$= \frac{R_H}{4} = \frac{1.09 \times 10^7}{4} = 2.725 \times 10^6 \text{ m}^{-1}$$

62. After breaking of the bond of I_2 molecule, the remaining energy would be distributed uniformly to iodine atoms as their kinetic energy, i.e.

E (energy of photon) = Bond energy + $2 \times$ kinetic energy

$$\Rightarrow \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{4500 \times 10^{-10}} = \frac{240 \times 10^3}{6.023 \times 10^{23}} + 2 \times E_k$$

$$\Rightarrow E_k = 2.16 \times 10^{20} \text{ J/atom}$$

63. The Bohr de-Broglie relationship is

$$2\pi r = n\lambda = \text{circumference of Bohr's orbit.}$$

i.e. number of complete waves formed in one complete revolution of electron in any Bohr orbit is equal to orbit number, hence three.

64. The expression for transition wavelength is given by Rydberg's equation :

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

Equating the transition wavelengths of H-atom and He^+ ion,

$$R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R_H \left(\frac{4}{2^2} - \frac{4}{4^2} \right)$$

Equating termwise on left to right of the above equation gives

$$n_1 = 1 \quad \text{and} \quad n_2 = 2$$

65. For H-atom, the energy of a stationary orbit is determined as

$$E_n = -\frac{k}{n^2} \quad \text{where, } k = \text{constant } (2.18 \times 10^{-18} \text{ J})$$

$$\Rightarrow \Delta E \text{ (} n=2 \text{ to } n=1) = k \left(1 - \frac{1}{4} \right) = \frac{3}{4} k$$

$$= 1.635 \times 10^{-18} \text{ J}$$

For a H-like species, energy of stationary orbit is determined as

$$E_n = -\frac{kZ^2}{n^2}$$

where, Z = atomic number

$$\Rightarrow \Delta E = kZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow \frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{k}{hc} Z^2 \left(\frac{1}{1} - \frac{1}{4} \right) = R_H Z^2 \times \frac{3}{4}$$

$$\Rightarrow Z^2 = \frac{4}{3R_H \lambda} = \frac{4}{3 \times 1.097 \times 10^7 \times 3 \times 10^{-8}} = 4.05$$

$$\Rightarrow Z = 2 \text{ (He}^+ \text{)}$$

66. For H-like species, the energy of stationary orbit is expressed as

$$E(X) = Z^2 \times E(H)$$

\Rightarrow For He⁺ ($Z = 2$)

$$E = -\frac{4 \times 21.7 \times 10^{-19}}{n^2} \text{ J}$$

For longest wavelength transition from 3rd orbit, electron must jump to 4th orbit and the transition energy can be determined as

$$\Delta E = +4 \times 21.7 \times 10^{-19} \left(\frac{1}{9} - \frac{1}{16} \right) \text{ J} = 4.22 \times 10^{-19} \text{ J}$$

Also, $\therefore \Delta E = \frac{hc}{\lambda}$

$$\therefore \lambda = \frac{hc}{\Delta E} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{4.22 \times 10^{-19}} \text{ m}$$

$$= 471 \times 10^{-9} \text{ m} = 471 \text{ nm}$$

67. Ten, the given value of n and l correspond to $3d$ -orbital which has five fold degeneracy level.

68. The 2nd configuration is against Hund's rule of maximum multiplicity which states that the singly occupied degenerate atomic orbitals must have electrons of like spins.

69. The required transition is $n_1 = 2$ to $n_2 = \infty$ and corresponding transition energy is

$$\Delta E = 21.7 \times 10^{-12} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ erg} = \frac{21.7}{4} \times 10^{-12} \text{ erg}$$

$$= 5.425 \times 10^{-12} \text{ erg}$$

The longest wavelength that can cause above transition can be determined as :

$$\lambda = \frac{hc}{\Delta E} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{5.425 \times 10^{-12} \times 10^{-7}}$$

$$= 3.66 \times 10^{-7} \text{ m} = 3.66 \times 10^{-5} \text{ cm}$$

70. Ionisation potential of H-like species

$$= E_1 = 2.17 \times 10^{-11} \text{ erg}$$

$$\Rightarrow \Delta E = 2.17 \times 10^{-11} \left(1 - \frac{1}{2^2} \right) \times 10^{-7} \text{ J}$$

$$= 1.6275 \times 10^{-18} \text{ J} \Rightarrow \lambda = \frac{hc}{\Delta E}$$

$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{1.6275 \times 10^{-18}} \text{ m}$$

$$= 122 \times 10^{-9} \text{ m} = 1220 \text{ \AA}$$

71. Transition energy = $[-2.41 - (-5.42)] \times 10^{-12} \text{ erg}$

$$= 3.01 \times 10^{-12} \text{ erg}$$

$$= 3.01 \times 10^{-19} \text{ J} \quad [\because 1 \text{ erg} = 10^{-7} \text{ J}]$$

Also, $\Delta E = \frac{hc}{\lambda}$

$$\Rightarrow \lambda = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{3.01 \times 10^{-19}} \text{ m}$$

$$= 660 \times 10^{-9} \text{ m} = 660 \text{ nm}$$

- Which of the following statements is incorrect?
 - When hydrogen atoms were excited, a line spectrum rather than a continuous spectrum was observed
 - It was assumed that electrons in the hydrogen atoms were allowed to have only discrete amounts of energy
 - In Balmer series, the emitted light falls in the visible region of spectrum in which the electron's final energy level is 2
 - Einstein postulated that light behaved as a particle called a photon, and the photoelectric effect was used to support this postulation
- Which of the following is not a legal set of quantum numbers for an electron in an atom?
 - $n = 5, l = 3, m_l = 2, m_s = 1/2$
 - $n = 3, l = 2, m_l = 3, m_s = -1/2$
 - $n = 1, l = 1, m_l = 0, m_s = -1/2$
 - $n = 6, l = 3, m_l = -3, m_s = 1/2$
- The first emission line in visible region in the emission spectrum of He^+ ion would correspond to which of the following electronic transition?
 - $6 \rightarrow 3$
 - $7 \rightarrow 4$
 - $5 \rightarrow 4$
 - $6 \rightarrow 4$
- Consider the following radial distribution function diagrams. Which of the following has the correct matching of curve and orbital?

- I (3s), II (3p), III (3d)
- I (3d), II (3p), III (3s)
- I (3p), II (3d), III (3s)
- I (3s), II (3d), III (3p)

- A one electron system has its electron revolving in the 3rd orbit. The light of maximum wavelength which can eject the electron from the third orbit has energy of 6.04 eV. Which of the following statement regarding the above mentioned species is (are) true?
 - The ionisation energy of the species is 54.36 eV
 - If the electron falls to second Bohr orbit, visible light would be emitted
 - The atomic number is 2
 - A visible light may bring about transition from 4th to higher orbit

Passage for Q.Nos. 6 to 8

A one electron species initially in the some excited state (n_i) is irradiated with a light of wavelength 121 nm when the electron is promoted to a further higher orbit (n_f). In returning back to the ground state, it gives an emission

spectrum containing 15 bright lines. Out of these 15 lines, 9 lines were found to have wavelengths smaller than 121 nm while 5 lines have wavelengths greater than 121 nm. Based on the above information, answer the following three questions.

- What is the value of n_i ?
 - 2
 - 3
 - 4
 - 5
- What is the ionisation energy of the given species in eV unit?
 - 13.6
 - 54.4
 - 122.4
 - 217.6
- Which electronic transition correspond to the emission of 2nd longest wavelength?
 - $6 \rightarrow 5$
 - $6 \rightarrow 4$
 - $5 \rightarrow 4$
 - $4 \rightarrow 3$

Assertion-Reason Type

Following two questions have assertion followed by the reason. Answer them according to the following options.

- Both assertion and reason are correct and reason is the correct explanation of the assertion
 - Both assertion and reason are correct but reason is not the correct explanation of assertion
 - Assertion is correct but reason is incorrect
 - Assertion is incorrect but reason is correct
- Assertion** In H-atom, photons of higher intensity is emitted when electron falls from 2nd to 1st orbit than when it falls from 4th to 2nd orbit.
Reason Transition energy for 2nd to 1st orbit is greater than for 4th to 2nd orbit.
 - Assertion** Emission spectrum of H-atom is a line spectrum rather a continuous spectrum.
Reason Emission spectrum of every pure atom is always a line spectrum.
 - Match the statements of Column I with values of Column II.

	Column I		Column II
A.	$n = 6$	p.	Ionisation energy is greater than 0.75 eV. [ionisation energy of hydrogen atom when in ground state is 13.6 eV]
B.	$n = 5$	q.	Has radius greater than the 5th Bohr's radius of He^+ .
C.	$n = 4$	r.	Has more than six lines.
D.	$n = 3$	s.	Has two or more lines in the visible region.

- In how many different ways, the electrons of the outermost orbital of carbon can be represented in box diagram format such that they all corresponds to the ground state electronic configuration?

Answers

- (c)
- (b)
- (d)
- (c)
- (a, c, d)
- (b)
- (c)
- (c)
- (d)
- (b)
- A \rightarrow q,r,s; B \rightarrow q,r,s; C \rightarrow p,q,s; D \rightarrow p
- (6)

3

Periodic Classification and Periodic Properties

History and Periodic Classification

- **Mendeleef's Periodic Law** According to Mendeleef, "The physical and chemical properties of the elements are a periodic function of their atomic weights." He arranged the elements in increasing order of atomic weights into groups and periods.
- **Drawbacks of Mendeleef's Periodic Table**
Anomaly is found in three pair of elements. Tellurium (Te) and iodine (I), argon (Ar) and potassium (K), nickel (Ni) and cobalt (Co) which were not in accordance of their chemical behaviour.
- **Moseley's Law and Long-Form (Modern) Periodic Table** From his X-ray diffraction experiments on a number of elements, Moseley proposed that "The physical and chemical properties of the elements are a periodic function of their atomic number or their electronic configuration".
- **Characteristic Features of Long Form of Periodic Table**
 - (i) The modern periodic table is divided into two main categories known as
 - (a) vertical columns–groups and
 - (b) horizontal rows–periods.
 - (ii) There are 18 groups. These groups are further subdivided into A-groups and B-groups.
 - (iii) Members of the same group have same valence shell configurations.
 - (iv) Elements of group IA to VIIA (1, 2, 13, 14, 15, 16, 17 groups) are known as representative elements. Members of group IB to VIIIIB (3, 4, 5, 6, 7, 8, 9, 10, 11 and 12) are known as transition elements.
 - (v) Elements of group 18 (also known as zero group) are noble gases.
 - (vi) There are seven horizontal rows in the periodic table, known as periods.
 - (vii) In a period, number of valence shell remains the same, however the number of electrons increases from left to right.

Periodic Properties

• Metallic and Non-metallic Character

- (i) The tendency of an element to lose electrons and form positive ions is called electropositive character or metallic character, e.g. alkali metals are the most electropositive elements.
- (ii) The tendency of an element to accept electrons to form an anion is called **non-metallic character** or electronegative character, e.g. chlorine, oxygen, nitrogen are all electronegative elements and they are called non-metals.
- (iii) In a period, metallic character of elements decreases from left to right, e.g. in 3rd period, Na on extreme left is most metallic and Cl on extreme right is most electronegative.
- (iv) In a group metallic character increases from top to bottom, e.g. in group 14, element at the top (carbon) is non-metal while element at the bottom (lead) is metal.

• Atomic Size and Atomic Radii

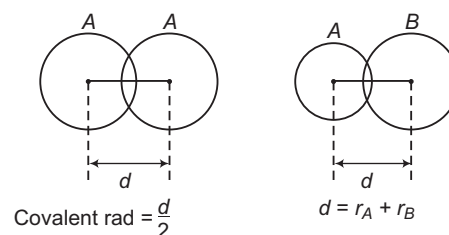
The distance from centre of the nucleus to the outermost shell is called radius of an atom. Atomic radius, therefore, depends on two important factors:

- (i) The orbit number of outermost shell and
- (ii) On effective nuclear charge.

- (a) Effective nuclear charge increases from left to right in a period and therefore, atomic radius decreases from left to right in a given period.
- (b) Orbit number in which the last electron enters increases successively from top to bottom in a group, hence atomic radius increases from top to bottom in a group.

• Covalent Radius and van der Waals' Radius

Covalent radius is defined in covalently bonded molecules as :



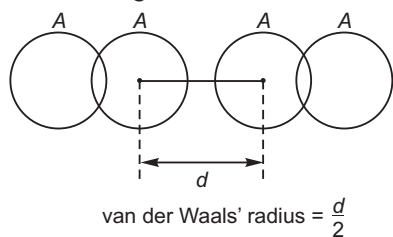
36 Periodic Classification and Periodic Properties

- (i) In case of **homonuclear diatomic molecule**, covalent radius is half of their internuclear distance.
- (ii) In case of **heteronuclear diatomic molecules**, covalent radius is defined as :

$$AB : \text{Internuclear distance} = r_A + r_B$$

where, r_A and r_B are covalent radii of A and B and if any one of them is known, other can be known.

- (iii) van der Waals' radius is defined as the half of the internuclear distance between two adjacent, non-bonded, like atoms. These types of radii are shown below in the diagram :



As shown above, for a given element, covalent radius is always less than its van der Waals' radius. Elements of 18th group do not form covalent bond therefore, for them the van der Waals' radius is the only radius and it is always greater than the covalent radius of any elements of the same period.

• Ionic Radius

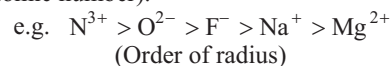
- (a) When a **cation is formed**, effective nuclear charge $\left(\frac{\text{number of protons}}{\text{number of electrons}}\right)$ increases resulting a decrease in radius than the radius of normal atom.
- (b) When an **anion is formed**, effective nuclear charge decreases, resulting an increase in radius than the radius of normal atom.

Comparison of cationic and anionic radius

Cationic radius	Anionic radius
Smaller than the radius of corresponding neutral atom. e.g. $\text{Mg} > \text{Mg}^{2+}$	Larger than the radius of corresponding neutral atom.
For same atom, cationic radius is inversely proportional to the magnitude of positive charge. e.g. $\text{Fe} > \text{Fe}^{2+} > \text{Fe}^{3+}$	For same atom, anionic radius is directly proportional to the magnitude of negative charge. e.g. $\text{O}^{2-} > \text{O}^- > \text{O}$
For isoelectronic cationic radius $\propto \frac{1}{Z}$ e.g. $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$	For isoelectronic species, anionic radius $\propto \frac{1}{Z}$ e.g. $\text{N}^{3-} > \text{O}^{2-} > \text{F}^-$

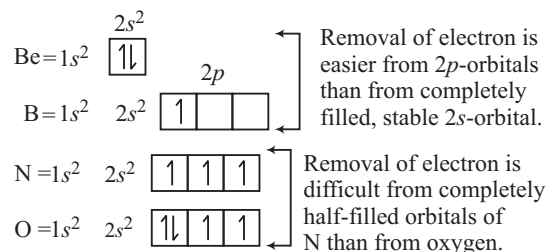
Remember

For a group of isoelectronic species involving cation, anion and neutral atom, radius is inversely proportional to Z (atomic number).



