CHEMICAL REACTIONS AND EQUATIONS

LAWS OF CHEMICAL COMBINATION

In order to understand the composition of the compounds, it is necessary to have a theory which accounts for both qualitative and quantitative observations during chemical change. These observations of chemical reactions were most significant in the development of a satisfactory theory of the nature of matter. These observations of chemical reactions are summarized in certain statements known as laws of chemical combination.

1. **Law of Conservation of Mass**

In simple terms, this law states that matter can neither be created nor destroyed. In other words, the total mass, that is, the sum of the total mass of reacting mixture and the products formed remains constant. Antoine Lavoisier gave this law in the year 1789 based on the data he obtained after carefully studying numerous combustion reactions.

$$C_3H_8 + 5O_2 \rightarrow 4H_2O + 3CO_2$$

The mass of C_3H_8 (propane) 44 and that of O_2 is 160. The total mass of the reactants is equal to 204.
The mass of H_2O is 72 and that of CO_2 is 132. The total mass of the products is 204. Since the masses of reactants and of products are same the mass is conserved in this reaction. To prove that the mass of the substances be conserved the chemical equations have to be balanced.

2. **Law of Definite Proportions**

Joseph Proust, a French chemist stated that the proportion of elements by weight in a given compound will always remain exactly the same. In simple terms we can say that, irrespective of its source, origin or its quantity, the percent composition of elements by weight in a given compound will always remain the same.

- 2 atoms of hydrogen combine with 1 atom of oxygen in water.

3. **Law of Multiple Proportions**

This law states that if two elements combine to form more than one compound, the masses of these elements in the reaction are in the ratio of small whole numbers. This law was given by Dalton in the year 1803.

- Carbon monoxide (CO): 12 parts by mass of carbon combines with 16 parts by mass of oxygen.
- Carbon dioxide (CO_2): 12 parts by mass of carbon combines with 32 parts by mass of oxygen.

Ratio of the masses of oxygen that combines with a fixed mass of carbon (12 parts): 16:32 or 1:2
Hydrogen and oxygen are known to form 2 compounds. The hydrogen content in one is 5.93%, and that of the other is 11.2%. Show that this data illustrates the law of multiple proportions.

SOLUTION

In the first compound: hydrogen = 5.93%
Oxygen = (100 –5.93) = 94.07%
In the first compound the number of parts of oxygen that combine with one part by mass of hydrogen $\frac{94.07}{5.93} = 15.86$ parts

In the second compound: hydrogen = 11.2%
Oxygen = (100 –11.2) = 88.88%
In the second compound the number of parts of oxygen that combine with one part by mass of hydrogen $\frac{88.8}{11.2} = 7.9$ parts.

Ratio of the masses of oxygen that combine with fixed mass of hydrogen: 15.86:7.9 or 2:1. This is consistent with the law of multiple proportions.

4. **Gay Lussac's Law of Gaseous Volumes**

In 1808, Gay–Lussac gave this law based on his observations. This law states that when gases are produced or combine in a chemical reaction, they do so in simple ratio by volume given that all the gases are at same temperature and pressure. This law can be considered as another form of law of definite proportions. The only difference between these two laws of chemical combination is that Gay–Lussac's Law is stated with respect to volume while law of definite proportions is stated with respect to mass.

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

1 vol. 3 vols. 2 vols.

1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia.

TYPES OF CHEMICAL CHANGES:

Chemical reactions and chemical changes are divided into four types depending on the nature of the substance.

1. Chemical combination (or) synthesis reaction
2. Chemical decomposition
3. Chemical displacement
4. Chemical double decomposition (or) precipitation reaction

1. Chemical combination

The chemical change in which two (or) more elements (or) compounds combine to form a new substance is called "chemical combination"

Examples:

(i) Magnesium burns in air with dazzling light; it gives white ash called Magnesium oxide.

$$\underset{\text{Magnesium}}{2Mg} + \underset{\text{Oxygen}}{O_2} \rightarrow \underset{\text{Magnesium oxide}}{2MgO}$$

(ii) When a glass rod dipped in concentrated hydrochloric acid is kept at the mouth of ammonia gas jar then White dense fumes of NH_4Cl will be formed.

