1. STOICHIOMETRY AND REDOX REACTIONS

THE MOLE AND EQUIVALENT CONCEPT

1. INTRODUCTION

Some important terminologies required to master the concepts of chemistry are as follows:

(a) **Chemical Equation:** It is the symbolic representation of a true chemical reaction. The equation provides qualitative and quantitative information about a chemical change in a simple manner. For e.g. in the reaction,

$$3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 6NaCl$$

The '+' sign on left hand side means 'react with' and on the right of arrow as 'produces'. The substances which react ae called 'reactants' and those produced in the reaction are called 'products' and they are represented on the LHS and RHS of the arrow respectively.

(b) **Thermo Chemical Equation:** The equations which represent chemical as well as thermal changes are called thermo chemical equations. The energy change is shown by putting value on the RHS of the reaction. For eg.

$$\text{(Exothermic)} : C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -ve$$

$$\text{(Endothermic)} : C(s) + 2S(s) \longrightarrow CS_2(g); \quad \Delta H = +ve$$

(c) **Molecule and Atom:** A molecule is defined as the smallest possible particle of a substance which has all the properties of that substance and can exist freely in nature. On the other hand an atom is the smallest particle of an element (made up of still smaller particles like electrons, protons, neutrons, etc.) which can take part in a chemical reaction. It may or may not exist free in nature.

(d) **Atomicity of an Element:** The term refers for the number of atoms present in one molecule of an element, e.g., atomicity of H_2, O_3, S_8, P_4 is 2, 3, 8 and 4 respectively.

(e) **Mole:** A mole is defined as the amount of matter that contains as many objects (atoms, molecules, electron, proton or whatever, objects we are considering) as the same number of atoms in exactly 12 g of C^{12}. This number is also known as **Avogadro's number (N_A)**. Avogadro's number = 6.023×10^{23} molecule/mole. Thus, 1 mole of an entities contains N_A particles of that entity.

Number of objects (N) in n mole = number of mole (n) × number of objects per mole (N_A)

$$N = n \times N_A = \frac{w}{M} \times N_A, \left[n = \frac{w}{M} \right]$$ where N_A is Avogadro's number.

(f) **Molar Mass:** The mass in gram of 1 mole of a substance is known as molar mass or molecular weight of substance.

(g) **Atomic Weight:** The atomic mass of an element is defined as the average relative mass of its atoms as compared to the mass of a carbon atom taken as 12. Note that the atomic weight of an element is a relative weight of one atom and not the absolute weight.

(h) **Gram Molecular Weight:** Molecular weight or gram molecular weight of a substance is weight of N-molecules of that substance in grams.

Illustration 1: Calculate the mass of single atom of sulphur and a single molecule of carbon dioxide.

(JEE MAIN)

Sol: Know the gram atomic and the molecular mass of sulphur and CO_2 and then divide by N_A.

Mass of one sulphur atom $= \dfrac{\text{Gram atomic mass}}{6.02\times10^{23}} = \dfrac{32}{6.02\times10^{23}} = 5.33\times10^{-23}\,\text{g}$

Formula of carbon dioxide = CO_2

Molecular mass of CO_2 = 12 + 2 × 16 = 44

Gram-molecular mass of CO_2 = 44 g

Mass of one molecule of CO_2 $= \dfrac{\text{Gram molecular mass}}{6.02\times10^{23}} = \dfrac{44}{6.02\times10^{23}} = 7.308\times10^{-23}\,\text{g}$

Illustration 2: How many electrons are present in 1.6 g of methane? **(JEE ADVANCED)**

Sol: Know the molar mass of methane, the moles and the no. of molecules.Then calculate no. of electrons for the solved no. of molecules.

Gram molecular mass of methane, (CH_4) = 12 + 4 = 16 g

Number of moles in 1.6 g of methane $= \dfrac{1.6}{16} = 0.1$

Number of molecule of methane in 0.1 mole $= 0.1\times6.023\times10^{23} = 6.02\times10^{22}$

One molecules of methane has = 6 + 4 = 10 electrons

So, 6.02×10^{22} molecules of methane have $= 10\times6.02\times10^{22}$ electrons $= 6.02\times10^{23}$ electrons

2. STOICHIOMETRY

The quantitative aspect, dealing with mass and volume relations among reactants and products is termed stoichiometry. Consider for example, the reaction represented by a balanced chemical equation:

Chemical Equation	$2H_2(g)$	+	$O_2(g)$	$\longrightarrow$	$2H_2O(g)$
Mole ratio :	2 mol or		1 mol or		2 mol or
Molecule ratio :	$2\times6.023\times10^{23}$ molecules or 2 molecules		$1\times6.023\times10^{23}$ molecules or 1 molecules		$2\times6.023\times10^{23}$ molecules or 2 molecules
Weight ratio :	4g		32g		36 g
Volume ratio :	2 vol		1 vol		2 vol

(valid only for gaseous state at same P and T)

The given reaction suggests the combination ratio of reactants and formation ratio of products in terms of:

(a) **Mole ratio:** 2 mol H_2 reacts with 1 mol of O_2 to form 2 mol of H_2O vapors.

(b) **Molecular ratio:** 2 molecule of H_2 reacts with 1 molecule of O_2 to form 2 molecules of H_2O vapors.

(c) **Weight ratio:** 4 g H_2 reacts with 32 g O_2 to form 36 g of H_2O vapors.

(d) Volume ratio: In gaseous state 2 volume H_2 reacts with 1 volume O_2 to form 2 volume H_2O vapors at same conditions of P and T.

Therefore, coefficients in the balanced chemical reaction can be interpreted as the relative number of moles, molecules or volume (if reactants are gases) involved in the reaction. These coefficients are called stoichiometrically equivalent quantities and may be represented as:

$$2 \text{ mol } H_2 \equiv 1 \text{ mol } O_2 \equiv 2 \text{ mol } H_2O$$

Or $\quad$ Mole of H_2: Mole of O_2: Mole of H_2O = 2: 1: 2

Where the symbol ≡ is taken to mean 'stoichiometrically equivalent to'. The stoichiometric relation can be used to give conversion factors for relating quantities of reactants and products in a chemical reaction.

2.1 Some Important Laws

(a) Law of conservation of mass: "In all physical and chemical changes, the total mass of the reactants is equal to that of the products" or "matter can neither be created nor destroyed."

(b) Law of constant composition/definite proportion: "A chemical compound is always found to be made up of the same elements combined together in the same fixed ratio by weight".

(c) Law of multiple proportions: "When two elements combine together to form two or more chemical compounds, then the weight of one of the elements which combine with a fixed weight of the other bear a simple ratio to one another".

(d) Law of reciprocal proportions: The ratio of the weights of two elements A and B which combine with a fixed weight of the third element C is either the same or a simple multiple of the ratio of the weights of A and B which directly combine with each other.

(e) Gay-Lussac's law of gaseous volumes: "When gases react together, they always do so in volumes which bear a simple ratio to one another and to the volumes of the products, if gaseous, all measurements are made under the same conditions of temperature and pressure".

Illustration 3: What mass of sodium chloride would be decomposed by 9.8 g of sulphuric acid, if 12 g of sodium bisulphate and 2.75 g of hydrogen chloride were produced in a reaction assuming that the law of conservation of mass is true? **(JEE MAIN)**

Sol: Apply the law of conservation of mass.