- **Ionisation Potential** Ionisation potential (or ionisation energy) is the amount of energy required to remove one or more electrons from the outermost shell of an isolated gaseous atom in their ground state. Ionisation energy is also known as ionisation potential because it is measured as the minimum potential difference required to remove the most loosely held electrons from the rest of the atom. It is measured in eV unit per atom or kJ per mole. Following trends are observed for ionisation energy in periodic table :

- Metals usually have low ionisation energy whereas non-metals have high ionisation energies. Inert gases have maximum ionisation energy in its period.
- In a period ionisation energy increases from left to right. In a group ionisation energy decreases from top to bottom.
- In a period, ionisation energy does not vary uniformly. Stability of electronic configuration alter the regular trends between adjacent elements in a period. Although B comes after Be in period, Be has higher ionisation energy.



Similarly, N has higher ionisation energy than O because N has completely half-filled, stable valence shell configuration :

However this anomaly applies only between adjacent elements in a period. Therefore, elements of G-2 has higher ionisation energy than elements of G-13 but of the same period. Similarly, elements of G-15 has higher ionisation energy than ionisation energy of G-16 elements from the same period.

- For a given element, values of successive ionisation energy increases, i.e. removal of an electron further require more energy than the energy required for removal of previous electron, i.e. for an element : $\text{IE}_1 < \text{IE}_2 < \text{IE}_3 \dots$

- **Electron Affinity** Electron affinity is the amount of energy released when an electron is added to an isolated,

neutral gaseous atom in the ground state. Electron affinity of an element depends on : (a) Extent of nuclear charge, i.e. effective nuclear charge. (b) Size of the atom. (c) Stability of valence shell electronic configuration.

If electron affinity is low, the electron is weakly bound to the nucleus and if the electron affinity is high, electron is strongly bound to the nucleus, e.g. electron affinity of chlorine is 3.79 eV which is higher than that of iodine, i.e. 3.28 eV. Periodic trend of electron affinity is :

- (i) In a period, it increases from left to right. Exception occurs in case of C and N. Carbon has greater electron affinity than nitrogen because later has stable valence shell configuration :

N = $\begin{array}{|c|c|c|} \hline & 2p^3 & \\ \hline \boxed{1} & \boxed{1} & \boxed{1} \\ \hline \end{array}$, has less affinity for electron.

C = $\begin{array}{|c|c|} \hline & 2p^2 & \\ \hline \boxed{1} & \boxed{1} \\ \hline \end{array}$, has greater affinity for electron than nitrogen.

- (ii) In a group, electron affinity decreases from top to bottom. Exception occur between fluorine and chlorine. Fluorine, due to smaller size and high electron density, has slightly smaller electron affinity than chlorine.
- (iii) Addition of 2nd electron is always an endothermic process.
- (iv) Noble gases have positive electron gain enthalpy, i.e. energy is required to add an electron into their valence shell.
- (v) Be, N also have positive electron gain enthalpy due to their stable electronic configuration.
- **Electronegativity** Electronegativity is the tendency of an atom to attract electron towards itself in a molecule or

compound. The value of electronegativity of an element describes the ability of its atom to complete for electrons with the other atom to which it is bonded. Electronegativity is however not the property of an isolated atom. In general,

- (i) Electronegativity increases from left to right in a period, ending at group 17.
- (ii) In a group electronegativity decreases from top to bottom.

The following Scales are used to measured electronegativity :

- (i) **Pauling Scale** The electronegativity value for other element are calculated as follows for a covalent bond between *A* and *B*

$$\chi_A - \chi_B = 0.208\sqrt{\Delta}$$

where, χ_A and χ_B are electronegativities of *A* and *B*

$$\Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$$

- (ii) **Mulliken Scale** According to this scale :

$$\chi = \frac{\text{Ionisation enthalpy} + \text{Electron gain enthalpy}}{2}$$

- **Inert Pair Effect** It is an effect, observed mainly in groups 13, 14 and 15. According to this effect, as we descend down in a group, the two electrons of *s*-orbital of the valence shell becomes inert, do not easily take part in bonding and the element show its oxidation state two unit less than the group oxidation number. Let us take the case of group 13. Al has +3, Ga has +3 as their stable oxidation state. In show both +1 and +3 oxidation state but Tl has only +1 as their stable oxidation state, because the two *s*-electrons of ns^2np^1 have become inert. Inert pair effect is the result of increase in effective nuclear charge on moving down in a group. Similar, phenomena is observed in group 14. Si, Ge show their usual oxidation state of +4, Sn has both +2 and +4 oxidation state but lead has +2 as their most stable oxidation state.

Topic 1 History and Periodic Classification

Objective Questions I (Only one correct option)

- The statement that is not correct for the periodic classification of elements, is (1992, 1M)
 - the properties of elements are the periodic functions of their atomic numbers
 - non-metallic elements are lesser in number than metallic elements
 - the first ionisation energies of elements along a period do not vary in a regular manner with increase in atomic number
 - for transition elements the *d*-subshells are filled with electrons monotonically with increase in atomic number

Objective Questions II

(One or more than one correct option)

- The statements that is/are true for the long form of the periodic table is/are (1988, 1M)
 - it reflects the sequence of filling the electrons in the order of sub-energy level *s*, *p*, *d* and *f*
 - it helps to predict the stable valency states of the elements
 - it reflects trends in physical and chemical properties of the elements
 - it helps to predict the relative ionicity of the bond between any two elements

38 Periodic Classification and Periodic Properties

Topic 2 Periodic Properties

Objective Questions I (Only one correct option)

- The ionic radii (in Å) of N^{3-} , O^{2-} and F^- respectively are (2015 Main)
(a) 1.36, 1.40 and 1.71 (b) 1.36, 1.71 and 1.40
(c) 1.71, 1.40 and 1.36 (d) 1.71, 1.36 and 1.40
- Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy? (2015 Main)
(a) CaSO_4 (b) BeSO_4
(c) BaSO_4 (d) SrSO_4
- Which among the following is the most reactive? (2015 Main)
(a) Cl_2 (b) Br_2
(c) I_2 (d) ICl
- Which one has the highest boiling point?
(a) He (b) Ne (c) Kr (d) Xe
- The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be (2013 Main)
(a) - 2.55 eV (b) - 5.1 eV
(c) - 10.2 eV (d) + 2.55 eV
- Which of the following represents the correct order of increasing first ionisation enthalpy for Ca, Ba, S, Se and Ar? (2013 Main)
(a) $\text{Ca} < \text{S} < \text{Ba} < \text{Se} < \text{Ar}$ (b) $\text{S} < \text{Se} < \text{Ca} < \text{Ba} < \text{Ar}$
(c) $\text{Ba} < \text{Ca} < \text{Se} < \text{S} < \text{Ar}$ (d) $\text{Ca} < \text{Ba} < \text{S} < \text{Se} < \text{Ar}$
- Identify the least stable ion amongst the following. (2002, 3M)
(a) Li^+ (b) Be^-
(c) B^- (d) C^-
- The set representing the correct order of first ionisation potential is (2001, 1M)
(a) $\text{K} > \text{Na} > \text{Li}$ (b) $\text{Be} > \text{Mg} > \text{Ca}$
(c) $\text{B} > \text{C} > \text{N}$ (d) $\text{Ge} > \text{Si} > \text{C}$
- The correct order of radii is (2000, 1M)
(a) $\text{N} < \text{Be} < \text{B}$ (b) $\text{F}^- < \text{O}^{2-} < \text{N}^{3-}$
(c) $\text{Na} < \text{Li} < \text{K}$ (d) $\text{Fe}^{3+} < \text{Fe}^{2+} < \text{Fe}^{4+}$
- The incorrect statement among the following. (1997(C), 1M)
(a) The first ionisation potential of Al is less than the first ionisation potential of Mg
(b) The second ionisation potential of Mg is greater than the second ionisation potential of Na
(c) The first ionisation potential of Na is less than the first ionisation potential of Mg
(d) The third ionisation potential of Mg is greater than third ionisation potential of Na
- Which of the following has the maximum number of unpaired electrons? (1996, 1M)
(a) Mg^{2+} (b) Ti^{3+}
(c) V^{3+} (d) Fe^{2+}
- Which has most stable +2 oxidation state? (1995, 1M)
(a) Sn (b) Pb (c) Fe (d) Ag
- Amongst the following elements (whose electronic configurations are given below), the one having the highest ionisation energy is (1990, 1M)
(a) $[\text{Ne}] 3s^2 3p^1$ (b) $[\text{Ne}] 3s^2 3p^3$
(c) $[\text{Ne}] 3s^2 3p^2$ (d) $[\text{Ar}] 3d^{10} 4s^2 4p^3$
- Which one of the following is the smallest in size? (1989, 1M)
(a) N^{3-} (b) O^{2-}
(c) F^- (d) Na^+
- The first ionisation potential of Na, Mg, Al and Si are in the order (1988, 1M)
(a) $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$ (b) $\text{Na} > \text{Mg} > \text{Al} > \text{Si}$
(c) $\text{Na} < \text{Mg} < \text{Al} > \text{Si}$ (d) $\text{Na} > \text{Mg} > \text{Al} < \text{Si}$
- The electronegativity of the following elements increases in the order (1987, 1M)
(a) C, N, Si, P (b) N, Si, C, P
(c) Si, P, C, N (d) P, Si, N, C
- Atomic radii of fluorine and neon in Angstrom units are respectively given by (1987, 1M)
(a) 0.72, 1.60 (b) 1.60, 1.60
(c) 0.72, 0.72 (d) None of these
- The first ionisation potential in electron volts of nitrogen and oxygen atoms are respectively given by (1987, 1M)
(a) 14.6, 13.6 (b) 13.6, 14.6
(c) 13.6, 13.6 (d) 14.6, 14.6
- The hydration energy of Mg^{2+} is larger than that of (1984, 1M)
(a) Al^{3+} (b) Na^+
(c) Be^{2+} (d) Mg^{3+}
- The element with the highest first ionisation potential is (1982, 1M)
(a) boron (b) carbon
(c) nitrogen (d) oxygen
- The correct order of second ionisation potential of carbon, nitrogen, oxygen and fluorine is (1981, 1M)
(a) $\text{C} > \text{N} > \text{O} > \text{F}$ (b) $\text{O} > \text{N} > \text{F} > \text{C}$
(c) $\text{O} > \text{F} > \text{N} > \text{C}$ (d) $\text{F} > \text{O} > \text{N} > \text{C}$

Objective Questions II

(One or more than one correct option)

- Ionic radii of (1999, 3M)
(a) $\text{Ti}^{4+} < \text{Mn}^{7+}$ (b) $^{35}\text{Cl}^- < ^{37}\text{Cl}^-$
(c) $\text{K}^+ > \text{Cl}^-$ (d) $\text{P}^{3+} > \text{P}^{5+}$
- The first ionisation potential of nitrogen and oxygen atoms are related as follows. (1989, 1M)
(a) The ionisation potential of oxygen is less than the ionisation potential of nitrogen
(b) The ionisation potential of nitrogen is greater than the ionisation potential of oxygen
(c) The two ionisation potential values are comparable
(d) The difference between the two ionisation potential is too large

- 24.** Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because (1989, 1M)
- the hydration energy of sodium sulphate is more than its lattice energy
 - the lattice energy of barium sulphate is more than its hydration energy
 - the lattice energy has no role to play in solubility
 - the hydration energy of sodium sulphate is less than its lattice energy

Assertion and Reason

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

- Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
 - Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
 - Statement I is true; Statement II is false.
 - Statement I is false; Statement II is true.
- 25. Statement I** Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.
Statement II The reaction between nitrogen and oxygen requires high temperature. (2015 Main)
- 26. Statement I** Pb^{4+} compounds are stronger oxidising agents than Sn^{4+} compounds.
Statement II The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'. (2008, 3M)
- 27. Statement I** Band gap in germanium is small.
Statement II The energy spread of each germanium atomic energy level is infinitesimally small. (2007, 3M)
- 28. Statement I** The first ionisation energy of Be is greater than that of B.
Statement II $2p$ -orbital is lower in energy than $2s$. (2000, (S), 1M)
- 29. Statement I** F-atom has a less negative electron affinity than Cl-atom.
Statement II Additional electrons are repelled more effectively by $3p$ -electrons in Cl-atom than by $2p$ -electrons in F-atom. (1998, 2M)

Fill in the Blanks

- 30.** Compounds that formally contain Pb^{4+} are easily reduced to Pb^{2+} . The stability of the lower oxidation state is due to (1997, 1M)
- 31.** Ca^{2+} has a smaller ionic radius than K^+ because it has (1993, 1M)
- 32.** On Mulliken scale, the average of ionisation potential and electron affinity is known as (1985, 1M)
- 33.** The energy released when an electron is added to a neutral gaseous atom is called (1982, 1M)

True/False

- 34.** The basic nature of the hydroxides of group 13 (III B) decreases progressively down the group. (1993, 1M)
- 35.** The decreasing order of electron affinity of F, Cl, Br is $\text{F} > \text{Cl} > \text{Br}$. (1993, 1M)
- 36.** In group IA of alkali metals, the ionisation potential decreases down the group. Therefore, lithium is a poor reducing agent. (1987, 1M)
- 37.** The softness of group IA metals increases down the group with increasing atomic number. (1986, 1M)

Subjective Questions

- 38.** Arrange the following ions in order of their increasing radii Li^+ , Mg^{2+} , K^+ , Al^{3+} . (1997, 1M)
- 39.** Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation. (1996, 2M)
- 40.** Arrange the following as stated :
 "Increasing order of ionic size" N^{3-} , Na^+ , F^- , O^{2-} , Mg^{2+} (1991, 1M)
- 41.** Explain the following :
 "The first ionisation energy of carbon atom is greater than that of boron atom whereas, the reverse is true for the second ionisation energy." (1989, 2M)
- 42.** Arrange the following in the order of their increasing size: Cl^- , S^{2-} , Ca^{2+} , Ar (1986, 1M)
- 43.** Arrange the following in order of their
 (i) decreasing ionic size Mg^{2+} , O^{2-} , Na^+ , F^-
 (ii) increasing first ionisation energy Mg, Al, Si, Na
 (iii) increasing bond length F_2 , N_2 , Cl_2 , O_2 (1985, 3M)

Topic 1

1. (d) 2. (b,c,d)

Topic 2

- | | | | |
|---------|---------|---------|---------|
| 1. (c) | 2. (b) | 3. (d) | 4. (d) |
| 5. (b) | 6. (c) | 7. (b) | 8. (b) |
| 9. (b) | 10. (b) | 11. (d) | 12. (b) |
| 13. (b) | 14. (d) | 15. (a) | 16. (c) |

- | | | | |
|---------------------------------------|-------------------------|-------------------------|-----------|
| 17. (a) | 18. (a) | 19. (b) | 20. (c) |
| 21. (c) | 22. (d) | 23. (a,b,c) | 24. (a,b) |
| 25. (a) | 26. (c) | 27. (c) | 28. (c) |
| 29. (c) | 30. (inert pair effect) | | |
| 31. (higher effective nuclear charge) | | | |
| 32. (electronegativity) | | 33. (electron affinity) | |
| 34. F | 35. F | 36. F | 37. T |

Topic 1 History and Periodic Classification

- (a) **Correct statement** According to Moseley's law, the properties of elements are the periodic function of their atomic numbers.