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrochloric acid}}{HCl} \rightarrow \underset{\text{Ammonium Chloride}}{NH_4Cl}$$

(iii) Calcium oxide combines with water to form calcium hydroxide.

$$\underset{\text{Calcium oxide}}{CaO} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Calcium hydroxide}}{Ca(OH)_2} .$$

Note: CaO is called quick lime.
$Ca(OH)_2$ is called slaked lime.

Other examples of chemical combination are

(1) $2Na + Cl_2 \rightarrow 2NaCl$
(2) $N_2 + 3H_2 \rightarrow 2NH_3 \uparrow$
(3) $S + O_2 \rightarrow SO_2 \uparrow$

2. Chemical decomposition:

The chemical change in which compound splits into two (or) more substances which may be either elements or compounds is called "chemical decomposition".

Examples:

(i) When lead nitrate is heated in a dry test tube, a reddish brown gas of nitrogen dioxide is evolved along with oxygen gas. A pale yellow substance which is lead oxide is left in the test tube.

$$\underset{\text{Lead Nitrate}}{2Pb(NO_3)_2} \longrightarrow \underset{\text{Nitrogen dioxide}}{4NO_2} \uparrow + \underset{\text{Oxygen}}{O_2} \uparrow + \underset{\text{Lead Oxide}}{2PbO}$$

(ii) Calcium carbonate on heating gives rise to two new substances, calcium oxide and carbon dioxide. These substances are also compounds. The properties of these two substances differ from those of calcium carbonate.

$$\underset{\text{calcium carboante}}{CaCO_3} \longrightarrow \underset{\text{Calcium oxide}}{CaO} + \underset{\text{Carbon dioxide}}{CO_2}$$

Other examples of chemical decomposition are:

$2NaNO_3 \rightarrow 2NaNO_2 + O_2 \uparrow$
$2HgO \rightarrow 2Hg + O_2 \uparrow$
$CuCO_3 \rightarrow CuO + CO_2 \uparrow$
$2KNO_3 \rightarrow 2KNO_2 + O_2 \uparrow$
$2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow$

3. Chemical displacement:

The reaction in which an element displaces another element from its compound and occupies its place forming a new compound is called chemical displacement.

Examples:

(i) Zinc displaces hydrogen gas when treated with dilute acids.

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Hydrogen chloride}}{2HCl} \longrightarrow \underset{\text{Zinc chloride}}{ZnCl_2} + \underset{\text{Hydrogen}}{H_2} \uparrow$$

(ii) When Zinc metal is added to copper sulphate solution. Zinc displaces copper from copper sulphate solution. Blue coloured solution turns colourless and red colour copper is deposited.

$$\underset{\substack{\text{copper sulphate}\\ \text{(Blue)}}}{CuSO_4} + \underset{\text{Zinc}}{Zn} \longrightarrow \underset{\substack{\text{Zinc sulphate}\\ \text{(colourless)}}}{ZnSO_4} + \underset{\substack{\text{Copper}\\ \text{(Red)}}}{Cu}$$

Other examples of chemical displacement are:

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

$Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$

$Br_2 + 2KI \rightarrow 2KBr + I_2$

$Mg + 2AgNO_3 \rightarrow Mg(NO_3)_2 + 2Ag$

4. Chemical double decomposition:

When solutions of two salts are mixed, there will be mutual exchange of radicals resulting in the formation of two new compounds. Such chemical reactions are called "chemical double decomposition".

Examples:

(i) When silver nitrate ($AgNO_3$) solution is added with sodium chloride solution, here the constituents of two compounds get mutually exchanged. So silver chloride and sodium nitrate solution will be formed.

$$\underset{\text{Silver Nitrate}}{AgNO_3} + \underset{\text{Sodium chloride}}{NaCl} \rightarrow \underset{\text{Silver chloride}}{AgCl} \downarrow + \underset{\text{Sodium Nitrate}}{NaNO_3}$$

(ii) When barium chloride solution is added to a solution of sodium sulphate in a test tube, white precipitate of Barium sulphate will be formed. Here barium and sodium exchange their ions to give two new compounds hence it is example of double decomposition.

$$\underset{\text{Barium chloride}}{BaCl_2} + \underset{\text{Sodium sulphate}}{Na_2SO_4} \longrightarrow \underset{\text{Barium Sulphate}}{BaSO_4} \downarrow + \underset{\text{Sodium Chloride}}{2NaCl}$$

Other examples of double decomposition are:

$2KI + Pb(NO_3)_2 \rightarrow PbI_2 + 2KNO_3$

$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$

Oxidation: The term "oxidation" means addition of oxygen (or) removal of hydrogen.