$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl$$

According to law of conservation of mass, Total mass of reactant = Total mass of product

Let the mass of NaCl decomposed be x, so

$$\begin{aligned} x + 9.8 &= 12 + 2.75 \\ &= 14.75 \\ x &= 4.95 \text{ g} \end{aligned}$$

Illustration 4: How much volume of oxygen will be required for complete combustion of 40 mL of acetylene (C_2H_2) and how much volume of carbon dioxide will be formed? All volumes are measured at NTP. **(JEE ADVANCED)**

Solution: Write the balanced chemical reaction and from the given data determine the volume.

$$\begin{array}{ccccccc} 2C_2H_2 & + & 5CO_2 & \rightleftharpoons & 4CO_2 & + & 2H_2O \\ 2\text{ vol} & & 5\text{vol} & & 4\text{ mol} & & \\ 40\text{ ml} & & \frac{5}{2}\times 40\text{ml} & & \frac{4}{2}\times 40\text{ml} & & \\ 40\text{ml} & & 100\text{ml} & & 80\text{ml} & & \end{array}$$

So, for complete combustion of 40 mL of acetylene, 100 mL of oxygen are required and 80 mL of carbon dioxide is formed.

2.2 Avogadro's Hypothesis

"Equal volumes of all gases/vapors under similar conditions of temperature and pressure contain equal number of molecules."

This statement leads to the following facts:

(a) One mole of all gases contain Avogadro's number of molecules, i.e., 6.023×10^{23} molecules.

(b) The volume of 1 mole of gas at NTP or STP is 22.4 litre.

(c) NTP or STP refers for $P = 1$ atm, $T = 0^{\circ}C$ or 273 K.

(d) Molecular weight = 2 × vapour density (for gaseous phase only)

It provides a method to determine the atomic weights of gaseous elements.

2.3 Dulong and Petit's Law

This law is valid for metals only. According to this law, atomic weight × specific heat (in cal/g) ≈ 6.4. Also, heavier the element, lesser will be its specific heat. Therefore, $C_{Hg} < C_{Cu} < C_{Al}$.

2.4 Equivalent Weight

For comparing reacting weights of substances participating in a chemical reaction, chemists coined the term 'equivalent weight'. The substances react in their equivalent weight ratios.

2.4.1 Equivalent Weight of an Element or Compound in a Non-Redox Change

Equivalent weight of an element is its weight which reacts with 1 part by weight of hydrogen, 8 parts by weight of oxygen and 35.5 parts by weight of chlorine. This definition leads to following important generalisations.

(a) **Equivalent weight of an element:** $'E' = \frac{\text{Atomic weight of element}}{\text{Valence of element}}$

(b) **Equivalent weight of an ionic compound:** $(E) = \frac{\text{Formula weight of compound}}{\text{Total charge on cationic or anionic part}}$

Also, Eq. wt. of compound E = Eq. wt. of I part + Eq. wt. of II part

(c) **Equivalent weight of an acid or base:**

$$E_{Acid} = \frac{\text{Molecular weight}}{\text{Basicity}}$$

Basicity = Number of H-atoms replaced from one molecule of acid

$$E_{Base} = \frac{\text{Molecular weight}}{\text{Acidity}}$$

Acidity = Number of OH-groups replaced from one molecule of base.

(d) **Equivalent weight of acid salt:** $= \frac{\text{Molecular weight of acid salt}}{\text{Replaceable H-atom in it}}$

An acid salt is one which has replaceable H-atom, e.g., $NaHCO_3$, $NaHSO_4$, Na_2HPO_4, Na_2HPO_3 is not an acid salt, since it does not have replaceable H-atom.

Note: An acid salt possesses acidity as well as basicity both.

(i) Equivalent weight of basic salt: $= \dfrac{\text{Molecular weight of basic salt}}{\text{Replacable OH gps in basic salt}}$

A basic salt is one which has replaceable OH gps e.g., $Ca(OH)Cl$, $Al(OH)_2Cl$, $Al(OH)Cl_2$ etc.

2.4.2 Equivalent Weight of an Element or Compound in a Redox Change

For a redox change, the equivalent weight of a substance is given by,

$$\text{Equivalent weight of an oxidant or reductant} = \frac{\text{Molecular weight}}{\text{Number of electrons lost or gained by one molecule of oxidant or reductant}}$$

2.4.3 Gram Equivalent Weight

The equivalent weight of a substance expressed in grams is called gram eq. wt. or one gram equivalent. Now we can define gram-equivalent (g meq) in gms of a substance whose equivalent weight is as follows: No. of equivalents $= \dfrac{g}{E}$

Illustration 5: An unknown element forms an oxide. What will be the equivalent mass of the element if the oxygen content is 20% by mass? **(JEE MAIN)**

Sol: Use the equation of equivalent weight.

$$\text{Equivalent mass of element} = \frac{\text{Mass of element}}{\text{Mass of oxygen}} \times 8 = \frac{80}{20} \times 8 = 32$$

Illustration 6: The equivalent weight of a metal is double than that of oxygen. How many times is the weight of its oxide greater that the weight of metal? **(JEE ADVANCED)**

Sol: First calculate the equivalent weight of the metal and from the molecular formula, determine the ratio.

Equivalent mass of metal = 16 = $\dfrac{x}{n}$

Where x= atomic mass of metal

N = valency of metal

Molecular formula of metal oxide = M_2O_n

$$\frac{\text{Mass of metal oxide}}{\text{Mass of metal}} = \frac{2(16n) + 16(n)}{2(16n)} = 1.5$$

2.5 The Limiting Reagent

The reagent producing the least number of moles of products is the limiting reagent. For example, consider a chemical reaction given below, containing 10 mol of H_2 and 7 mol of O_2. Since, 2 mol H_2 reacts with 1 mol O_2, thus,

	$2H_2(g)$	+ $O_2(g)$ $\longrightarrow$	$2H_2O(V)$
Moles before reaction	10	7	0
Moles after reaction	0	2	10

It is thus, evident that the reaction stop only after consumption of 5 moles of O_2 since, no further amount of H_2 is left to react with unreacted O_2. The substance that is completely consumed in a reaction is called **limiting reagent** because it determines or limits, the amount of product. The other reactants present in excess are sometimes called as **excess reagents**.

Calculation of limiting reagent

(a) By calculating the required amount by the equation and comparing it with given amount. [Useful when only two reactants are there]

(b) By calculating amount of anyone product obtained taking each reactant one by one irrespective of other reactants. The one giving least product is limiting reagent.

(c) Divide given moles of each reactant by their stoichiometric coefficient, the one with least ratio is limiting reagent. [Useful when numbers of reactants are more than two].

2.6 Reaction Yield

The theoretical yield of a product is the maximum quantity that can be expected on the basis of stoichiometry of a chemical equation. The percentage yield is the percentage of a theoretical yield actually achieved. The lower yield of a chemical reaction is due to side reactions.

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Illustration 7: 10 mL N_2 and 25 mL H_2 at same P and T are allowed to react to give NH_3 quantitatively. Predict (i) the volume of NH_3 formed, (ii) limiting reagent. **(JEE MAIN)**

Sol: Frame the reaction and lay down the conditions, due to which volume of NH_3 can be found which leads to the limiting reagent.

$$\begin{array}{llll} & N_2 & +3H_2 \longrightarrow & 2NH_3 \\ \text{V at t} = 0 & 10 & 25 & 0 \\ \text{V at final condition} & \left[10 - \frac{25}{3}\right] & 0 & \frac{50}{3} \end{array}$$

$\therefore$ Volume of $2NH_3$ formed $= \frac{50}{3}$ mL

Limiting reagent is H_2.