(b) **Correct statement** The whole *s*-block, *d*-block, *f*-block and heavier *p*-block elements are metal.

(c) **Correct statement** Trend is not regular, Be has higher first ionisation energy than B, nitrogen has higher first ionisation energy than oxygen.

(d) **Incorrect statement** *d*-subshells are not filled monotonically, regularity break at chromium and copper.
- (a) **Incorrect** Electrons are not filled in sub-energy levels *s*, *p*, *d* and *f* in the same sequence.

(b) **Correct** Number of valence shell electrons usually determine the stable valency state of an element.

(c) **Correct** Physical and chemical properties of elements are periodic function of atomic number which is the basis of modern, long form of periodic table.

(d) **Correct** Relative ionicity of the bond between any two elements is function of electronegativity difference of the bonded atoms which in turn has periodic trend in long form of periodic table.

Topic 2 Periodic Properties

- Number of electrons in N^{3-} , $= 7 + 3 = 10$
 Number of electrons in O^{2-} $= 8 + 2 = 10$
 Number of electrons in F^- $= 9 + 1 = 10$
 Since, all the three species have each 10 electrons, hence they are isoelectronic species.

It is considered that, in case of isoelectronic species as the negative charge increases, ionic radii increases and therefore the value of ionic radii are

$$\text{N}^{3-} = 1.71 \quad (\text{highest among the three})$$

$$\text{O}^{2-} = 1.40$$

$$\text{F}^- = 1.36 \quad (\text{lowest among the three})$$

Time Saving Technique There is no need to mug up the radius values for different ions. This particular question can be solved through following time saving.

Trick The charges on the ions indicate the size as $\text{N}^{3-} > \text{O}^{2-} > \text{F}^-$. Thus, you have to look for the option in which the above trend is followed. Option(c) is the only one in which this trend is followed. Hence, it is the correct answer.

- As we move down the group, size of metal increases. Be has lower size while SO_4^{2-} has bigger size, that's why BeSO_4 breaks easily and lattice energy becomes smaller but due to lower size of Be, water molecules are gathered around and hence hydration energy increases.

On the other hand, rest of the metals, i.e Ca, Ba, Sr have bigger size and that's why lattice energy is greater than hydration energy.

Time Saving Technique In the question of finding hydration energy only check the size of atom. Smaller sized atom has more hydration energy. Thus, in this question Be is placed upper most in the group has lesser size and not comparable with the size of sulphates. Hence, BeSO_4 is the right response.

- Cl_2 , Br_2 and I_2 are homonuclear diatomic molecule in which electronegativity of the combining atoms is same, so they are more stable and less reactive, whereas, I and Cl have different electronegativities and bond between them are polarised and reactive. Therefore, interhalogen compounds are more reactive.

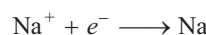
Time Saving Technique In this type of question of halogen, only go through the polarity of the molecules.

As we know, diatomic molecule does not have polarity but molecules with dissimilar sizes have polarity resulting in more reactivity.

- As we move down the group of noble gases, molecular mass increases by which dipole produced for a moment and hence London forces increases from He to Xe.

Therefore, more amount of energy is required to break these forces, thus boiling point also increases from He and Xe.

- $\text{Na} \longrightarrow \text{Na}^+ + e^-$ First IE



Electron gain enthalpy of Na^+ is reverse of (IE)

Because reaction is reverse so

$$\Delta H(\text{eq}) = -5.1 \text{ eV}$$

- Ionisation energy increases along a period from left to right and decreases down a group. The position of given elements in the periodic table is as

Group No.	2	16	18
	Ca	S	Ar
	Ba	Se	

Thus, the order of increasing ΔH_{IE_1} is

$$\text{Ba} < \text{Ca} < \text{Se} < \text{S} < \text{Ar}$$

- Be^- is the least stable ion, Be ($1s^2 2s^2$) has stable electronic configuration, addition of electron decreases stability.
- In a group, ionisation energy decreases down the group
 $\text{Be} > \text{Mg} > \text{Ca}$
- Among isoelectronic species, greater the negative charge, greater the ionic size, hence $\text{F}^- < \text{O}^{2-} < \text{N}^{3-}$.

10. (a) **Correct statement** In a period, element of 2nd group has higher first ionisation potential than element of group 13.
 (b) **Incorrect statement** Mg^+ require less energy for further ionisation than Na^+ because of noble gas configuration of Na^+ .
 (c) **Correct statement** Ionisation energy increases from left to right in a period.
 (d) **Correct statement** Mg^{2+} has noble gas configuration, require greater energy for further ionisation than Na^{2+} .
11. $\text{Mg}^{2+} = 1s^2 2s^2 2p^6 =$ no unpaired electron
 $\text{Ti}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 =$ one unpaired electron
 $\text{V}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 =$ two unpaired electrons
 $\text{Fe}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 =$ four unpaired electrons
12. Pb has most stable +2 oxidation state due to inert pair effect.
 13. $[\text{Ne}] 3s^2 3p^3$ has highest ionisation energy, periodic trend.
 14. Among isoelectronic species, the relation in size is
 cation < neutral < anion

Hence, Na^+ has smallest size.

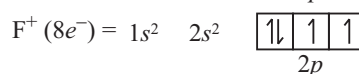
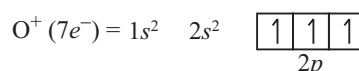
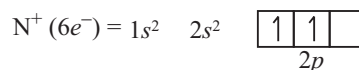
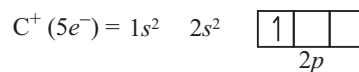
15. Ionisation energy increases from left to right in a period. However, exception occur between group 2 and group 13 elements on account of stability of electronic configuration of valence shell.



\Rightarrow The desired order is $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$

16. Electronegativity increases from left to right in a period and decreases from top to bottom in a group. Variation is more rapid in group than in a period, hence the desired order is Electronegativity : $\text{Si} < \text{P} < \text{C} < \text{N}$
17. Atomic radius of noble gases are greater than halogens of same period, hence (a) is the correct answer.
18. First ionisation energy of oxygen is less than that of nitrogen on the ground of stability of valence shell configuration, hence (a) is the correct answer.
19. Hydration energy depends on charge of ion and ionic radius. Higher the charge, greater the hydration energy. On the other hand, smaller the size, greater the hydration energy. Charge is considered first for comparison. Hence, Mg^{2+} has higher hydration energy than Na^+ .

20. Nitrogen has highest ionisation potential due to exceptional stability of its valence shell configuration mentioned in question 21.
21. For second ionisation potential, electron will have to be removed from valence shell of the following ions:



In general, ionisation energy increases from left to right in a period. However, exception occur between adjacent atoms in a period, greater amount energy is required for removal of electron from completely half-filled or completely filled orbital than the same for adjacent atom with either less than completely half-filled or less than completely filled orbital. Therefore, ionisation potential of O^+ is greater than that of F^+ . Also ionisation potential of N^+ is greater than C^+ but less than both O^+ and F^+ (periodic trend). Hence, overall order is 2nd IP : $\text{O} > \text{F} > \text{N} > \text{C}$.

22. (a) $\text{Ti}^{4+} > \text{Mn}^{7+}$ is the correct order of size due to lower positive charge on Ti^{4+} .
 (b) $^{37}\text{Cl}^- = ^{37}\text{Cl}^-$: Isotopes with same charge have same size because isotopes differ in compositions of nuclei which do not affect the atomic/ionic radius.
 (c) $\text{K}^+ < \text{Cl}^-$ is the correct order. Among isoelectronic species, anion has greater size than cation.
 (d) $\text{P}^{3+} > \text{P}^{5+}$ is the correct order. For the same elements, lower the positive charge, larger the ions.
23. (a) and (b) are infact the same statements and both are correct. N has slightly greater ionisation energy than oxygen which is against periodic trend. This exception is due to completely half-filled ($2p^3$) orbital in nitrogen that makes ionisation slightly difficult than oxygen.
 (c) Also correct : Although N has greater first ionisation potential than oxygen, two values of ionisation potentials are comparable since they are adjacent in a period, i.e. electrons are removed from same orbit during ionisation.
 (d) Incorrect – opposite to (c). of the bonded atoms which in turn has periodic trend in long form of periodic table.

42 Periodic Classification and Periodic Properties

24. (a) **Correct** For greater solubility, hydration energy must be greater than lattice energy.
 (b) **Correct** Greater lattice energy discourage dissolution of a salt.
 (c) **Incorrect** When a salt dissolve, energy is required to break the lattice, which comes from hydration process.
 (d) **Incorrect** Explained in (A).
25. Statement I and II are true and Statement II is the correct explanation of statement I.
26. Statement I is true. Stronger oxidising agent is one which itself can easily be reduced. Pb^{4+} is unstable, due to inert pair effect, can easily be reduced to stable Pb^{2+} , hence a stronger oxidising agent than Sn^{4+} .
 Statement II is false. Due to inert pair effect, the higher oxidation states of group 14 elements becomes less stable for heavier member.
27. Both statements I and II are true and Statement II is the correct explanation of statement I.
28. Statement I is true Be has higher first ionisation energy than B which is against periodic trend.
 Statement II is false $2s$ -orbital is lower in energy than $2p$, Aufbau's principle.
29. Statement I is true; Statement II is false.
 F atom has slightly lower affinity for the electron than chlorine. It is due to the reason that additional electrons are repelled more effectively by $2p$ -electrons in F than by $3p$ -electrons in Cl-atom.
30. Inert pair effect-favours lower oxidation state.
31. Higher effective nuclear charge due to greater p/e ratio.
32.
$$\text{Electronegativity} = \frac{\text{IP} + \text{EA}}{2} \quad (\text{Mulliken formula})$$
33. Electron affinity-definition.
34. Basic nature of hydroxides increases down a group.
35. Cl has maximum electron affinity, hence the correct order is $\text{Cl} > \text{F} > \text{Br}$
36. Ionisation potential decreases down the group but this is not the only criteria of reducing power.
37. In a group, size increases from top to bottom.
38. $\text{Li}^+ < \text{Al}^{3+} < \text{Mg}^{2+} < \text{K}^+$
 Size decreases from left to right in a period and it increases from top to bottom in a group. Variation is more pronounced in group than in period.
39. $\text{Zn} = 3d^{10} 4s^2$,
 $\text{Cu} = 3d^{10} 4s^1$
 The first ionisation energy is greater for Zn but reverse is true for 2nd ionisation energy.
40. Ionic size

$$\text{Mg}^{2+} < \text{Na}^+ < \text{F}^- < \text{O}^{2-} < \text{N}^{3-}$$

 Already explained in question 1 (i).
41. The first ionisation energy of carbon is greater than the same of boron as predicted from periodic trend. However, for 2nd

$$\text{B}^+ = 1s^2 \begin{array}{|c|} \hline \uparrow\downarrow \\ \hline \end{array} \text{;} \text{ more stable than } \text{C}^+ = 1s^2 \text{ } 2s^2 \begin{array}{|c|c|c|} \hline \uparrow & & \\ \hline \end{array} \text{ } 2p^1$$

 ionisation trend is reversed due to stability of completely filled $2s$ -orbital of B^+ :
42. Size $\text{Ca}^{2+} < \text{Ar} < \text{Cl}^- < \text{S}^{2-}$
 Explained in (i), question 6.
43. (i) Mg^{2+} , O^{2-} , Na^+ and F^- are all isoelectronic, has 10 electrons each. Among isoelectronic species, the order of size is cation $<$ neutral $<$ anion.
 Also, between cations, higher the charge, smaller the size and between anions, greater the negative charge, larger the size. Therefore, the decreasing order of ionic radii : $\text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+}$
 (ii) First ionisation energy increases from left to right in a period. However, exception occur between group 2 and 13 and group 15 and 16 where trend is reversed on the grounds of stability of completely filled and completely half-filled orbitals. Therefore,
 Ionisation energy (1st) : $\text{Na} < \text{Al} < \text{Mg} < \text{Si}$
 (iii) If the atoms are from same period, bond length is inversely proportional to bond order. In a group, bond length is related directly to atomic radius. Therefore,
 bond length $\text{N}_2 < \text{O}_2 < \text{F}_2 < \text{Cl}_2$

$N_0/2$ atom of $X(g)$ are converted into $X^+(g)$ by energy E_1 . $N_0/2$ atoms of $X(g)$ are converted into $X^-(g)$ by energy E_2 . Hence, ionisation potential and electron affinity of $X(g)$ are

- (a) $\frac{2E_2}{N_0}, \frac{2(E_1 - E_2)}{N_0}$ (b) $\frac{2E_1}{N_0}, \frac{2E_2}{N_0}$
 (c) $\frac{(E_1 - E_2)}{N_0}, \frac{2E_2}{N_0}$ (d) None is correct

The electron affinities of N, O, S and Cl are such that

- (a) $N < O < S < Cl$ (b) $O < N < Cl < S$
 (c) $O \approx Cl < N \approx S$ (d) $N < S < O < Cl$

If Aufbau and Hund's rule are not used, then incorrect statement is

- (a) K^+ would be coloured ion
 (b) Na will be in same s-block (if these rules are true)
 (c) Cu would be s-block element
 (d) Magnetic moment of Cr(24) would be zero

The compound vanadium has magnetic moment of 1.73 BM. The vanadium chloride has the formula

- (a) VCl_2 (b) VCl_3 (c) VCl_4 (d) VCl_5

Which of the following can be acceptable electronic configuration of carbon atom in the ground state?