We can define oxidation in terms of electrons as loss of electrons, loss of electrons is called oxidation.

In terms of oxidation state: Increase in positive charge is called oxidation.

Reduction: The term "reduction" means addition of hydrogen (or) removal of oxygen.

We can define oxidation in terms electrons i.e., gain of electrons also.

OIL	**RIG**
Oxidation **I**s **L**oss of electrons	**R**eduction **I**s **G**ain of electrons

Redox reactions

In a chemical reaction if oxidation and reduction occur simultaneously such reactions are called redox reactions, and the substance which gains electrons is termed the oxidizing agent, and the substance which looses electrons is called reducing agent

E.g.: $Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$

In the above reaction two electrons (negative charges) are transferred from the iron atom to the copper atom; thus the iron becomes positively charged (is oxidized) by loss of two electrons while the copper receives the two electrons and becomes neutral (is reduced).

Oxidation Number

Oxidation number (or oxidation state) of an element may be defined as the charge which an atom of an element has in its ion or appears to have when present in the combined state with other atoms. Oxidation number is also known as oxidation state and defined the state of oxidation of an element in that compound.

To determine the oxidation number of an atom in an ion or a molecule, the following set of rules has been formulated.

1. The oxidation number of all atoms of different elements in their respective elementary states and allotropic forms is taken as zero.
   Example: Hydrogen exists as H_2, oxygen exists as O_2, O_3. Phosphorous exists as P_4, sulphur as S_8 molecule, carbon exists as graphite, diamond etc. They have the oxidation state equal to zero.
2. The oxidation number of hydrogen is $+1$ when it forms compounds with non–metals and -1 with metals i.e. metal hydrides.
   Example: In HCl, HNO_3, H_2S etc the oxidation number of hydrogen is taken as $+1$
   In NaH, MgH_2, AlH_3 the oxidation state of hydrogen is -1.
3. The oxidation number of alkali metals (group 1) and alkaline earth metals (group 2) is $+1$ and $+2$ respectively.
4. The oxidation number of oxygen is -2 in most of the compounds. In peroxides such as H_2O_2, BaO_2, Na_2O_2, it is -1 and in super oxides like KO_2 the oxidation state of oxygen is $-\frac{1}{2}$ oxygen exhibits positive charge when it combines with fluorine. Ex: OF_2.
5. The most electronegative atom Fluorine exhibits an oxidation state of -1 in all its compounds, while other halogens (Cl, Br, I) exhibit -1 only in halides and exhibit, variable positive oxidation states in other compounds like ClO_2, $HClO_3$ etc.
6. The sum of the oxidation state in a molecule is equal to zero and that of ion is equal to its charge. Example: In H_2SO_4, the sum of oxidation states of all the elements put together is equal to zero.
   In SO_4^{-2}; the sum of oxidation states of all the elements put together is equal to its charge – 2.
7. In general metals have positive oxidation states and non–metals have negative oxidation. Using the known oxidation states, the oxidation state of unknown is calculated.
8. The oxidation state of representative elements should not exceed the group number. For example, sulphur belongs to VI group so its oxidation state should not exceed $+6$.