Illustration 8: A chloride of an element contains 49.5% chlorine. The specific heat of the element is 0.056. Calculate the equivalent mass, valency and atomic mass of the element. **(JEE ADVANCED)**

Sol: Calculate mass of the metal from the given percentage and the equivalent mass of the metal. Using the Dulong and Petit's law, specific heat gives the atomic mass of the metal and then the valency can be found.

Mass of chlorine in the metal chloride = 49.5%

Mass of metal = (100 – 49.5) = 50.5

$$\text{Equivalent mass of the metal} = \frac{\text{Mass of metal}}{\text{Mass of chlorine}} \times 35.5 = \frac{50.5}{49.5} \times 35.5 = 36.21$$

According to Dulong and Petit's law,

$$\text{Approximate atomic mass of the metal} = \frac{6.4}{\text{Specific heat}} = \frac{6.4}{0.056} = 114.3$$

$$\text{Valency} = \frac{\text{Approximate atomic mass}}{\text{Equivalent mass}} = \frac{114.3}{36.21} = 3.1 \approx 3\text{ v}$$

Hence, exact atomic mass = 36.21 × 3 = 108.63

3. METHODS OF EXPRESSING CONCENTRATION OF SOLUTION

(a) Strength of Solution: Amount of solute present in one litre solution

$$S = \frac{\text{Weight of solute}}{\text{Volume of solution in litre}} = \frac{w}{V\text{ in (l)}}$$

$$= \text{Normality} \times \text{Equivalent weight}$$

$$= \text{Molarity} \times \text{Molecular weight}$$

(b) Mass Percentage or Percent by Mass:

$$\%(w/w)\text{ Mass percentage of solute} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

(c) Percent Mass by Volume: $\%(w / v) = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$

(d) Parts Per Million (ppm): $= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$

(e) Molarity: It is expressed as moles of solute contained in one litre of solution or it is also taken as millimoles of solute in 1000 cc(mL) of solution. It is denoted by M.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Litres of solution}} = \frac{\text{Millimoles of solute}}{\text{Millilitres of solution}}; \qquad M = \frac{n_B}{V_{lt}} = \frac{g_B / m_B}{V_{lt}}$$

(f) Molality: It is the number of mole present in 1kg solvent.

$$\text{Molality(m)} = \frac{\text{No. of moles of solute}}{\text{Weight (in kg) of solvent}}$$

Let w_A grams of the solute of molecular mass m_A be present in w_B grams of the solvent, then

$$\text{Molality(m)} = \frac{w_A}{m_A \times w_B} \times 1000$$

(g) Normality: It is define as number of equivalent of a solute present in one litre of solution.

$$N = \frac{\text{Equivalent of solute}}{\text{Volume of solution in litre}} = \frac{\text{Weight of solute}}{\text{Equivalent weight of solute} \times \text{V in litre}}$$

$$N = \frac{w}{E \times V\text{ in (l)}} = \frac{w \times 1000}{E \times V\text{ in mL}}$$

Note: A striking fact regarding equivalent and milli equivalent is equivalent and milli equivalent of reactants react in equal number to give same number of equivalent or milli equivalent of products separately.

(h) Formality: Since molecular weight of ionic solids is not determined accurately due to their dissociative nature and therefore molecular weight of ionic solid is often referred as formula weight and molarity as formality. $\text{Formality} = \frac{\text{Wt. of solute}}{\text{Formula wt.} \times \text{V(in l)}}$ i.e., molarity

(i) Specific Gravity of Solution: $= \dfrac{\text{Weight of solution}}{\text{Volume of solution}}$ i.e., weight of 1 mL solution.

MASTERJEE CONCEPTS

- Molality, % by weight, mole fractions are independent of temperature since these involve weights.
- Rest all, i.e., normality, molarity, % by volume, % by strength and strength are temperature dependent, normally decrease with increase in temperature since volume of solution increases with T.
- Molar solution having normality 1N and molarity 1M respectively.
- On diluting a solution, eq. meq. mole or m mole of solute do not change however N and M change.

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(j) Mole Fraction: It is the fractional part of the moles that is contributed by each component to the total number of moles that comprises the solution. In containing n_A moles of solvent and n_B moles of solute. Mole fraction of B $= x_B = \dfrac{n_B}{n_A + n_B}$

Mole fraction of A $= x_B = \dfrac{n_A}{n_A + n_B}$

(k) Ionic Strength: The ionic strength (μ) of the solution obtained by mixing two or more ionic compounds is given by: $\mu = \frac{1}{2}\Sigma cZ^2$. Where c is the concentration (molarity) of that ion and Z is its valence.

Illustration 9: 30 mL of 0.1 N $BaCl_2$ is mixed with 40 mL of 0.2 N $Al_2(SO_4)_3$. How many g of $BaSO_4$ are formed? **(JEE MAIN)**

Sol: Frame the reaction and place the given data to find the milliequivalents at the end of the reaction. Using the formula below, weight of $BaSO_4$ can be found.

	$BaCl_2$	$+ Al_2(SO_4)_3 \longrightarrow$	$BaSO_4$	$+ AlCl_3$
Meq. before reaction	$30 \times 0.1 = 3$	$40 \times 0.2 = 8$	$0 = 0$	$0 = 0$
Meq. after reaction	0	5	3	3

3 Meq. of $BaCl_2$ reacts with 3 Meq. of $Al_2(SO_4)_3$ to produce 3 Meq. of $BaSO_4$ and 3 Meq. of $AlCl_3$

$$\therefore \quad \text{Meq. of } BaSO_4 \text{ formed} = \frac{w_{BaSO_4}}{E_{BaSO_4}} \times 1000 = 3$$

$$w_{BaSO_4} \text{ formed} = \frac{3 \times 233}{2 \times 1000} = 0.3495 \text{ g}$$

Illustration 10: 500 mL of aM solution and 250 mL of bM solution of the same solute are mixed and diluted to 2 litre. The diluted solution shows the molarity 1.6 M. If a: b is 2: 5, then calculate a and b. **(JEE ADVANCED)**

Sol: Using the mixture molarity formula $\dfrac{M_1 \times V_1 + M_2 \times V_2}{V_1 + V_2}$, a and b is calculated.

$\frac{500\times a+250\times b}{2000}=1.6$; 500 a + 250 b = 3200

If, $\frac{a}{b}=\frac{2}{5}$ then $\frac{500\times b\times 2}{5}$ + 250 b = 3200; 450 b = 3200; b = 7.11

Similarly, $500a+\frac{250\times 5a}{2}=3200$; $\therefore$ $a=\frac{3200}{1125}$ = 2.84

4. SOME CHARACTERISTIC APPLICATION OF MOLE CONCEPT

4.1 Gravimetric Analysis

Gravimetric analysis is an analytical technique based on the measurement of mass of solid substances and or volume of gaseous species. Gravimetric analysis is divided into three parts.

(a) **Mass–Mass Relationship:** It relates the mass of a species (reactant or product) with the mass of another species (reactants or products)

Let us consider a chemical reaction,

$$2NaHCO_{3(s)}\xrightarrow{\Delta}Na_2CO_{3(s)}+H_2O+CO_{2(g)}$$

Suppose the mass of $NaHCO_3$ being heated is 'x' g and we want to calculate the weight of Na_2CO_3 being produced by heating of 'a' g $NaHCO_3$.