- (a) $1s^2 2s^2 \underbrace{\downarrow \downarrow \downarrow}_{2p}$ (b) $1s^2 2s^2 \underbrace{\uparrow \uparrow \uparrow}_{2p}$
 (c) $1s^2 2s^2 \underbrace{\uparrow \downarrow \downarrow}_{2p}$ (d) $1s^2 2s^2 \underbrace{\downarrow \downarrow \downarrow}_{2p}$

Which of the following statement is(are) correct regarding periodic table?

- (a) In a period, ionisation energy increases monotonically from left to right
 (b) Electronegativity increases from left to right
 (c) Electron affinity decreases monotonically from top to bottom in a group
 (d) Transition elements starts only from fourth period of the periodic table

Passage for Q.Nos. 7 to 9

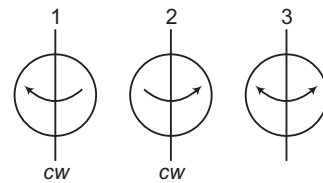
Let's consider a hypothetical planet "pseudo Earth" which is similar to our earth in several aspects. The similarities are

On pseudo earth:

- (i) There are same number of elements as on our earth and they are known by the same name.
 (ii) Pauli's exclusion principal, Hund's Rule and Aufbau principle are known to the people of pseudo earth in the same manner as we know on our earth.
 (iii) They classify elements as representative, transition and inner-transition elements in the same manner as we classify on our earth.

However, there is one basic difference in understanding the electron's spin on these two earths. On our earth the electron can have only two spin directions, 'clock wise (1)

and anti-clockwise (2), while on pseudo earth there is an additional possible value of spin quantum number called neutral spin (3) in which electron is believed to be fluctuating harmonically between clockwise and anti-clockwise directions, about its axis. Answer the following three question based on the above information.



The first noble gas on pseudo earth would be

- (a) He (b) H (c) Li (d) Ne

The long form of periodic table on this pseudo earth will have how many groups?

- (a) 18 (b) 24 (c) 27 (d) 36

On pseudo earth, atomic number of the first transition metal would be

- (a) 21 (b) 26 (c) 29 (d) 31

Assertion-Reason Type

Following two questions have Assertion followed by the Reason. Answer them according to the following options.

- (a) Both Assertion and Reason are correct and Reason is the correct explanation of the Assertion.
 (b) Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion.
 (c) Assertion is correct but Reason is incorrect.
 (d) Assertion is incorrect but Reason is correct.

Assertion Nitrogen has higher first ionisation energy than oxygen.

Reason Atomic radius of nitrogen is smaller than that of oxygen.

Assertion $SnCl_2$ is a good reducing agent while $PbCl_2$ is stable although both Sn and Pb belongs to same group of periodic table.

Reason Pb show inert pair effect.

Match the statements of Column I with values of Column II.

Column I	Column II
A. Be ($Z = 4$)	p. Paramagnetic
B. C ($Z = 6$)	q. Diamagnetic
C. Mg^{2+} ($Z = 12$)	r. No valence shell orbital without electron
D. N ($Z = 7$)	s. Has higher IE than both elements, on left and right in the period.

In ground state of oxygen, in how many ways its p -electrons can be represented in box diagram without violating either Hund's rule or Pauli's exclusion principle?

Answers

1. (b) 2. (d) 3. (a) 4. (c) 5. (a,b,d) 6. (a,c) 7. (c) 8. (c) 9. (d) 10. (c)
 11. (a) 12. $A \rightarrow q,s; B \rightarrow p; C \rightarrow q,r,s; D \rightarrow p,r,s$ 13. (6)

4

Chemical Bonding

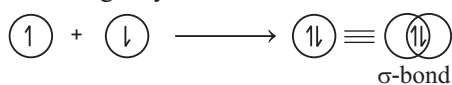
Preliminary Concepts of Electrovalent and Covalent Bonding Including Bonding

- Chemical bonds are formed as a result of instability of individual isolated atoms. Through chemical bonding, atoms or ions associate and gain stability. There are three important types of chemical bonds by which atoms or ions connect to one another:

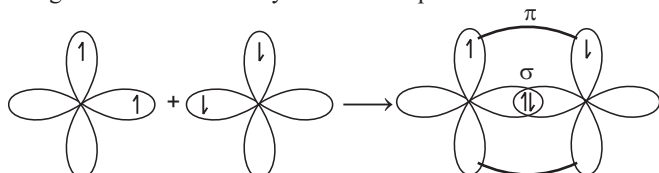
(i) Covalent bond (ii) Ionic bond

(iii) Metallic bond

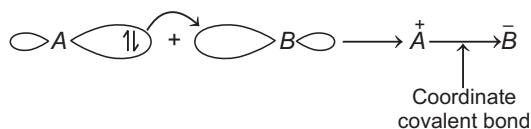
- Covalent Bond** This type of bond is formed by sharing of electrons of the valence shell. Sharing of electrons may occur in following ways:



Sigma bond is formed by direct overlap of orbitals as shown.



Pi (π) covalent bond is formed by sidewise (or lateral) overlapping of atomic p -orbitals as shown above in the diagram.



Properties of covalent system are explained with the help of various theories of which the two most common are valence shell electron pair repulsion theory and molecular orbital theory.

• Highlights of MOT

(i) Bond order

$$= \frac{\text{No. of bonding electrons} - \text{No. of antibonding electrons}}{2}$$

(ii) If there is any unpaired electrons in the molecular orbitals, system will be paramagnetic otherwise diamagnetic. For paramagnetic system,

$$\text{spin-only magnetic moment } (\mu) = \sqrt{n(n+2)} \text{ BM}$$

where n = Number of unpaired electrons

(iii) A system with zero bond order means that system does not exist.

- Ionic Bond** This type of bond is formed by transfer of electrons from a highly electropositive element to a highly electronegative element, viz.



• Salient Features of Ionic Bonding

- In ionic bonding, the oppositely charged ions are held together by very strong electrostatic force of attraction.
- In solid state, each cation surrounds itself with anions and each anion with cations. These very large number of ions are arranged in an ordinary network called ionic crystals.
- Ionic compounds are good conductors of electricity in fused state or in aqueous solution.
- Ionic compounds have very high melting and boiling points.
- Ionic compounds develop some extent of covalency under the following conditions:

- If the cation has very small size or high charge, e.g. Li^+ or Al^{3+} .
- If the anion has very large size or high negative charge, e.g. I^- or S^{2-} .
- If the cation has partially or fully filled d or f orbitals in penultimate shell.

The above factors lowers the ionic character and makes physical properties characteristic of ionic compounds inferior.

Metallic Bond Metallic bonding is a strong cohesive interaction developed between positively charged metal ions and the sea of free electrons existing in metals. These cohesive force of attraction is responsible for all the special characteristics of metals.

VBT, Hybridisation and VSEPR Theory

- **Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)** This theory is based on the concepts of hybridisation of atomic orbitals. According to this theory, pure atomic orbitals do not take part in bonding, rather the valence shell orbitals first hybridise and the resulting hybrid orbitals are involved in bond formation. Based on the geometries of hybrid orbitals at the central atom, molecular structure is proposed and physiochemical properties are interpreted.

Summary of molecular geometries and hybridisation

Total Number of independent electron pairs	Number of independent bonding electron pairs	Number of non-bonding electron pairs	Orbital geometry	Molecular geometry	Distortion*	Hybridisation	Bond angle	Examples
2	2	0	Linear	Linear	No	sp	180°	CO ₂ , BeCl ₂
3	3	0	Trigonal planar	Trigonal planar	Possible	sp^2	120°	BF ₃ , NO ₃ ⁻ , GaI ₃
3	2	1	Trigonal planar	Bent (non-linear)	Always	sp^2	120°	NO ₂ ⁻ , SO ₂ , SnCl ₂
4	4	0	Tetrahedral	Tetrahedral	Possible	sp^3	109°	CH ₄ , SO ₄ ²⁻ , CF ₄
4	3	1	Tetrahedral	Trigonal pyramidal	Always	sp^3	109°	SO ₃ ⁻ , NH ₃
4	2	2	Tetrahedral	Bent or V-shaped	Always	sp^3	109°	H ₂ O, OF ₂ , NH ₂ ⁻
5	5	0	Trigonal Bipyramidal	Trigonal bipyramidal	Possible	sp^3d	90° and 120°	PF ₅ , PCl ₅
5	4	1	Trigonal bipyramidal	See-saw	Always	sp^3d	90° and 120°	SF ₄ , TeCl ₄ , XeO ₂ F ₂
5	3	2	Trigonal bipyramidal	T-shaped	Always	sp^3d	90°	IF ₃
5	2	3	Trigonal bipyramidal	Linear	Never	sp^3d	180°	I ₃ ⁻ , IF ₂ ⁻
6	6	0	Octahedral (square bipyramidal)	Octahedral	Possible	sp^3d^2	90°	SF ₆ , PF ₆ ⁻
6	5	1	Octahedral	Square pyramidal	Always	sp^3d^2	90°	IF ₅ , BrF ₅
6	4	2	Octahedral	Square planar	Possible	sp^3d^2	90°	XeF ₄ , ICl ₄ ⁻ , BrF ₄ ⁻

NOTE

Under distortion possible means that the bond angle will be distorted when the outer atoms are not identical, e.g. CH₄ is tetrahedral with all other atoms identical, no distortion, but in CH₂F₂, tetrahedral geometry but outer atoms are different, bond angles will be distorted, i.e. some will be slightly greater than 109° and some smaller than 109°.

- **Note on Molecular Geometry** The following types of molecules are non-polar:

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AB_2 -linear, AB_3 -trigonal planar, AB_4 -tetrahedral, AB_5 -trigonal bipyramidal, AB_6 -octahedral, AB_4 -square planar, AB_2C_2 -symmetric and square planar. Some examples of these categories:

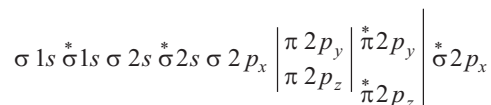
Type	Shape	Examples
AB_2	Linear	BeCl ₂ , CO ₂ , CS ₂
AB_3	Trigonal planar	BF ₃ , SO ₃ , GaF ₃
AB_4	Tetrahedral	CH ₄ , CCl ₄ , SiF ₄
AB_5	Pentagonal bipyramidal	PCl ₅ , AsF ₅
AB_6	Octahedral (Square bipyramidal)	SF ₆ , SeF ₆
AB_4	Square planar	XeF ₄

Any other molecule having a single “central atom” will be polar as long as the electronegativities of elements that make it up are not same. This includes molecules that have the above mentioned geometries but dissimilar outer atoms, e.g. CH₃F, OCS, BeFCl, etc.

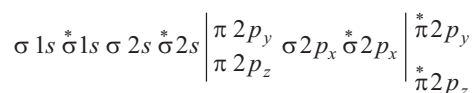
Resonance, LCAO, MOT, Other Bonding Types

- Molecular Orbital Theory (MOT)** According to MOT, atomic orbitals first combines to form molecular orbitals which finally participate in bond formation. Combination of atomic orbitals in fact pertains to combination of electronic waves and it may occur in two ways known as constructive interference and destructive interference. Constructive interference leads to formation a resultant wave that is called “bonding” molecular orbitals while destructive interference gives rise to ‘antibonding’ molecular orbitals. Potential energy of a bonding molecular orbital is always less than the potential energies of atomic orbitals combined and potential energy of an antibonding molecular orbital is always greater than the potential energies of atomic orbitals combined. After bond formation, electrons occupy these molecular orbitals. Molecular orbitals are filled by electrons in increasing order of energies. During filling of molecular orbitals, both Hund’s rule and Pauli exclusion principle are obeyed. The increasing order of energy of molecular orbitals in a diatomic system are

(i) For oxygen and heavier system,



(ii) For nitrogen and lighter system,



(Starred molecular orbitals denote antibonding molecular orbitals)

Electron filling in molecular orbitals of second period homonuclear diatomic molecules are shown below:

Li ₂	Be ₂	B ₂	N ₂	O ₂
				— $\sigma^* 2p_x$
		— $\sigma^* 2p_x$	— $\sigma^* 2p_x$	$\frac{1}{1} \frac{1}{1} \pi^* 2p_y, \pi^* 2p_z$
		— $\sigma 2p_x$	$\frac{1}{1} \sigma 2p_x$	$\frac{1}{1} \frac{1}{1} \pi 2p_y, \pi 2p_z$
	— $\pi 2p_y, \pi 2p_z$	$\frac{1}{1} \frac{1}{1} \pi 2p_y, \pi 2p_z$	$\frac{1}{1} \frac{1}{1} \pi 2p_y, \pi 2p_z$	$\frac{1}{1} \sigma 2p_x$
— $\sigma^* 2s$	$\frac{1}{1} \sigma^* 2s$	$\frac{1}{1} \sigma^* 2s$	$\frac{1}{1} \sigma^* 2s$	$\frac{1}{1} \sigma^* 2s$
$\frac{1}{1} \sigma 2s$	$\frac{1}{1} \sigma 2s$	$\frac{1}{1} \sigma 2s$	$\frac{1}{1} \sigma 2s$	$\frac{1}{1} \sigma 2s$
$\frac{1}{1} \sigma^* 1s$	$\frac{1}{1} \sigma^* 1s$	$\frac{1}{1} \sigma^* 1s$	$\frac{1}{1} \sigma^* 1s$	$\frac{1}{1} \sigma^* 1s$
$\frac{1}{1} \sigma 1s$	$\frac{1}{1} \sigma 1s$	$\frac{1}{1} \sigma 1s$	$\frac{1}{1} \sigma 1s$	$\frac{1}{1} \sigma 1s$

Topic 1 Preliminary Concepts of Electrovalent and Covalent Bonding Including Bonding

Objective Questions I (Only one correct option)