The moles of $NaHCO_3=\frac{x}{84}$

According to the above balanced equation 2 moles of $NaHCO_3$ upon heating gives 1 mole of Na_2CO_3

(b) **Mass–Volume Relationship:** It relates the mass of a species (reactant or product) and the volume of a gaseous species (reactant or product) involved in a chemical reaction. Suppose we are provided with 'a' gms of $NaHCO_3$ in a vessel of capacity VL and the vessel is heated, so that decomposes as $2NaHCO_3\xrightarrow{\Delta}Na_2CO_3+H_2O+CO_2$

Now, we want to calculate the volume of CO_2 gas being reduced.

Moles of $NaHCO_3$ taken $=\frac{X}{84}$

Now, since 2 moles of $NaHCO_3$ gives 1 mole of CO_2 at STP. Thus

Moles of CO_2 produced $=\frac{1}{2}\times\frac{X}{84}$

As we know that 1 mole of any gas at STP occupies a volume of 22.4 L.

So, volume of CO_2 produced $=\left(\frac{1}{2}\times\frac{X}{84}\times 22.4\right)L$

(i) **Volume–Volume Relationship:** It relates the volume of gaseous species (reactants or products) with the volume of another gaseous species (reactant or product) involved in a chemical reaction.

Illustration 11: An ore containing Mn_2O_3 is analysed for the manganese content by quantitatively converting the manganese to Mn_3O_4 and weighing it. A 1.52 g sample of ore yields 0.126 g Mn_3O_4. Calculate the percent of Mn and Mn_2O_3 in the sample. **(JEE ADVANCED)**

Sol: From the given data, find out the amount of Mn_2O_3 and calculate the %.

Equate the no. of moles of Mn_2O_3 with the no. of moles of Mn and hence find % of Mn. $3Mn_2O_3\longrightarrow 2Mn_3O_4$

Mole ratio $Mn_2O_3 : Mn_3O_4 :: 3 : 2$

$\therefore$ Moles of $Mn_2O_3 = \frac{3}{2}$ × Moles of $Mn_3O_4 = \frac{3}{2} \times \frac{0.126}{229} = 5.253 \times 10^{-4}$

$\therefore$ Amount of $Mn_2O_3 = 8.253 \times 10^{-4} \times 158 = 0.13$ g

$\therefore$ % of $Mn_2O_3 = \frac{0.13}{1.52} \times 100 = 8.58$

Also, $Mn_2O_3 \longrightarrow 2Mn$

$\therefore$ Mole of Mn = 2 × Mole of Mn_2O_3 = $2 \times 8.253 \times 10^{-4} = 16.51 \times 10^{-3}$

$\therefore$ Amount of Mn $= 16.51 \times 10^{-3} \times 55$

$\therefore$ % Mn $= \frac{0.09}{1.52} \times 100 = 5.29$

Illustration 12: A 1.0 g sample of pure organic compound containing chlorine is fused with Na_2O_2 convert chlorine to NaCl. The sample is then dissolved in water, and the chloride precipitated with $AgNO_3$, giving 1.96 g of AgCl. If the molecular weight of organic compound is 147, how many chlorine atoms does each molecule contain?

(JEE MAIN)

Sol: Calculate the moles of chloride ions in silver chloride and the organic compound; and compare the ratio.

Moles of AgCl = Moles of chloride= $\frac{1.96}{143.5} = 0.0136$

Moles of organic compound = $\frac{1}{147} = 6.8 \times 10^{-3}$

Chlorine atoms in each molecules of organic compound = $\frac{0.0136}{6.5 \times 10^{-3}} = 2$

4.2 Volumetric Analysis

It is the process of determination of conc. of a solution with the help of another solution of known conc. It may also be defined as experimental method of determination of volume of a solution of known strength needed for a definite volume of another solution of unknown strength.

Titration: It is an operation forming the basis of volumetric analysis. The addition of measured amount of a solution of one reagent (called the **titrant**) from a burette to a definite amount of another reagent (called **analyte**) until the reaction between them is complete, i.e., till the second reagent (analyte) is completely used up, i.e., upto end point.

Type of Titrations: There are four general classes of volumetric titrations.

(a) **Acid-Base Titration:** Acid or base solutions are titrated against a standard solution of a strong base or strong acid using suitable acid-base indicator.

(b) **Precipitation Titration:** In such titration, the titrant forms an insoluble product with analyte e.g., titration of chloride ions against $AgNO_3$ solution.

(c) **Complexometric Titrations:** In such titrations, the titrant is a complexing agent and forms a water-soluble complex with the analyte, usually containing a metal ion. The titrant is often a chelating agent, e.g., ethylenediaminetetraacetic acid (EDTA).

(d) **Redox Titrations:** These involves the titration of an oxidizing agent against a reducing agent or vice versa.

Standard Solution: It is the solution of known strength.

Primary Standard Solution: The solution for which conc. is known is called primary standard solution.

Note: For primary standard solution,

(a) Solute should not be reactive towards solvent or air.

(b) Solute should not be hygroscopic.

(c) Temperature should be constant.

In **acids**, oxalic acid ($H_2C_2O_2.2H_2O$), benzoic acid (C_6H_5COOH), sulphamic acid (HNH_2SO_3), etc. are taken as primary standard solution.

In **bases**, washing soda ($NaCO_3.10H_2O$), borax ($Na_2B_4O_7$), etc are taken as primary standard solution.

In **oxidizing agents**, only potassium dichromate ($K_2Cr_2O_7$) is taken as primary standard solution.

In **reducing agents**, hypo ($Na_2S_2O_3.5H_3O$), Mohr's salt ($FeSO_4.(NH_3)_2SO_4.6H_2O$), sodium oxalate ($Na_2C_2O_4$), etc are taken as primary standard solutions.

End point: End point of titration is normally detected by a sudden change in color of the solution.

Indicator: These compound mixed in the solution in very small amount, which responses the sudden change in color of the solution and show the end point of titration. In acid–base titration, the indicators used are either weak organic acid or weak organic bases. Some examples are

Acidic Indicator: Phenolphthalein, litmus paper etc.

Basic Indicator: Methyl orange, methyl red, etc.

Acid	**Base**	**Indicator**
Strong	Strong	Any
Strong	Weak	Methyl orange, methyl red, etc
Weak	Strong	Phenolphthalein etc

Principle of Titration: Titration means stoichiometry and hence its problems may be solved by mole as well as equivalent concept. But for simplicity equivalent concept is preferred, according to which the number of g-equivalents of all reactants reacted will be equal and the same number of g-equivalents of each products will form. The number of g-equivalents of substances may be determined by using the following formulae:

$$\text{Number of g-equivalents} = \frac{\text{Wt.(in gm)}}{\text{Gm. eq.wt.}} = \frac{VS}{1000} = \frac{\text{Vol. of gas}}{\text{Eq. vol.}} = \text{Mole} \times x - \text{factor}$$

Where, S = strength in normality

Illustration 13: 30 mL of a certain solution of Na_2CO_3 and $NaHCO_3$, required 12 mL of 0.1 N H_2SO_4 using phenolphthalein as indicator. In presence of methyl orange, 30 mL of same solution required 40 mL of 0.1 N H_2SO_4. Calculate the amount of Na_2CO_3 per litre in mixture. **(JEE MAIN)**

Sol: Use titration principles to understand the numerical. Find out the milliequivalents of H_2SO_4 and Na_2CO_3.

Phenolphthalein as indicator:

Meq. of H_2SO_4 used = 12 × 0.1 = 1.2 for 30 mL mixture

$$\therefore \quad \frac{1}{2}\text{ Meq. of } Na_2CO_3 \text{ in 30 mL mixture} = 1.2 \qquad \text{...(i)}$$

Methyl orange as indicator: This time fresh solution is titrated with H_2SO_4 using methyl orange as indicator. By equating the data of the bases with the required acid, solve the milliequivalents and then calculate the strength of the bases.

Meq. of Na_2CO_3 + Meq. of $NaHCO_3$ = Meq. of H_2SO_4 used

= 40 × 0.1 = 4 ...(ii)

By Eq. (i)

Meq. of Na_2CO_3 = 2.4

$$\therefore \quad \frac{w}{53} \times 1000 = 2.4$$

or $\quad w_{Na_2CO_3} = 0.1272 \text{ g in } 30 \text{ mL}$

$\therefore$ Strength of Na_2CO_3 = 4.24 g litre^{-1}

Also, Meq. of $NaHCO_3$ = 4 – 2.4 = 1.6; $\frac{w}{84} \times 1000 = 1.6$

$\therefore \quad w_{NaHCO_3} = 0.1344 \text{ g in } 30 \text{ mL}$

Strength of $NaHCO_3$ $= \frac{0.1344 \times 1000}{30}$ = 4.48 g litre^{-1}

Illustration 14: 0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. Iodine liberated required 150 cm^3 of 0.10N solution of thiosulphate solution for titration.

Find the percentage of $K_2Cr_2O_7$ in the mixture. **(JEE MAIN)**

Solution: Determine the equivalent weight of chromate and permanganate solution and compare the mili. Eq of each components to determine the % of chromate.

Reactions of $K_2Cr_2O_7$ and $KMnO_4$ with KI may be given as :

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow 4K_2SO_4 + Cr_2\left(SO_4\right)_3 + 7H_2O + 3I_2$$
$$2KMnO_4 + 8H_2SO_4 + 10KI \rightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2$$

Thus equivalent wt. of $K_2Cr_2O_7$ = $\frac{294}{6} = 49$

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

m.eq. of $K_2Cr_2O_7$ + m.eq. of $KMnO_4$ = m.eq. of I_2 = m.eq of hypo.

Let the mass of $K_2Cr_2O_7$ = x g

Mass of $KMnO_4$ = (0.5-x)g

$$\frac{x}{49} + \frac{(0.5-x)}{31.6} = 150 \times 0.1 \times 10^{-3} \; x = 0.0732$$

$$\% \text{ of } K_2Cr_2O_7 = \frac{0.0732}{0.5} \times 100 = 14.64$$

4.3 Double Indicators Titration

For the titration of alkali mixtures (e.g., NaOH + Na_2CO_3) or (Na_2CO_3 + $NaHCO_3$), two indicators phenolphthalein and methyl orange are used. This will be discussed in detail in Ionic Equilibrium.

4.4 Eudiometry

Eudiometry or gas analysis involves the calculation based on gaseous reactions in which the amounts of gases are represented by their volumes, measured at STP. Some basic assumptions for calculations

(a) Gay-Lussac's law of volume combination holds good.

(b) For non-reacting mixture. Amagat's law holds good. According to this, the total volume of a non-reacting gaseous mixture is equal to the sum of partial volumes of all the component gases. The volume of solids or liquids is considered to be negligible in comparison to the volumes of gases.

Thus, we can summarize the above points as – eudiometry involves volume measurement during the reaction. Since, Volume of gas, V is directly proportional to number of moles at constant P, T and thus, volume ratio of gases can be directly used in place of mole ratio for analysis.

Illustration 15: A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 litre at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, calculate the mole fraction of C_2H_4 and C_2H_6 in the mixture. **(JEE MAIN)**

Sol: Using the Ideal gas equation, find out no. of moles. Frame the balanced combustion reactions of the hydrocarbons and lay down the values.Calculate the mole fraction accordingly.

For a gaseous mixture of C_2H_6 and C_2H_4

$$PV = nRT$$

$\therefore$ $1 \times 40 = n \times 0.082 \times 400$

Total mole of (C_2H_6 + C_2H_4) = 1.2195

Let mole of C_2H_6 and C_2H_4 be a and b respectively.

$$a + b = 1.2195 \quad \text{...(i)}$$

$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

$\therefore$ Mole of O_2 needed for complete reaction of mixture = 7a/2 + 3b

$$\therefore \quad \frac{7a}{2} + 3b = \frac{130}{32} \quad \text{...(ii)}$$

By Eqs. (i) and (ii), a = 0.808

b = 0.4115

$\therefore$ Mole fraction of C_2H_6 = $\frac{0.808}{1.2195} = 0.66$ and Mole fraction of C_2H_4 = 0.34

4.5 To Represent Concentration of H_2O_2 Solution

(a) **In percentage:** The amount of H_2O_2 present in 100 mL H_2O_2 solution is H_2O_2 concentration in percentage of H_2O_2 solution.

(b) **In volume:** The volume of O_2 at STP given by 1 mL H_2O_2 solution on decomposition is H_2O_2 concentration of H_2O_2 in volume.

Note:

(i) Direct conversions can be made by using following relations

- % strength $= \frac{17}{56} \times$ volume strength
- Volume strength = 5.6 × Normality
- Volume strength = 11.2 × Molarity

(ii) The volume strength of H_2O_2 solution decreases on long standing due to decomposition of H_2O_2 and O_2.

Illustration 16: Report the concentration of 1.5 N solution of H_2O_2 in terms of volume. **(JEE MAIN)**

Sol: From the given equivalent of H_2O_2, calculate the weight and then the volume of O_2. This itself can solve the volume strength of H_2O_2.

$\because$ Equivalent of H_2O_2 in 1 litre solution = 1.5

$\therefore$ $w_{H_2O_2}$ in 1 litre solution $= 1.5 \times \frac{34}{2} = 25.5$ g

$\therefore$ Volume of O_2 obtained by 1000 mL H_2O_2 solution $= \frac{22400 \times 25.5}{68} = 8400$ mL

$\therefore$ Volume strength of H_2O_2 $= \frac{8400}{1000} = 8.4$

4.6 To Represent the Concentration of Oleum

(100 – X%) of oleum means 'X' g H_2O reacts with equivalent amount of free SO_3 to give H_2SO_4.

Illustration 17: 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. The solution requires 26.7 mL of 0.4N NaOH for complete neutralization. Find the % of free SO_3 in the sample of oleum. Also report % of oleum solution.

(JEE ADVANCED)

Sol: Principle of titration is used. Equation of oleum and the base in terms of their milliequivalents is done wherein the amount of oleum is found. % of SO_3 is thus found. Reaction of SO_3 with H_2O gives H_2SO_4. Lay down the calculated and the given values and solve the % of oleum.

Fuming H_2SO_4 contains H_2SO_4 and SO_3. Both react with NaOH. Let a g and b g SO_3 be present.

For reaction, $\therefore$ Meq. of H_2SO_4 + Meq. of SO_3 = Meq. of NaOH; $\frac{a}{98/2} \times 1000 + \frac{b}{80/2} \times 1000 = 26.7 \times 0.4$

$\therefore$ $80a + 98b = 41.87$ ...(i)

Also, $a + b = 0.5$ ...(ii)

$\therefore$ % of SO_3 $= \frac{0.1039}{0.5} \times 100 = 20.78\%$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

80 g SO_3 = 18 g H_2O

$\therefore$ 20.78 g SO_3 $= \frac{18 \times 20.78}{80} = 4.68$

% of oleum = 100 + 4.68 = 104.68%

4.7 To Determine Hardness of Water

Water, which gives foams easily with soap is called soft water and if not then hard water. The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of Ca and Mg. The extent of hardness is known as **degree of hardness** defined usually as the no. of parts by weight of $CaCO_3$ present per million parts by weight of water. Hardness is expressed in ppm i.e., 1 ppm = 1 part of $CaCO_3$ in 10^6 part of hard water.