- The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is (2015 Main)
(a) ion-ion interaction (b) ion-dipole interaction
(c) London force (d) hydrogen bond
- The nodal plane in the π -bond of ethene is located in
(a) the molecular plane (2002, 3M)
(b) a plane parallel to the molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon-carbon σ -bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon-carbon σ -bond
- Amongst H_2O , H_2S , H_2Se and H_2Te , the one with the highest boiling point is (2000, 1M)
(a) H_2O because of hydrogen bonding
(b) H_2Te because of higher molecular weight
(c) H_2S because of hydrogen bonding
(d) H_2Se because of lower molecular weight
- Arrange the following compounds in order of increasing dipole moment, toluene (I), *m*-dichlorobenzene (II), *o*-dichlorobenzene (III), *p*-dichlorobenzene (IV) (1996, 1M)
(a) $\text{I} < \text{IV} < \text{II} < \text{III}$ (b) $\text{IV} < \text{I} < \text{II} < \text{III}$
(c) $\text{IV} < \text{I} < \text{III} < \text{II}$ (d) $\text{IV} < \text{II} < \text{I} < \text{III}$
- The number and type of bonds between two carbon atoms in CaC_2 are (1996, 1M)
(a) one sigma (σ) and one pi (π) bonds
(b) one sigma (σ) and two pi (π) bonds
(c) one sigma (σ) and one half pi (π) bonds
(d) one sigma (σ) bond
- The molecule which has zero dipole moment is (1989, 1M)
(a) CH_2Cl_2 (b) BF_3
(c) NF_3 (d) ClO_2
- Element *X* is strongly electropositive and element *Y* is strongly electronegative. Both are univalent. The compound formed would be (1980, 1M)
(a) X^+Y^- (b) X^-Y^+
(c) $X - Y$ (d) $X \rightarrow Y$
- Which of the following compound is covalent? (1980, 1M)
(a) H_2 (b) CaO
(c) KCl (d) Na_2S
- The total number of electrons that take part in forming the bonds in N_2 is (1980, 1M)
(a) 2 (b) 4 (c) 6 (d) 10
- The compound which contains both ionic and covalent bonds is (1979, 1M)
(a) CH_4 (b) H_2 (c) KCN (d) KCl

Objective Questions II

(One or more than one correct option)

- Dipole moment is shown by (1986, 1M)
(a) 1, 4-dichlorobenzene (b) *cis*-1, 2-dichloroethene
(c) *trans*-1, 2-dichloroethene (d) *trans*-1, 2-dichloro-2-pentene

Assertion and Reason

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

- (a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I
(c) Statement I is correct; Statement II is incorrect
(d) Statement I is incorrect; Statement II is correct
- Statement I** LiCl is predominantly a covalent compound.
Statement II Electronegativity difference between Li and Cl is too small. (1998, 2M)

Fill in the Blanks

- There are π bonds in a nitrogen molecule. (1982, 1M)

True/False

- All molecules with polar bonds have dipole moment. (1985, $\frac{1}{2}$ M)
- Linear overlapping of two atomic *p*-orbitals leads to a sigma bond. (1983, 1M)

Subjective Questions

- Arrange the following ions in order of their increasing radii: Li^+ , Mg^{2+} , K^+ , Al^{3+} . (1997, 1M)
- Between Na^+ and Ag^+ , which is stronger Lewis acid and why? (1997, 3M)
- In the reaction, $\text{I}^- + \text{I}_2 \longrightarrow \text{I}_3^-$, which is the Lewis acid? (1997, 1M)
- Explain the difference in the nature of bonding in LiF and LiI . (1996, 2M)
- The dipole moment of KCl is 3.336×10^{-29} C-m which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl . (1993, 2M)

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21. Give reasons in two or three sentences only for the following :
“Hydrogen peroxide acts as an oxidising as well as a reducing agent.” (1992, 1M)
22. State four major physical properties that can be used to distinguish between covalent and ionic compounds. Mention the distinguishing features in each case. (1978, 2M)

Topic 2 VBT, Hybridisation and VSEPR Theory

Objective Questions I (Only one correct option)

1. The correct statement for the molecule, CsI_3 is (2014 Main)
(a) it is a covalent molecule
(b) it contains Cs^+ and I_3^- ions
(c) it contains Cs^{3+} and I^- ions
(d) it contains Cs^+ , I^- and lattice I_2 molecule
2. The species having pyramidal shape is (2010)
(a) SO_3 (b) BrF_3
(c) SiO_3^{2-} (d) OSF_2
3. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is (2010)
(a) 1 and diamagnetic (b) 0 and diamagnetic
(c) 1 and paramagnetic (d) 0 and paramagnetic
4. The species having bond order different from that in CO is
(a) NO^- (b) NO^+ (2007, 3M)
(c) CN^- (d) N_2
5. Among the following, the paramagnetic compound is
(a) Na_2O_2 (b) O_3 (2007, 3M)
(c) N_2O (d) KO_2
6. Which of the following contains maximum number of lone pairs on the central atom? (2005, 1M)
(a) ClO_3^- (b) XeF_4
(c) SF_4 (d) I_3^-
7. Number of lone pair(s) in XeOF_4 is/are (2004, 1M)
(a) 0 (b) 1 (c) 2 (d) 3
8. Which of the following are isoelectronic and isostructural ?
 $\text{NO}_3^-, \text{CO}_3^{2-}, \text{ClO}_3^-, \text{SO}_3$ (2003, 1M)
(a) $\text{NO}_3^-, \text{CO}_3^{2-}$ (b) $\text{SO}_3, \text{NO}_3^-$
(c) $\text{ClO}_3^-, \text{CO}_3^{2-}$ (d) $\text{CO}_3^{2-}, \text{SO}_3$
9. Among the following, the molecule with the highest dipole moment is (2003, 1M)
(a) CH_3Cl (b) CH_2Cl_2
(c) CHCl_3 (d) CCl_4
10. Which of the following molecular species has unpaired electron (s)? (2002, 3M)
(a) N_2 (b) F_2 (c) O_2^- (d) O_2^{2-}
11. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3 . (2002, 3M)
(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
12. The correct order of hybridisation of the central atom in the following species NH_3 , $[\text{PtCl}_4]^{2-}$, PCl_5 and BCl_3 is (2001, 1M)
(a) dsp^2 , dsp^3 , sp^2 and sp^3
(b) sp^3 , dsp^2 , sp^3d and sp^2
(c) dsp^2 , sp^2 , sp^3 and dsp^3
(d) dsp^2 , sp^3 , sp^2 and dsp^3
13. The common features among the species CN^- , CO and NO^+ are (2001, 1M)
(a) bond order three and isoelectronic
(b) bond order three and weak field ligands
(c) bond order two and acceptors
(d) isoelectronic and weak field ligands
14. The hybridisation of atomic orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ are (2000, 1M)
(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
15. In the compound $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$, the C_2-C_3 bonds is of (1999, 2M)
(a) $sp-sp^2$ (b) sp^3-sp^3
(c) $sp-sp^3$ (d) sp^2-sp^3
16. The geometry of H_2S and its dipole moment are (1999, 2M)
(a) angular and non-zero (b) angular and zero
(c) linear and non-zero (d) linear and zero
17. The geometry and the type of hybrid orbital present about the central atom in BF_3 is (1998, 2M)
(a) linear, sp (b) trigonal planar, sp^2
(c) tetrahedral, sp^3 (d) pyramidal, sp^3
18. Which one of the following compounds has sp^2 - hybridisation? (1997, 1M)
(a) CO_2 (b) SO_2 (c) N_2O (d) CO
19. Among KO_2 , AlO_2^- , BaO_2 and NO_2^+ , unpaired electron is present in (1997 C, 1M)
(a) NO_2^+ and BaO_2 (b) KO_2 and AlO_2^-
(c) Only KO_2 (d) Only BaO_2
20. The cyanide ion CN^- and N_2 are isoelectronic, but in contrast to CN^- , N_2 is chemically inert because of (1997 C, 1M)
(a) low bond energy
(b) absence of bond polarity
(c) unsymmetrical electron distribution
(d) presence of more number of electron in bonding orbitals

21. Among the following species, identify the isostructural pairs.
 $\text{NF}_3, \text{NO}_3^-, \text{BF}_3, \text{H}_3\text{O}^+, \text{N}_3\text{H}$ (1996, 1M)
 (a) $[\text{NF}_3, \text{NO}_3^-]$ and $[\text{BF}_3, \text{H}_3\text{O}^+]$
 (b) $[\text{NF}_3, \text{N}_3\text{H}]$ and $[\text{NO}_3^-, \text{BF}_3]$
 (c) $[\text{NF}_3, \text{H}_3\text{O}^+]$ and $[\text{NO}_3^-, \text{BF}_3]$
 (d) $[\text{NF}_3, \text{H}_3\text{O}^+]$ and $[\text{N}_3\text{H}, \text{BF}_3]$
22. Which one of the following molecules is planar? (1996, 1M)
 (a) NF_3 (b) NCl_3 (c) PH_3 (d) BF_3
23. The maximum possible number of hydrogen bonds a water molecule can form is (1992, 1M)
 (a) 2 (b) 4 (c) 3 (d) 1
24. The type of hybrid orbitals used by the chlorine atom in ClO_2^- is (1992, 1M)
 (a) sp^3 (b) sp^2
 (c) sp (d) None of these
25. The molecule which has pyramidal shape is (1989, 1M)
 (a) PCl_3 (b) SO_3 (c) CO_3^{2-} (d) NO_3^-
26. Which of the following is paramagnetic? (1989, 1M)
 (a) O_2^- (b) CN^-
 (c) CO (d) NO^+
27. The $\text{Cl}-\text{C}-\text{Cl}$ angle in 1, 1, 2, 2-tetrachloroethene and tetrachloromethane respectively will be about (1988, 1M)
 (a) 120° and 109.5° (b) 90° and 109.5°
 (c) 109° and 90° (d) 109.5° and 120°
28. The molecule that has linear structure is (1988, 1M)
 (a) CO_2 (b) NO_2
 (c) SO_2 (d) SiO_2
29. The species in which the central atom uses sp^2 -hybrid orbitals in its bonding is (1988, 1M)
 (a) PH_3 (b) NH_3 (c) CH_3^+ (d) SbH_3
30. Of the following compounds, which will have a zero dipole moment? (1987, 1M)
 (a) 1, 1-dichloroethylene
 (b) *cis*-1, 2-dichloroethylene
 (c) *trans*-1, 2-dichloroethylene
 (d) None of the above
31. The hybridisation of sulphur in sulphur dioxide is (1986, 1M)
 (a) sp (b) sp^3 (c) sp^2 (d) dsp^2
32. The bond between two identical non-metal atoms has a pair of electrons (1986, 1M)
 (a) unequally shared between the two
 (b) transferred fully from one atom to another
 (c) with identical spins
 (d) equally shared between them
33. On hybridisation of one s and one p -orbital we get (1984, 1M)
 (a) two mutually perpendicular orbitals
 (b) two orbitals at 180°
 (c) four orbitals directed tetrahedrally
 (d) three orbitals in a plane
34. Carbon tetrachloride has no net dipole moment because of (1983, 1M)
 (a) its planar structure
 (b) its regular tetrahedral structure
 (c) similar sizes of carbon and chlorine atoms
 (d) similar electron affinities of carbon and chlorine
35. The ion that is isoelectronic with CO is (1982, 1M)
 (a) CN^- (b) O_2^+ (c) O_2^- (d) N_2^+
36. Among the following, the linear molecule is (1982, 1M)
 (a) CO_2 (b) NO_2 (c) SO_2 (d) ClO_2
37. If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atomic number < 21) are (1981, 1M)
 (a) pure p (b) sp -hybridised
 (c) sp^2 -hybridised (d) sp^3 -hybridised

Objective Questions II

(One or more than one correct option)

38. The molecules that will have dipole moment are (1992, 1M)
 (a) 2, 2-dimethyl propane (b) *trans*-2-pentene
 (c) *cis*-3-hexene (d) 2, 2, 3, 3-tetramethyl butane
39. Which of the following have identical bond order? (1992, 1M)
 (a) CN^- (b) O_2^-
 (c) NO^+ (d) CN^+
40. The linear structure assumed by (1991, 1M)
 (a) SnCl_2 (b) CS_2 (c) NO_2^+ (d) NCO^-
 (e) SO_2
41. CO_2 is isostructural with (1986, 1M)
 (a) HgCl_2 (b) C_2H_2 (c) SnCl_2 (d) NO_2

Match the Columns

42. Match the orbital overlap figures shown in Column I with the description given in Column II and select the correct answer using the codes given below the Columns. (2014 Adv.)

	Column I		Column II
A.		1.	$p-d$ π antibonding
B.		2.	$d-d$ σ bonding
C.		3.	$p-d\pi$ bonding
D.		4.	$d-d$ σ antibonding

Codes

A B C D A B C D

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- (a) 4 3 2 1 (b) 1 2 3 4
(c) 2 3 1 4 (d) 4 1 2 3

43. Match each of the diatomic molecules in Column I with its property/properties in Column II. (2009)

Column I		Column II	
A.	B ₂	p.	Paramagnetic
B.	N ₂	q.	Undergoes oxidation
C.	O ₂ ⁻	r.	Undergoes reduction
D.	O ₂	s.	Bond order ≥ 2
		t.	Mixing of 's' and 'p' orbitals

Codes

- | | A | B | C | D |
|-----|------------|------------|------------|------------|
| (a) | q, r, s | p, r, t, s | q, r, t | p, q, t |
| (b) | p, q, r, t | q, r, s, t | p, q, r, t | p, r, s, t |
| (c) | q, r, s, t | p, q, r | r, s, t | p, q, r, t |
| (d) | p, q, s, t | p, q, s | p, t | q, r, t |

Fill in the Blanks

44. Among N₂O, SO₂, I₃⁺ and I₃⁻, the linear species are (1997 C, 1M)
45. When N₂ goes to N₂⁺, the N—N bond distance ... , and when O₂ goes to O₂⁺ the O—O bond distance (1996, 1M)
46. The two types of bonds present in B₂H₆ are covalent and (1994, 1M)
47. The kind of delocalisation involving sigma bond orbitals is called..... (1994, 1M)
48. The valence atomic orbitals on C in silver acetylide ishybridised. (1990, 1M)
49. The shape of CH₃⁺ is (1990, 1M)
50. hybrid orbitals of nitrogen atom are involved in the formation of ammonium ion. (1982, 1M)
51. Pair of molecules which forms strongest intermolecular hydrogen bonds is (SiH₄ and SiF₄, acetone and CHCl₃, formic acid and acetic acid) (1981, 1M)
52. The angle between two covalent bonds is maximum in (CH₄, H₂O, CO₂) (1981, 1M)

True/False

53. The dipole moment of CH₃F is greater than that of CH₃Cl. (1993, 1M)
54. H₂O molecule is linear. (1993, 1M)
55. The presence of polar bonds in a polyatomic molecule suggests that the molecule has non-zero dipole moment. (1990, 1M)
56. sp³ hybrid orbitals have equal s and p character. (1987, 1M)
57. In benzene, carbon uses all the three p-orbitals for hybridisation. (1987, 1M)

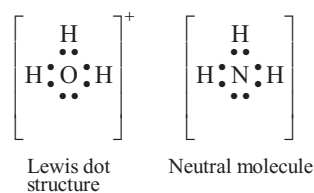
58. SnCl₂ is a non-linear molecule. (1985, $\frac{1}{2}$ M)

Integer Type Questions

59. A list of species having the formula XZ₄ is given below (2014 Adv.)
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
60. The total number of lone-pair of electrons in melamine is (2013 Adv.)
61. Based on VSEPR theory, the number of 90° F—Br—F angles in BrF₅ is (2010)

Subjective Questions

62. Predict whether the following molecules are isostructural or not. Justify your answer.
(i) NMe₃ (ii) N(SiMe₃)₃ (2005, 2M)
63. On the basis of ground state electronic configuration, arrange the following molecules in increasing O—O bond length order. KO₂, O₂, O₂[AsF₆] (2004, 2M)
64. Draw the shape of XeF₄ and OSF₄ according to VSEPR theory. Show the lone pair of electrons on the central atom. (2004, Main, 2M)
65. Using VSEPR theory, draw the shape of PCl₅ and BrF₅. (2003, 2M)
66. Draw the molecular structures of XeF₂, XeF₄ and XeO₂F₂, indicating the location of lone pair(s) of electrons. (2000, 3M)
67. Interpret the non-linear shape of H₂S molecule and non-planar shape of PCl₃ using valence shell electron pair repulsion (VSEPR) theory. (Atomic number : H = 1, P = 15, S = 16, Cl = 17) (1998, 4M)
68. Using the VSEPR theory, identify the type of hybridisation and draw the structure of OF₂. What are the oxidation states of O and F? (1997, 3M)
69. 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 H₃O⁺ and NH₃.