Note: The reason for choosing $CaCO_3$ as the standard to express hardness, inspite of the fact that $CaCO_3$ is not soluble in water but its molecular weight is 100 which makes calculation easy.

4.8 Mass Balance Equations

The principle of mass balance is based on the law of conservation of mass, i.e., the number of atoms of an element remains constant in a chemical reaction.

4.9 Charge Balance Equations

The principle of charge balance equations is based on the principle of electroneutrality, i.e., all solution are electrically neutral since sum of positive charges equals the sum of negative charges.

4.10 Saponification Value

It is the amount of KOH in mg required to neutralize a fatty acid obtained by the hydrolysis of 1 g of oil.

REDOX REACTIONS

1. INTRODUCTION

Molecular Equations: $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

The reactants and products have been written in molecular forms; thus, the equation is termed as **molecular equation**.

Ionic Equations: The reactions in which the reactants and products are present in the form of ions are called **ionic reactions**.

For example: $2Fe^{3+} + 6Cl^- + Sn^{2+} + 2Cl^- \rightarrow 2Fe^{2+} + 4Cl^- + Sn^{4+} + 4Cl^-$

Or $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$

Illustration 18: Represent the following equation in ionic form. **(JEE MAIN)**

$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7H_2O + K_2SO_4$

Sol: Knowing the oxidation numbers of the elements present, balanced ionic form can be represented. In this equation except H_2O, all are ionic in nature. Representing these compounds in ionic forms,

$$2K^+ + Cr_2O_7^{2-} + 14H^+ + 7SO_4^{2-} + 6Fe^{2+} + 6SO_4^{2-} \longrightarrow$$

$$6Fe^{3+} + 9SO_4^{2-} + 2Cr^{3+} + 3SO_4^{2-} + 2K^+ + SO_4^{2-} + 7H_2O$$

$2K^+$ ions and $13SO_4^{2-}$ ions are common on both sides, so these are cancelled. The desired ionic equation reduces to, $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2-} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

Phenomenon of Oxidation and Reduction:

Oxidation or de-electronation is a process which liberates electrons.

Reduction or electronation is a process which gains electrons.

Oxidation	Reduction
a. $M \longrightarrow M^{n+} + ne^-$	$M^{n+} + ne^- \longrightarrow M$
b. $M^{n_1+} \longrightarrow M^{n_2+} + (n_2 - n_1)e^- \quad (n_2 > n_1)$	$M^{n_2+} + (n_2 - n_1)e^- \longrightarrow M^{n_1+} \quad (n_2 > n_1)$
c. $A^{n-} \longrightarrow A + ne^-$	$A + ne^- \longrightarrow A^{n-}$
d. $A^{n_1-} \longrightarrow A^{n_2-} + (n_1 - n_2)e^-$	$A^{n_2^-} + (n_1 - n_2)e^- \longrightarrow A^{n_2^-}$

Note: M may be an atom or a group of atoms; A may be atom or a group of atoms.

Oxidizing and Reducing Agent:

(a) If an element is in its highest possible oxidation state in a compound, it can function as an oxidizing agent, e.g. $KMnO_4, K_2Cr_2O_7, HNO_3, H_2SO_4, HClO_4$ etc.

(b) If an element is in its lowest possible oxidation state in a compound, it can function as a reducing agent, e.g. H_2S, $FeSO_4, Na_2S_2O_3, SnCl_2$ etc.

(c) If an element is in its intermediate oxidation state in a compound, it can function both as an oxidizing agent as well as reducing agent, e.g. $H_2O_2, H_2SO_3, HNO_3, SO_2$ etc.

(d) If highly electronegative element is in its higher oxidation state in a compound, that compound can function as a powerful oxidizing agent, e.g. $KClO_4, KClO_3, KIO_3$ etc.

(e) If an electronegative element is in its lowest possible oxidation state in a compound or in free state, it can function as a powerful reducing agent, e.g. I^-, Br^-, N_3^- etc.

2. MODERN CONCEPT OF OXIDATION AND REDUCTION

According to the modern concept, loss of electrons is oxidation whereas gain of electrons is reduction. Oxidation and reduction can be represented in a general way as shown below:

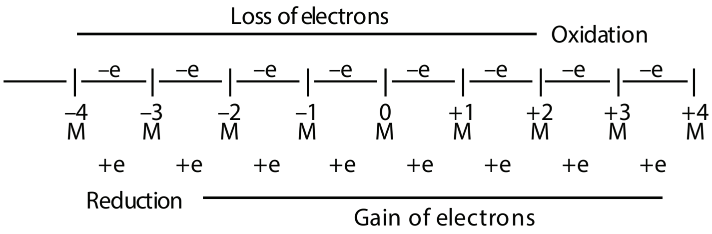


Figure 1.1: Oxidation and Reduction

MASTERJEE CONCEPTS

- In a redox process the valency of the involved species changes. The valency of a reducing agent increases while the valency of an oxidising agent decreases in a redox reaction. The valency of a free element is taken as zero.
- Redox reaction involves two half reactions, one involving loss of electron or electrons (oxidation) and the other involving gain of electron or electrons (reduction).

Saurabh Gupta (JEE 2010, AIR 443)

3. ION ELECTRON METHOD FOR BALANCING REDOX REACTIONS

This method involves the following steps:

(a) Divide the complete equations into two half reactions

- **(i)** One representing oxidation
- **(ii)** The other representing reduction

(b) Balance the atoms in each half reaction seperately according to the following steps

- **(i)** Balance all atoms other than oxygen and hydrogen
- **(ii)** To balance oxygen and hydrogen

(c) **Acidic Medium**

- **(i)** Add H_2O to the side which is oxygen deficient to balance oxygen atoms
- **(ii)** Add H^+ to the side which is hydrogen deficient to balance H atoms

(d) Basic Medium

- **(i)** Add OH^- to the side which has less negative charge
- **(ii)** Add H_2O to the side which is oxygen deficient to balance oxygen atoms
- **(iii)** Add H^+ to the side which is hydrogen deficient

Illustration 19: $H_2C_2O_4 + KMnO_4 \longrightarrow CO_2 + K_2O + MnO + H_2O$ **(JEE MAIN)**

Sol:

Step 1: Select the oxidant, reductant atoms and write their half reactions, one representing oxidation and other reduction. i.e., $C_2^{+3} \longrightarrow 2C^{+4} + 2e^-$

$$5e^- + Mn^{+7} \longrightarrow Mn^{+2}$$

Step 2: Balance the no. of electrons and add the two equation.

$$5C_2^{+3} \longrightarrow 10C^{+4} + 10e^-$$

$$\begin{array}{c} 10e^- + 2Mn^{+7} \longrightarrow 2Mn^{+3} \\ \hline 5C_2^{+3} + 2Mn^{+7} \longrightarrow 10C^{+4} + 2Mn^{+2} \end{array}$$

Step 3: Write complete molecule of the reductant and oxidant from which respective redox atoms were obtained.

$$5H_2C_2O_4 + 2KMnO_4 \longrightarrow 10CO_2 + 2MnO$$

Step 4: Balance other atoms if any (except H and O).