- (i) O₂²⁻ (ii) CO₃²⁻
(iii) CN⁻ (iv) NCS⁻ (1983, 4M)

Topic 3 Resonance, LCAO, MOT, Other Bonding Types

Objective Questions I (Only one correct option)

- Assuming $2s-2p$ mixing is not operative, the paramagnetic species among the following is (2014 Adv.)
(a) Be_2 (b) B_2 (c) C_2 (d) N_2
- Stability of the species Li_2 , Li_2^- and Li_2^+ increases in the order of (2013 Main)
(a) $\text{Li}_2 < \text{Li}_2^+ < \text{Li}_2^-$ (b) $\text{Li}_2^- < \text{Li}_2^+ < \text{Li}_2$
(c) $\text{Li}_2 < \text{Li}_2^- < \text{Li}_2^+$ (d) $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$
- In which of the following pairs of molecules/ions both the species are not likely to exist? (2013 Main)
(a) H_2^+ , He_2^{2-} (b) H_2^- , He_2^{2-}
(c) H_2^{2+} , He_2 (d) H_2^- , He_2^{2+}
- Hyperconjugation involves overlap of which of the following orbitals? (2008, 3M)
(a) $\sigma-\sigma$ (b) $\sigma-p$ (c) $p-p$ (d) $\pi-\pi$
- According to MO theory, (2004, 1M)
(a) O_2^+ is paramagnetic and bond order greater than O_2
(b) O_2^+ is paramagnetic and bond order less than O_2
(c) O_2^+ is diamagnetic and bond order is less than O_2
(d) O_2^+ is diamagnetic and bond order is more than O_2
- Molecular shape of SF_4 , CF_4 and XeF_4 are (2000, 1M)
(a) the same, with 2, 0 and 1 lone pair of electrons respectively
(b) the same, with 1, 1 and 1 lone pair of electrons respectively
(c) different, with 0, 1 and 2 lone pair of electrons respectively
(d) different, with 1, 0 and 2 lone pair of electrons respectively
- In compounds of type ECl_3 , where $E = \text{B, P, As or Bi}$, the angles $\text{Cl}-E-\text{Cl}$ is in order (1999, 2M)
(a) $\text{B} > \text{P} = \text{As} = \text{Bi}$
(b) $\text{B} > \text{P} > \text{As} > \text{Bi}$
(c) $\text{B} < \text{P} = \text{As} = \text{Bi}$
(d) $\text{B} < \text{P} < \text{As} < \text{Bi}$
- The correct order of increasing C—O bond length of CO , CO_3^{2-} , CO_2 is (1999, 2M)
(a) $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$
(b) $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$
(c) $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$
(d) $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$
- Which contains both polar and non-polar bonds?
(a) NH_4Cl (b) HCN (1997, 1M)
(c) H_2O_2 (d) CH_4
- Which one among the following does not have the hydrogen bond? (1983, 1M)
(a) Phenol (b) Liquid NH_3
(c) Water (d) HCl

Objective Question II

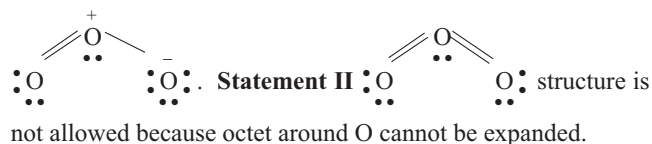
(One or more than one correct option)

- Hydrogen bonding plays a central role in which of the following phenomena? (2014 Adv.)
(a) Ice floats in water
(b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
(c) Formic acid is more acidic than acetic acid
(d) Dimerisation of acetic acid in benzene
- Which one of the following molecules is expected to exhibit diamagnetic behaviour? (2013 Main)
(a) C_2 (b) N_2
(c) O_2 (d) S_2

Assertion and Reason

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

- Statement I is correct; Statement II is correct; Statement II is the correct explanation of Statement I.
 - Statement I is correct; Statement II is correct; Statement II is not the correct explanation of Statement I.
 - Statement I is correct; Statement II is incorrect.
 - Statement I is incorrect; Statement II is correct.
13. **Statement I** The electronic structure of O_3 is



(1998, 2M)

Match the Columns

14. Match the reactions in Column I with nature of the reactions/type of the products in Column II. (2007, 6M)

Column I	Column II
A. $\text{O}_2^- \longrightarrow \text{O}_2 + \text{O}_2^{2-}$	1. Redox reaction
B. $\text{CrO}_4^{2-} + \text{H}^+ \longrightarrow$	2. One of the products has trigonal planar structure
C. $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \longrightarrow$	3. Dimeric bridged tetrahedral metal ion
D. $\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \longrightarrow$	4. Disproportionation

Codes

	A	B	C	D	A	B	C	D
(a)	2	1, 4	3	4	(b)	1, 4	3	1, 2
(c)	2	3	1	4	(d)	3	4	2, 3

52 Chemical Bonding

Subjective Questions

15. Write the MO electron distribution of O_2 . Specify its bond order and magnetic property. (2000, 3M)

16. Arrange the following as stated.

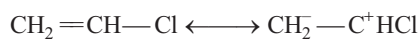
“Increasing strength of hydrogen bonding ($X-H-X$).”

O, S, F, Cl, N

(1991, 1M)

17. What effect should the following resonance of vinyl chloride have on its dipole moment?

(1987, 1M)



Topic 1

- | | | | |
|---------|---------|------------|---------|
| 1. (b) | 2. (a) | 3. (a) | 4. (b) |
| 5. (b) | 6. (b) | 7. (a) | 8. (a) |
| 9. (c) | 10. (c) | 11. (b, d) | 12. (c) |
| 13. (2) | 14. F | 15. T | |

Topic 2

- | | | | |
|---------|------------|------------|---------------|
| 1. (b) | 2. (d) | 3. (a) | 4. (a) |
| 5. (d) | 6. (d) | 7. (b) | 8. (a) |
| 9. (a) | 10. (c) | 11. (a) | 12. (b) |
| 13. (a) | 14. (b) | 15. (d) | 16. (a) |
| 17. (b) | 18. (b) | 19. (c) | 20. (b) |
| 21. (c) | 22. (d) | 23. (b) | 24. (a) |
| 25. (a) | 26. (a) | 27. (a) | 28. (a) |
| 29. (c) | 30. (c) | 31. (c) | 32. (d) |
| 33. (b) | 34. (b) | 35. (a) | 36. (a) |
| 37. (c) | 38. (b, c) | 39. (a, c) | 40. (b, c, d) |

- | | |
|--|--|
| 41. (a, b) | 42. $A \rightarrow 2; B \rightarrow 3; C \rightarrow 1; D \rightarrow 4$ |
| 43. $A \rightarrow p, q, r, t; B \rightarrow q, r, s, t; C \rightarrow p, q, r, t; D \rightarrow p, r, s, t$ | |
| 44. N_2O, I_3^- | 45. increases, decreases |
| 46. three centre bond-two electrons | |
| 47. hyperconjugation | |
| 48. sp | 49. Triangular planar |
| 51. $HCOOH$ and CH_3COOH | 52. CO_2 |
| 53. F | 54. F |
| 55. F | 56. F |
| 57. F | 58. T |
| 59. (4) | 60. (6) |
| 61. (0) | |

Topic 3

- | | | | |
|---------|--|---------------|------------|
| 1. (c) | 2. (b) | 3. (c) | 4. (b) |
| 5. (a) | 6. (d) | 7. (b) | 8. (a) |
| 9. (c) | 10. (d) | 11. (a, b, d) | 12. (a, b) |
| 13. (a) | 14. $A \rightarrow 1, 4; B \rightarrow 3; C \rightarrow 1, 2; D \rightarrow 1$ | | |

Topic 1 Preliminary Concepts of Electrovalent and Covalent Bonding Including Bonding

1. Ion-ion interaction is dependent on the square of distance, i.e. ion-ion interaction $\propto \frac{1}{r^2}$

Similarly, ion-dipole interaction $\propto \frac{1}{r^3}$

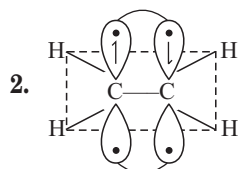
London force $\propto \frac{1}{r^6}$ and dipole-dipole interaction $\propto \frac{1}{r^3}$

Superficially it seems as both ion-dipole interaction and hydrogen bonding vary with the inverse cube of distance between the molecules but when we look at the exact expressions of field (force) created in two situations, it comes as

$$|E| \text{ or } |F| = \frac{2|P|}{4\pi \epsilon_0 r^3} \quad (\text{In case of ion-dipole interaction})$$

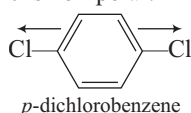
$$\text{and } F = \frac{2q^2r - 4q^2a}{4\pi \epsilon_0 r^3} \quad (\text{In case of dipole-dipole interaction})$$

From the above, it is clear that the ion-dipole interaction is the better answer as compared to dipole-dipole interaction, i.e. hydrogen bonding.

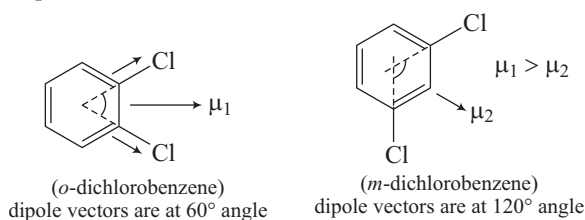


Pi bond is formed by the *p*-orbitals whose lobes have minima in the plane of molecule, hence molecular plane is the nodal plane of pi-bond.

3. H-bond is the strongest intermolecular force. All are different with 1, 0 and 2 lone pairs of electrons at central atom.
4. *p*-dichlorobenzene is non-polar.



The two dipole vectors cancelling each other giving zero resultant dipole moment. *o*-dichlorobenzene has greater dipole moment than *meta* isomer.



Toluene is less polar than both *ortho* and *para* dichlorobenzene. Therefore, the increasing order of dipole moment is

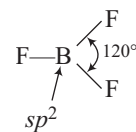
p-dichlorobenzene < toluene < *m*-dichlorobenzene < *o*-dichlorobenzene

5. The carbide (C_2^{2-}) ion has the following bonding pattern:

$:\bar{C}\equiv\bar{C}:$ one sigma and two pi bonds.

6. BF_3 has triangular planar arrangement.

Three identical vectors acting in outward direction at equal angles in a plane cancel each other giving zero resultant, hence non-polar.



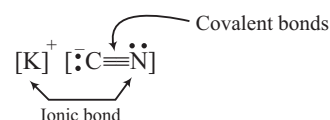
7. Strongly electropositive, univalent *X* will form an 1 : 1 ionic compound with strongly electronegative, univalent *Y*.



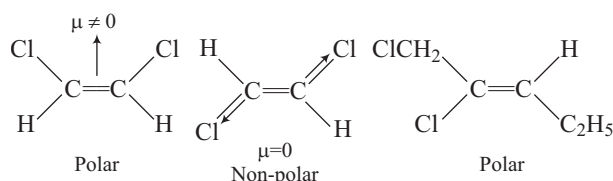
8. H_2 is a covalent, diatomic molecule with a sigma covalent bond between two hydrogen atoms.

9. N_2 has triple bond and each covalent bond is associated with one pair of electrons, therefore, six electrons are involved in forming bonds in N_2 .

10. In KCN, the bonding between potassium ion and cyanide ion is ionic while carbon and nitrogen are covalently bonded in cyanide ion as:



11. 1, 4-dichlorobenzene is non-polar, individual dipole vectors cancel each other.



12. Statement I is correct but Statement II is incorrect. The covalency in $LiCl$ is due to small size of Li^+ ion which brings about large amount of polarisation in bond.

13. These are 2π -bonds in a nitrogen molecule.

14. The resultant of individual bond dipoles may or may not be non-zero.

15. Linear overlapping of *p*-orbitals form sigma bond while sidewise overlapping of two *p*-orbitals forms a pi bond.

16. $Li^+ < Al^{3+} < Mg^{2+} < K^+$

17. Ag^+ is stronger Lewis acid because it can easily accommodate lone pair of electrons from Lewis base. On the other hand, Na^+ has noble gas configuration, cannot accept lone pair of electron, not at all a Lewis acid.

54 Chemical Bonding

18. I_2 is Lewis acid because I^- coordinate its one lone pair to I_2 .
19. Both LiF and LiI are expected to be ionic compounds. However, LiI is predominantly covalent because of small size of Li^+ and large size of iodide ion. A smaller cation and a larger anion introduces covalency in ionic compound.
20. Dipole moment is calculated theoretically as

$$\mu = q \cdot d$$

Here, $q = 1.6 \times 10^{-19}$ C and $d = 2.6 \times 10^{-10}$ m

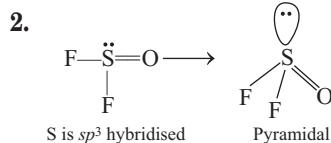
$$\mu_{\text{Theo}} = 1.6 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.16 \times 10^{-29} \text{ cm}$$

$$\% \text{ ionic character} = \frac{\mu_{\text{obs}}}{\mu_{\text{Theo}}} \times 100 = \frac{3.336 \times 10^{-29}}{4.16 \times 10^{-29}} \times 100 = 80.2\%$$

21. In hydrogen peroxide (H_2O_2), oxygen is in -1 oxidation state, can be oxidised to O_2 (zero oxidation state) or can be reduced to H_2O (-2 oxidation state of oxygen). Hence, H_2O_2 can act as both oxidising agent and reducing agent. With strong oxidising agent like $KMnO_4$, H_2O_2 acts as a reducing agent while with strong reducing agent like $H_2C_2O_4$, it acts as an oxidising agent.
22. (i) **Melting points** Ionic compounds have higher melting points than covalent compounds.
 (ii) **Boiling points** Ionic compounds have higher boiling points than covalent compounds.
 (iii) **Solubility** Ionic compounds have greater solubility in water than a covalent compound.
 (iv) **Conductivity in aqueous solution** Ionic compounds have greater electrical conductivity in aqueous solution while covalent compounds are usually non-conducting.