In above example K is unbalanced, therefore,

$$5H_2C_2O_4 + 2KMnO_4 \longrightarrow 10CO_2 + 2MnO + K_2O \text{ (Mentioned as product)}$$

Step 5: Balance O atom using H_2O on desired side.

$$5H_2C_2O_4 + 2KMnO_4 \longrightarrow 10CO_2 + 2MnO + H_2O + 5H_2O$$

4. OXIDATION STATE AND OXIDATION NUMBER

4.1 Oxidation State

It is defined as the charge (real or imaginary) which an atom appears to have when it is in combination. In the case of electrovalent compounds, the oxidation number of an element or radical is the same as the charge on the ion.

4.2 Oxidation Number

- **(a)** Oxidation number of an element in a particular compound represents the number of electrons lost or gained by an element during its change from free state into that compound or Oxidation number of an element in a particular compound represent the extent of oxidation or reduction of an element during its change from free state into that compound.
- **(b)** Oxidation number is given positive sign if electrons are lost. Oxidation number is given negative sign if electrons are gained.
- **(c)** Oxidation number represent real change in case of ionic compounds. However, in covalent compounds it represents imaginary charge.

Rules for Calculation of Oxidation Number:

Following rules have been arbitrarily adopted to decide oxidation number of elements on the basis of their periodic properties.

(a) In uncombined state or free state, oxidation number of an element is zero.

(b) In combined state oxidation number of-

- **(i)** F is always –1.
- **(ii)** O is –2. In peroxide it is –1, in superoxides it is –1/2. However in F_2O it is +2.
- **(iii)** H is +1. In ionic hydrides it is –1. (i.e., IA, IIA and IIIA metals).
- **(iv)** Halogens as halide is always –1.
- **(v)** Sulphur as sulphide is always –2.
- **(vi)** Metal is always +ve.
- **(vii)** Alkali metals (i.e., IA group – Li, Na, K, Rb, Cs, Fr) is always +1.
- **(viii)** Alkaline earth metals (i.e., IIA group – Be, Mg, Ca, Sr, Ba, Ra) is always +2.

(c) The algebraic sum of the oxidation number of all the atoms in a compound is equal to zero. e.g. $KMnO_4$.

Ox. no. of K + Ox. no. of Mn + (Ox. no. of O) × 4 = 0

$(+1) + (+7) + 4x(-2) = 0$

(d) The algebraic sum of all the oxidation no. of elements in a radical is equal to the net charge on the radical. e.g. CO_3^{-2}.

Oxidation no. of C + 3 × (Oxidation no. of O) = –2(4) + 3x (–2) = –2

(e) Oxidation number can be zero, +ve, –ve (integer or fraction)

(f) Maximum oxidation no. of an element is = Group no. (Except O and F)

Minimum oxidation no. of an element is = Group no. –8 (Except metals)

Redox reactions involve oxidation and reduction both. Oxidation means loss of electrons and reduction means gain of electrons. Thus redox reactions involve electron transfer and the number of electrons lost are same as the number of electrons gained during the reaction. This aspect of redox reaction can serve as the basis of a pattern for balancing redox reactions.

Oxidation number of Mn in $KMnO_4$: Let the oxidation number of Mn be x. Now we know that the oxidation numbers of K is +1 and that of O is –2.

$$\begin{array}{ccc} K & Mn & O_4 \\ +1 & +x & +4\times -2 \end{array} \quad \text{or} \quad \begin{array}{ccc} K & Mn & O_4 \\ +1 & +x & -8 \end{array}$$

Now to the sum of oxidation numbers of all atoms in the formula of the compound must be zero, i.e. +1 +x – 8 = 0. Hence, the oxidation number of Mn in $KMnO_4$ is +7.

Illustration 20: What is the oxidation number of Cr in $K_2Cr_2O_7$? **(JEE MAIN)**

Sol: Let the Ox. no. of Cr in $K_2Cr_2O_7$ be x.

We know that, Ox. no. of K = +1

Ox. no. of O = –2

So, 2(Ox. no. K) + 2(Ox. no. Cr) + 7(Ox. no. O) = 0

$$2(+1) \quad 2(x) \quad 7(-2) \quad = 0$$

or $$+2 + 2x - 14 = 0$$

or $2x = +14 - 2 = +12$

or $x = +\frac{12}{2} = +6$ Hence, oxidation number of Cr in is +6.

Illustration 21: H_2S act only as reductant, whereas SO_2 acts as oxidant and reductant both. **(JEE ADVANCED)**

Sol: Oxidation number of S is –2 in H_2S. It can increase only oxidation number up to +6.

Oxidation number of S is +4 in SO_2. It can increase or decrease as it lies between maximum (+6) and minimum (–2) oxidation number of S.

Illustration 22: Which compound amongst the following has the highest oxidation number of Mn? $KMnO_4$, K_2MnO_4, MnO_2 and Mn_2O_3. **(JEE MAIN)**

Sol:

		Ox. no. of Mn
$KMnO_4$	+1+x-8=0 x=+7	+7
K_2MnO_4	+2+x-8=0 x=+6	+6
MnO_2	x-4=0 x=+4	+4
Mn_2O_3	2x-6=0 x=+3	+3

Thus, the highest oxidation number for Mn is in $KMnO_4$.

4.3 Balancing of Redox Reactions by Oxidation State Method

This method is based on the fact that the number of electrons gained during reduction must be equal to the number of electrons lost during oxidation. Following steps must be followed while balancing redox equations by this method.

(a) Write the skeleton equation (if not given, frame it) representing the chemical change.

(b) With the help of oxidation number of elements, find out which atom is undergoing oxidation/reduction, and white separate equations for the atom undergoing oxidation/reduction.

(c) Add the respective electrons on the right for oxidation and on the left for reduction equation. Note that the net charge on the left and right side should be equal.

(d) Multiply the oxidation and reduction reactions by suitable integers so that total electrons lost in one reaction is equal to the total electrons gained by other reaction.

(e) Transfer the coefficients of the oxidizing and reducing agents and their products as determined in the above step to the concerned molecule or ion.

(f) By inspection, supply the proper coefficient for the other formulae of substances not undergoing oxidation and reduction to balance the equation.

Illustration 23: $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow Cr^{3+} + I_2$ **(JEE MAIN)**

Sol: (i) Find the oxidation state of atoms undergoing redox change

$$\overset{+6x2}{Cr_2}\,O_7^{2-} + \overset{-1}{I^-} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{0}{I_2}$$

(ii) Balance the number of atoms undergoing redox change.

$$\overset{(+6)x2}{Cr_2}\,O_7^{2-} + \overset{2x(-1)}{2I^-} \longrightarrow \overset{(+3)x2}{2Cr^{3+}} + \overset{0x2}{I_2}$$

(iii) Find the change in oxidation state and balance the change in oxidation states by multiplying the species with a suitable integer.

$$\overset{+12}{Cr_2}O_7^{2-} + \overset{-2}{2I^-} \longrightarrow \overset{+6}{2Cr^{3+}} + \overset{0}{I_2}$$

Change in ox. state = 6　　Change in ox. state = 2×3

As the decrease in oxidation state if chromium is 6 and increase in oxidation state of iodine is 2, so we will have to multiply I^- / I_2 by 3 equalize the changes in oxidation state.

$$Cr_2O_7^{2-} + 6I^- \longrightarrow 2Cr^{3+} + 3I_2$$

(iv) Find the total charges on both the sides and also find the difference of charges.

Charge on LHS $= -2 + 6 \times (-1) = -8$

Charge on RHS $= 2 \times (+3) = +6$

Difference in charge $= +6 - (-8) = 14$

(v) Now, as the reaction is taking place in acidic medium, we will have to add the ions, to H^+ the side falling short in positive charges, so we will add $14H^+$ and LHs to equalize the charges on both sides.

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2$$

(vi) To equalize the H and O atoms, add $7H_2O$ on RHS

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

Illustration 24: Balance the following equation by oxidation number method:

$$Cl_2 + IO_3^- + OH^- \longrightarrow IO_4^- + Cl^- + H_2O$$

(JEE ADVANCED)

Sol: Writing oxidation numbers of all atoms,

$$\overset{0}{Cl_2} + \overset{+5}{I}\,\overset{-2}{O_3^-} + \overset{-2}{O}\,\overset{+1}{H^-} \longrightarrow \overset{+7}{I}\,\overset{-2}{O_4^-} + \overset{-1}{Cl^-} + \overset{+1}{H_2}\,\overset{-2}{O}$$

Oxidation numbers of Cl and I have changed.

$$\overset{0}{Cl_2} \longrightarrow 2\overset{-1}{Cl^-} \quad ...(i)$$

$$\overset{+5}{I}O_3^- \longrightarrow \overset{+7}{I}O_4^- \quad ...(ii)$$

Decrease in Ox. no. of Cl = 2 units per Cl_2 molecule

Increase in Ox. no. of I = 2 units per IO_3^- molecule

$$Cl_2 + IO_3^- \longrightarrow IO_4^- + 2Cl^-$$

To balance oxygen, $2OH^-$ ions be added on LHS and one H_2O molecule on RHS. Hence, the balanced equation is

$$Cl_2 + IO_3^- + 2OH^- \longrightarrow IO_4^- + 2Cl^- + H_2O$$

5. TYPES OF REACTIONS

The redox reactions are of the following types:

(a) Combination reactions: A compound is formed by chemical combination of two or more elements. The combination of an element or compound with oxygen is called combustion. The combustion and several other combinations which involve change in oxidation state are called redox reactions.

e.g.,

$$\overset{-4}{C}\overset{+1}{H}_4 + 2\overset{0}{O}_2 \longrightarrow \overset{+4}{C}\overset{-2}{O}_2 + 2\overset{+1}{H}_2\overset{-2}{O}$$

$$\overset{0}{C}(s) + \overset{0}{O}_2(g) \longrightarrow \overset{+4}{C}\overset{-2}{O}_2(g)$$

$$3\overset{0}{Mg} + \overset{0}{N}_2 \longrightarrow \overset{+2}{Mg}_3\overset{-3}{N}_2$$

$$\overset{0}{H}_2 + \overset{0}{Cl}_2 \longrightarrow 2\overset{+1}{H}\overset{-1}{Cl}$$

(b) Decomposition reactions: Decomposition is the reverse process of combination, it involves the breakdown of the compound into two or more components. The product of decomposition must contain at least one component in elemental state.

e.g.,

$$2\overset{+1}{H}_2\overset{-2}{O}(g) \xrightarrow{\Delta} 2\overset{0}{H}_2(g) + \overset{0}{O}_2(g);$$

$$2NaH(s) \xrightarrow{\Delta} 2\overset{0}{Na}(s) + \overset{0}{H}_2(g)$$

$$2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O}_3(s) \longrightarrow 2\overset{+1}{K}\overset{-1}{Cl} + 3\overset{0}{O}_2(g)$$

In above example, there is no change in oxidation state of potassium. Thus, it should be noted that the decomposition does not result into change in the oxidation number of each element.

(c) Displacement reactions: The reactions in which an atom or ion in a compound is displaced by another atom or ion are called displacement reactions. The displacement reactions are of 2 types:

(i) Metal displacement: In these reactions, a metal in a compound is replace by another metal in an uncombined state. It is found that a metal with stronger reducing character can displace the other metal having a weaker reducing character.

e.g.,

$$\overset{+3}{Cr}_2\overset{-2}{O}_3 + 2\overset{0}{Al}(s) \longrightarrow \overset{+3}{Al}_2\overset{-2}{O}_3(s) + 2\overset{0}{Cr}(s)$$

$$\overset{+2}{Cu}\overset{+6}{S}\overset{-2}{O}_4 + \overset{0}{Zn}(s) \longrightarrow \overset{+2}{Zn}\overset{+6}{S}\overset{-2}{O}_4(aq) + \overset{0}{Cu}(s)$$

(ii) Non-metal displacement: These displacement reactions generally involve redox reactions, where the hydrogen is displaced. Alkali and alkaline earth metals are highly electropositive, they displace hydrogen from cold water.

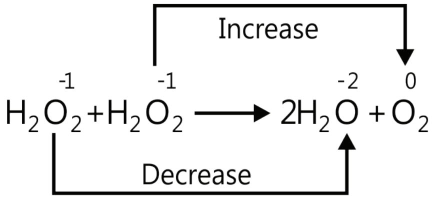
$$2\overset{0}{Na}(s) + 2\overset{+1}{H}_2\overset{-2}{O}(l) \longrightarrow 2\overset{+1}{Na}\overset{-2}{O}\overset{+1}{H}(aq) + \overset{0}{H}_2(g)$$

$$\overset{0}{Ca}(s) + 2\overset{+1}{H}_2\overset{-2}{O}(l) \longrightarrow \overset{+1}{Ca}(\overset{-2}{O}\overset{+1}{H})_2(aq) + \overset{0}{H}_2(g)$$

(d) Disproportionation and Oxidation–Reduction: One and the same substance may act simultaneously as an oxidizing agent with the result that a part of it gets oxidized to a higher state and rest of it is reduced to lower state of oxidation. Such a reaction, in which a substance undergoes simultaneous oxidation and reduction is called disproportionation and the substance is said to **disproportionate**.

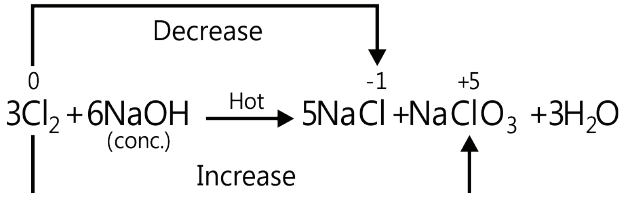
The following are some of the examples of disproportionation:

(a)



$$\overset{-1}{H_2O_2} + \overset{-1}{H_2O_2} \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O_2}$$

(b)



$$3\overset{0}{Cl_2} + \underset{\text{(conc.)}}{6NaOH} \xrightarrow{\text{Hot}} 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$$

(e) Oxidation state of chlorine lies between –1 to +7; thus out of ClO^-, ClO_2^-, ClO_3, ClO_4^-; ClO_4^- does not undergo disproportionation because in this oxidation state of chlorine is highest, i.e., +7. Disproportionation of the other oxoanions are:

$$3\overset{+1}{Cl}O^- \longrightarrow 2\overset{-1}{Cl} + \overset{+5}{Cl}O_3^-$$

$$6\overset{+3}{Cl}O_2^- \longrightarrow 4\overset{+5}{Cl}O_3^- + 2\overset{-1}{Cl^-}\ ; \qquad 4\overset{+5}{Cl}O_3^- \longrightarrow \overset{-1}{Cl^-} + 3\overset{+7}{Cl}O_4^-$$