Topic 2 VBT, Hybridisation and VSEPR Theory

1. I_3^- is an ion made up of I_2 and I^- which has linear shape. While Cs^+ is an alkali metal cation.



SO_3 is planar (S is sp^2 hybridised), BrF_3 is T-shaped and SiO_3^{2-} is planar (Si is sp^2 hybridised).

3. For molecules lighter than O_2 , the increasing order of energies of molecular orbitals is

$$\sigma 1s \sigma^* 1s \sigma 2s \sigma^* 2s \left[\begin{array}{l} \pi 2p_y \\ \pi 2p_z \end{array} \right] \sigma 2p_x \sigma^* 2p_x \left[\begin{array}{l} \pi 2p_y \\ \pi 2p_z \end{array} \right] \dots$$

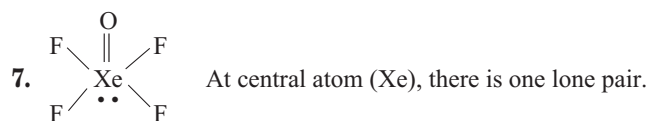
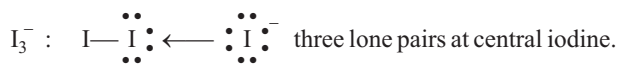
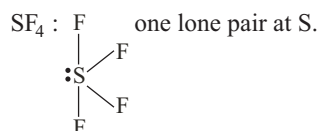
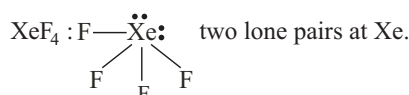
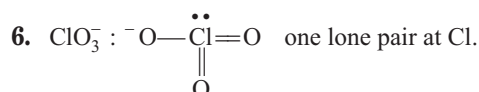
where, $\pi 2p_y$ and $\pi 2p_z$ are degenerate molecular orbitals, first singly occupied and then pairing starts if Hund's rule is obeyed. If Hund's rule is violated in B_2 , electronic arrangement would be

$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \left[\begin{array}{l} \pi 2p_y^2 \\ \pi 2p_z \end{array} \right]$$

No unpaired electron-diamagnetic.

$$\text{Bond order} = \frac{\text{bonding electrons} - \text{antibonding electrons}}{2} = \frac{6 - 4}{2} = 1$$

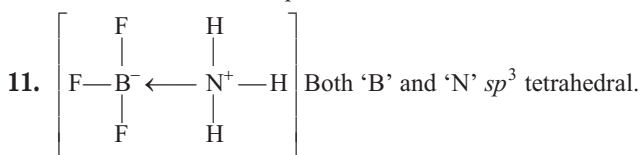
4. The bond order of $CO = 3$. NO^+ , CN^- and N_2 are isoelectronic with CO , have the same bond order as CO . NO^- ($16e^-$) has bond order of 2.
5. O_2^- in KO_2 has 17 electrons, species with odd electrons are always paramagnetic.



8. NO_3^- and CO_3^{2-} both have 32 electrons, central atom sp^2 hybridised, triangular planar.

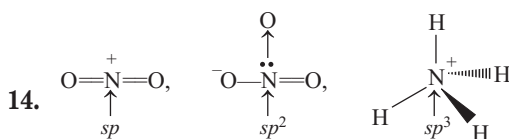
9. CH_3Cl has the highest dipole moment.

10. O_2^- has odd number(17) of electrons, therefore it must contain at least one unpaired electron.



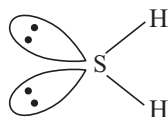
12. $NH_3 = sp^3$, $[PtCl_4]^{2-} = dsp^2$, $PCl_5 = sp^3d$, $BCl_3 = sp^2$

13. All three have 14 electrons (iso electronic) with bond order of three.

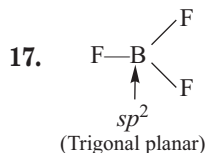


15. $^1CH_2 = ^2CH - ^3CH_2 - ^4CH_2 - ^5C \equiv ^6CH$
 Hybridisation at $C_2 = sp^2$ and at $C_3 = sp^3$.

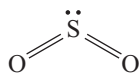
16. H_2S has sp^3 hybridised sulphur, therefore, angular in shape with non-zero dipole moment.



(Non-linear, polar molecule)



18. Sulphur in SO_2 is sp^2 -hybridised.

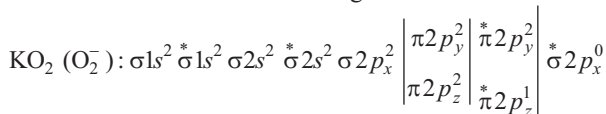


Electron pair = 2 (σ -bonds) + 1 (lone pair) = 3

Hybridisation = sp^2

Carbon in CO_2 is sp -hybridised, N in N_2O is sp -hybridised, carbon in CO is sp -hybridised.

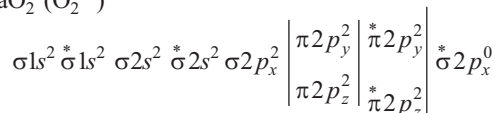
19. Molecular orbital electronic configuration are



Has one unpaired electron in $\pi^* 2p$ orbital.

AlO_2^- has both oxygen in O^{2-} state, therefore, no unpaired electron is present.

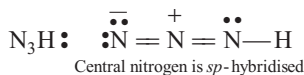
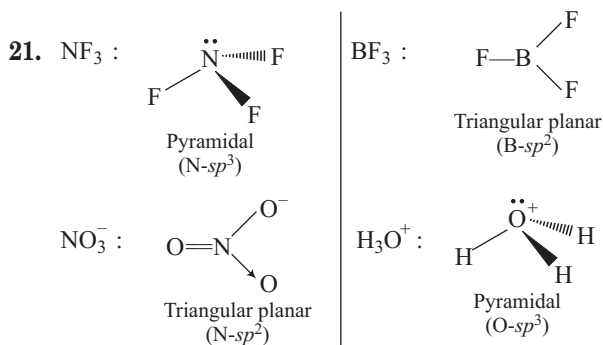
$\text{BaO}_2 (\text{O}_2^{2-})$



Has no unpaired electron.

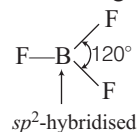
NO_2^+ has $[\text{O}=\text{N}=\text{O}]$ bonding, hence no unpaired electron.

20. N_2 is a neutral, non-polar, inert molecule while CN^- is a highly polar, highly active ion.



Therefore, $\text{NF}_3, \text{H}_3\text{O}^+$ and $\text{BF}_3, \text{NO}_3^-$ pairs have same shape.

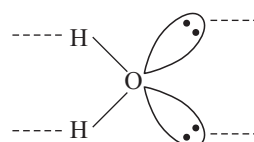
22. BF_3 has triangular planar arrangement.



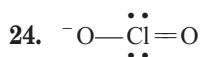
sp^2 -hybridised

There identical vectors acting in outward direction, at equal angles in a plane, cancel each other giving zero resultant, hence non-polar.

23. A water molecule can form at the most four H-bonds.



Four sites of H-bonding

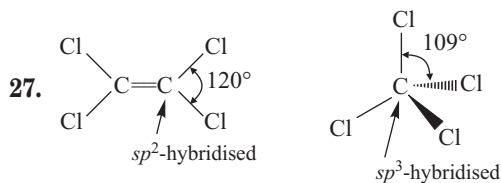


electron pairs at Cl = 2 (σ -bonds) + 2 (lone-pairs) = 4

Hybridisation at Cl = sp^3

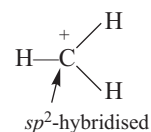
25. PCl_3 has sp^3 -hybridised phosphorus, with one lone pair. Therefore, molecule has pyramidal shape like ammonia.

26. O_2^- has odd number of electrons, hence it is paramagnetic.



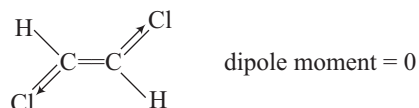
28. CO_2 is linear because carbon is sp -hybridised.

29. In CH_3^+ , there are only three electron pairs around carbon atom giving sp^2 -hybridisation state.

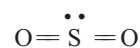


sp^2 -hybridised

30. Dipole vectors in *trans*-1, 2-dichloroethylene are at 180° and directed in opposite direction, cancelling each other.



31. In SO_2 , the Lewis-dot structure is



Electron pairs at S = 2 (σ -bonds) + 1 (lone-pair) = 3 sp^2 hybridised.

NOTE

π -bonded electrons are not present in hybrid orbitals, therefore not counted in electron pairs. Rather π bonds are formed by lateral overlapping of pure p -orbitals.

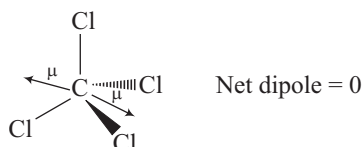
56 Chemical Bonding

32. Bonds between identical non-metal is purely covalent due to same electronegativities of the bonded atoms. Hence, the bonded atoms have equal holds on the shared pair of electrons.

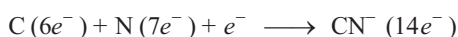
33. Hybridisation of one 's' and one 'p' orbitals gives two sp hybrid orbitals oriented linearly at 180°.



34. CCl₄ has a regular tetrahedral shape.

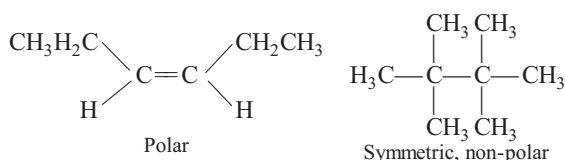
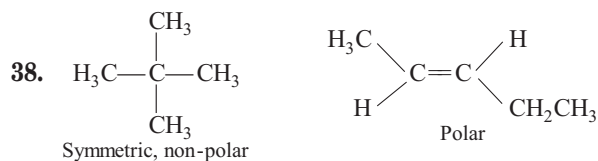


35. CO has a total of 14 electrons and CN⁻ also has 14 electrons.

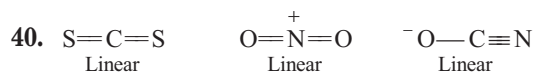


36. CO₂ is a linear molecule because of sp²-hybridisation around carbon atom.

37. For non-polar MX₃, it must have triangular planar arrangement, i.e. there should be sp²-hybridisation around M.

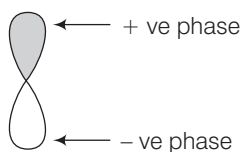


39. CN⁻ and NO⁺ are isoelectronic, have the same bond order of 3.

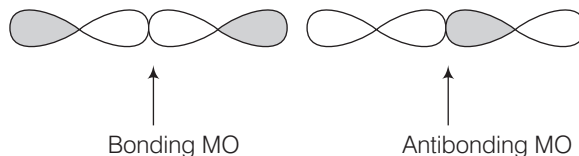


41. CO₂, HgCl₂, C₂H₂ are all linear.

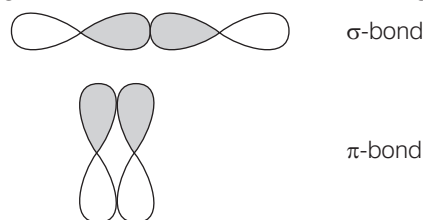
42. **PLAN** This problem includes basic concept of bonding. It can be solved by using the concept of molecular orbital theory.



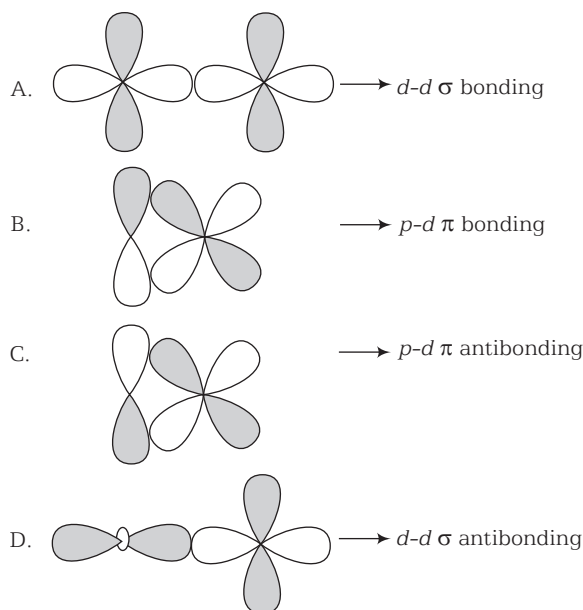
Any orbital has two phase +ve and -ve. In the following diagram, +ve phase is shown by darkening the lobes and -ve by without darkening the lobes.



When two same phase overlap with each other, it forms bonding molecular orbital otherwise antibonding.



On the basis of above two concepts, correct matching can be done as shown below:



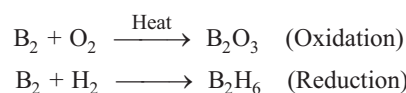
∴ A → 2, B → 3, C → 1, D → 4

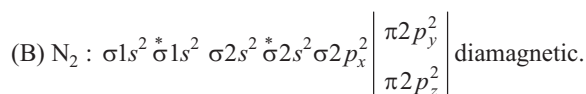
Hence, (c) is the correct option.

43. (A) $B_2 : \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \left| \begin{array}{l} \pi 2p_y^1 \\ \pi 2p_z^1 \end{array} \right|$ paramagnetic.

$$\text{Bond order} = \frac{6 - 4}{2} = 1$$

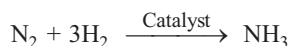
Bond is formed by mixing of s and p orbitals. B₂ undergoes both oxidation and reduction as



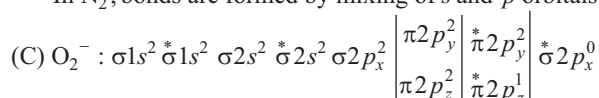


$$\text{Bond order} = \frac{10 - 4}{2} = 3 > 2$$

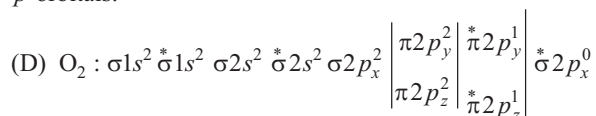
N_2 undergoes both oxidation and reduction as



In N_2 , bonds are formed by mixing of s and p orbitals.



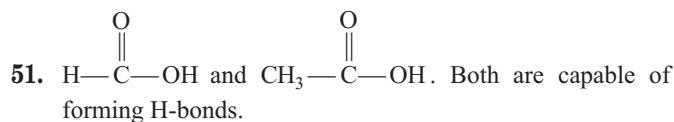
Paramagnetic with bond order = 1.5. O_2^- undergoes both oxidation and reduction and bond involves mixing of s and p -orbitals.



Paramagnetic with bond order = 2.

O_2 undergoes reduction and the bond involves mixing of s and p -orbitals.

44. N_2O and I_3^- are linear species.
 45. Bond order in N_2 is 3 while same in N_2^+ is 2.5, hence bond distance increases as N_2 goes to N_2^+ .
 Bond order in O_2 is 2 while same in O_2^+ is 2.5, hence bond distance decreases as O_2 goes to O_2^+ .
 46. Three centred-2 electrons.
 47. Hyperconjugation involves delocalisation of σ -electrons.
 48. sp -hybridised.
 49. Triangular planar. Carbon in CH_3^+ is sp^2 hybridised.
 50. sp^3 -hybrid orbital holding the lone pair is involved in formation of ammonium ion.

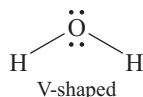


52. CO_2 , it is 180° .

53. Dipole moment (μ) = $q \cdot d$

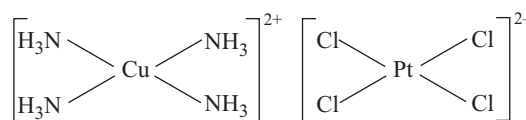
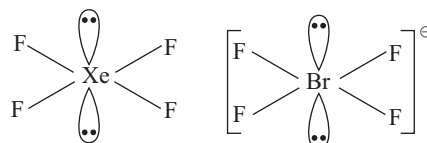
Since electronegativity of F and Cl are very close, it is the internuclear distance (d) that decides dipole moment here. Hence, C—Cl bond has greater dipole moment than the C—F bond.

54. H_2O is V-shaped molecule.

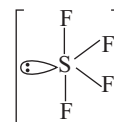


55. Explained in 2.

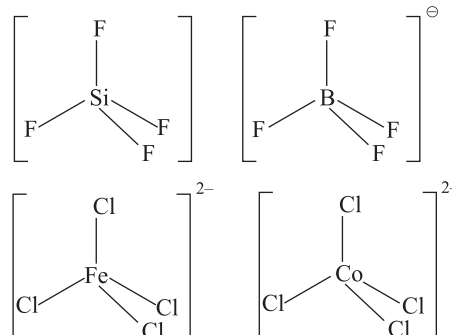
56. In sp^3 -hybrid orbital, there is 25 % s -character and 75 % p -character.
 57. Carbon in benzene is sp^2 -hybridised, i.e. uses only two of its p -orbitals in hybridisation.
 58. Sn in $SnCl_2$ has sp^2 -hybridisation.
 59. **PLAN** This problem includes concept of hybridisation using VBT, VSEPR theory, etc.,
 XeF_4 , BrF_4^- , $[Cu(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$ are square planar as shown below:



SF_4 (See-saw) as shown below:

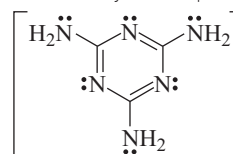


SiF_4 , BF_4^- , $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ are tetrahedral as shown below:



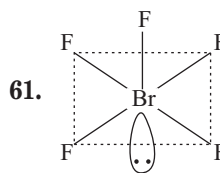
Hence, correct integer is 4.

60. **PLAN** Melamine is a heterocyclic compound.



Each nitrogen atom has one pair of lone pair

Thus, in all six lone pairs.



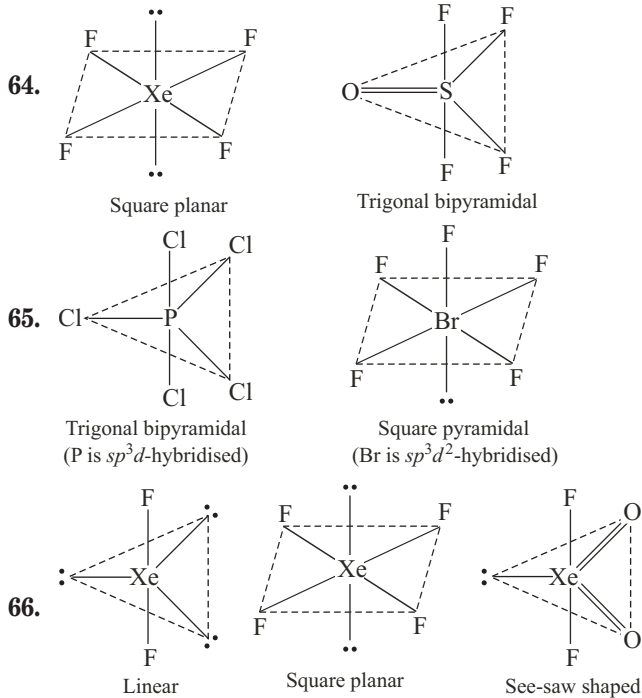
Lone pair would push the Br—F bond pairs in upward direction and all Br—F bond angles will contract.

58 Chemical Bonding

62. No, (i) NMe_3 is pyramidal while (ii) $\text{N}(\text{SiMe}_3)_3$ is planar. In the latter case, $p\pi - d\pi$ back bonding between N and Si makes N sp^2 -hybridised.

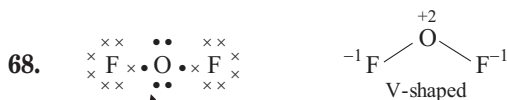
63. Bond order : $\text{O}_2^- = 1.5$, $\text{O}_2 = 2$, $\text{O}_2^+ = 2.5$

Bond length : $\text{O}_2^+ < \text{O}_2 < \text{O}_2^-$

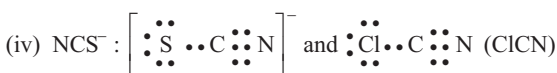
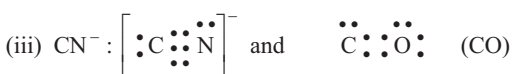
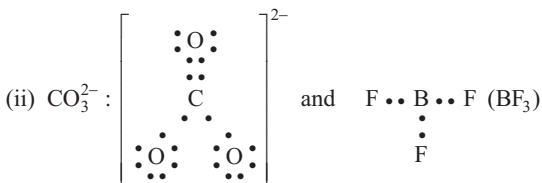
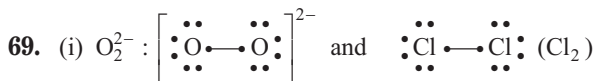


67. In H_2S , S is sp^3 -hybridised with two lone pairs of electrons on it giving V-shaped (water like) shape. In PCl_3 , P is sp^3 -hybridised with one lone pair of electrons on it.

Therefore, PCl_3 is pyramidal in shape.



Electron pair = $P = 2 + 2 = 4$
Hybridisation = sp^3



Topic 3 Resonance, LCAO, MOT, Other Bonding Types

1. **PLAN** This problem can be solved by using the concept involved in molecular orbital theory. Write the molecular orbital electronic configuration keeping in mind that there is no $2s-2p$ mixing, then if highest occupied molecular orbital contain unpaired electron then molecule is paramagnetic otherwise diamagnetic.

Assuming that no $2s-2p$ mixing takes place the molecular orbital electronic configuration can be written in the following sequence of energy levels of molecular orbitals

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \pi 2p_x \equiv \pi 2p_y,$$

$$\pi^* 2p_x \equiv \pi^* 2p_y, \sigma^* 2p_z$$

(a) $\text{Be}_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$ (diamagnetic)

(b) $\text{B}_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^0, \pi 2p_y^0$
(diamagnetic)

(c) $\text{C}_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^1, \pi 2p_y^1, \pi^* 2p_x^0, \pi^* 2p_y^0, \sigma^* 2p_z^0$ (paramagnetic)

(d) $\text{N}_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2, \pi 2p_y^2, \pi^* 2p_x^0, \pi^* 2p_y^0, \sigma^* 2p_z^0$ (diamagnetic)

Hence, (c) is the correct choice.

2. Li_2 ($3 + 3 = 6$) = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2$
Bond order = $\frac{N_b - N_a}{2} = \frac{4 - 2}{2} = 1$

Li_2^+ ($3 + 3 - 1 = 5$) = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^1$

Bond order = $\frac{3 - 2}{2} = \frac{1}{2} = 0.5$

Li_2^- ($3 + 3 + 1 = 7$) = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^1$

Bond order = $\frac{4 - 3}{2} = \frac{1}{2} = 0.5$

Stability order is $\text{Li}_2^- < \text{Li}_2^+ < \text{Li}_2$ (because Li_2^- has more number of electrons in antibonding orbitals which destabilises the species).

3. Species having zero or negative bond order do not exist.

H_2^{2+} ($1 + 1 - 2 = 0$) = $\sigma 1s^0$

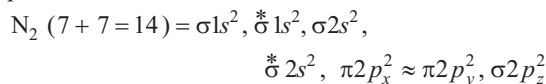
Bond order = 0

He_2 ($2 + 2 = 4$) = $\sigma 1s^2, \sigma^* 1s^2$

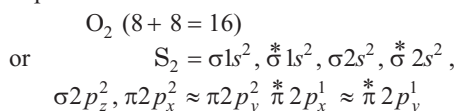
Bond order = $\frac{N_b - N_a}{2} = \frac{2 - 2}{2} = 0$

So, both H_2^{2+} and He_2 do not exist.

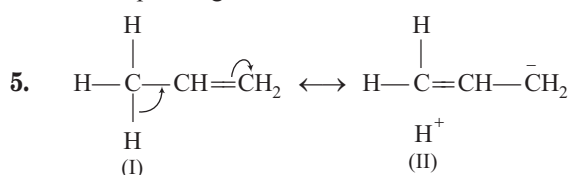
4. $C_2 (6 + 6 = 12) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2$
 Since, all the electrons are paired, it is a diamagnetic species.



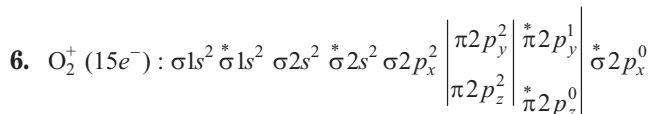
It is also a diamagnetic species because of the absence of unpaired electrons.



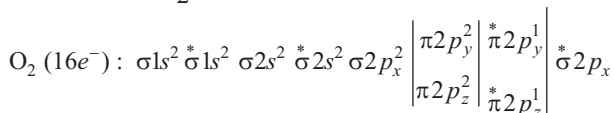
Due to the presence of two unpaired electrons, O_2 and S_2 both are paramagnetic molecules.



I and II are hyperconjugation structures of propene and involves σ -electrons of C—H bond and p -orbitals of pi bond in delocalisation.

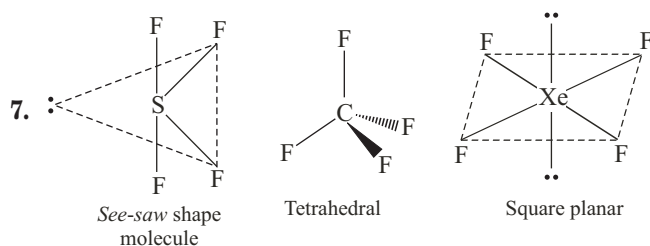


Bond order = $\frac{10 - 5}{2} = 2.5$; paramagnetic.



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

Hence, (a) is the correct answer.



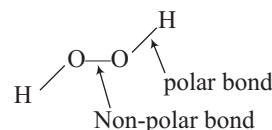
8. When $E = B$ in BCl_3 , bond angle is 120° . When $E = P, As$ or Bi in ECl_3 , hybridisation at E will be sp^3 . Also, if central atoms are from same group, bond angle decreases down the group provided all other things are similar. Hence, the order of bond angles is $BCl_3 > PCl_3 > AsCl_3 > BiCl_3$

9. Bond length $\propto \frac{1}{\text{Bond order}}$

$$\text{Bond order} : CO_2 = 2, CO = 3, CO_3^{2-} = 1 + \frac{1}{3} = \frac{4}{3}$$

Therefore, order of bond length is $CO_3^{2-} < CO_2 < CO$

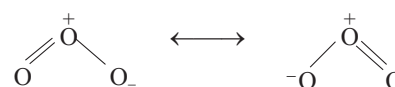
10. H_2O_2



11. HCl does not form hydrogen bond. For formation of hydrogen bond, atleast one hydrogen atom must be bonded to one of the three most electronegative atom O, N and F.

12. **PLAN** This problem can be solved by using concept of H-bonding and applications of H-bonding.

13. Statement I is correct, given structure is one of the resonance structure of ozone.

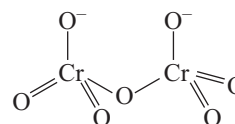


Statement II is also correct because oxygen cannot expand its octet. It is also the explanation for the given structure of ozone.

14. (A) In the reaction : $O_2^- \longrightarrow O_2 + O_2^{2-}$

Oxygen on reactant side is in $-\frac{1}{2}$ oxidation state. In product side, one of the oxygen is in zero oxidation state, i.e. oxidised while the other oxygen is in -1 oxidation state, i.e. reduced. Hence, in the above reaction, oxygen ($O^{-1/2}$) is simultaneously oxidised and reduced disproportionated.

- (B) In acidic medium, CrO_4^{2-} is converted into $Cr_2O_7^{2-}$ which is a dimeric, bridged tetrahedral.

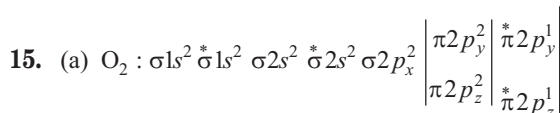


- (C) $MnO_4^- + NO_2^- + H^+ \longrightarrow Mn^{2+} + NO_3^-$

The above is a redox reaction and a product NO_3^- has trigonal planar structure.

- (D) $NO_3^- + H_2SO_4 + Fe^{2+} \longrightarrow Fe^{3+} + NO$

The above is a redox reaction.



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

16. Strength of hydrogen bonding in $X-H-X$ depends on electronegativity as well as size of X . X with higher electronegativity and smaller size forms stronger H-bond. Hence, increasing order of strength of H-bond is



17. Resonance in vinyl chloride increases polar character of the molecule.