Summarizing the above rules:

RULES FOR ASSIGNING OXIDATION NUMBERS	
ELEMENTAL FORM	Since only one kind of atoms are present. There is no difference in their electronegavities; the cumulative oxidation number will be equal to zero.
ATOMIC IONS	Equal to the charge on the ion – Na^{+}, Mg^{+2}, Al^{+3}, etc.
GROUP 1A **Li, Na, K, Rb, Cs**	Always +1
GROUP 2A **Be, Mg, Ca, Sr, Ba**	Always +2
HYDROGEN	+1 when bonded with non–metals, –1 when bonded with metals
OXYGEN	–1 in peroxides (O_2^{-2}), in all other compounds as oxides (O^{-2}), when bonded with fluorine it exhibits +2
FLUORINE	Always –1
NEUTRAL COMPOUNDS	The sum of all oxidation numbers of atoms or ions in a neutral compound is equal to zero.
IONIC COMPOUNDS	The sum of all oxidation numbers of atoms or ions in an ionic compound is equal to the charge on the polyatomic ion.

If the oxidation state of element exceeds the group number, peroxy linkage exists.
Let's work at these examples

1. Calculate the oxidation state of the underlined element
   i) : $H\underline{N}O_3$ The oxidation state of $H = +1$ as it is combining with non–metals; 0 = –2
   $H\underline{N}O_3$

$+1+x+-2(3)=0$
$+1+x+-6=0$
$x=+5$
So the oxidation state of nitrogen = 5.
ii) $H\underline{N}O_4$
$+1+x+-2(4)=0$
$+1+x-8=0$
$x=+7$
As nitrogen belongs to V group or 15^{th} group its oxidation state should not exceed $+5$. We need to calculate assuming there is peroxy linkage so for two of oxygen atoms the oxidation state is taken as -1.
$H\underline{N}O_4$
$+1+x+(-2)\times 2+(-1)\times 2=0$
$+1+x-6=0$
$x=+5$
This shows that HNO_4 (per nitric acid) has one peroxy bond.
iii) $\underline{S}O_4^{-2}$
$x+(-2)\times 4=-2$
$x-8=-2$
$x=-2+8=\pm 6$
Oxidation number of s in SO_4^{2-} is $+6$.

The number of electrons that must be added to or subtracted from an atom in a combined state to convert it to the elemental form; i.e., in calcium chloride ($CaCl_2$) the oxidation number of Ca is +2 and of Cl is –1.Many elements can exist in more than one oxidation state. It is dependent on periodic table group number.

Oxidation Number Method

During a redox reaction, the total increase in oxidation number must be equal to total decrease in oxidation number. This is the basic principle for balancing chemical equations. In addition, the number of atoms of each kind on one side of the equation must be equal to the number of atoms of the corresponding elements on the other side (the law of conservation of mass should not be violated). The following steps should be followed:

Steps for balancing redox equations by oxidation number method

♦ **First step:** Write the skeleton redox reaction.
♦ **Second step:** Indicate the oxidation number of atoms in each compound above the symbol of the element.
♦ **Third step:** Identify the element or elements, which undergo a change in oxidation number, one whose oxidation number increases (reducing agent) and the other whose oxidation number decreases (oxidizing agent).
♦ **Fourth step:** Calculate the increase or decrease in oxidation numbers per atom. Multiply this number of increase/decrease of oxidation number, with the number of atoms, which are undergoing change.
♦ **Fifth step:** Equate the increase in oxidation number with decrease in oxidation number on the reactant side by multiplying the formulae of the oxidizing and reducing agents.
♦ **Sixth step:** Balance the equation with respect to all other atoms except hydrogen and oxygen.
♦ **Seventh step:** Finally, balance hydrogen and oxygen.
♦ **Eighth step:** For reactions taking place in acidic solutions, add H^+ ions to the side deficient in hydrogen atoms.
♦ **Ninth step:** For reactions taking place in basic solutions, add H_2O molecules to the side deficient in hydrogen atoms and simultaneously add equal number to OH^- ions on the other side of the equation.

Illustration 16: **Zinc metal reacts with hydrochloric acid to produce zinc chloride and hydrogen gas.**
Solution: **Step: 1** The skeleton equation is:

$$Zn + HCl \longrightarrow ZnCl_2 + H_2$$

Step: 2 Oxidation number of various atoms involved in the reaction

$$\overset{0}{Zn} + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Zn}\ \overset{-1}{Cl_2} + \overset{0}{H_2}$$

Step: 3 The oxidation number of zinc has increased from 0 to +2 while that of hydrogen has decreased from +1 to 0. However, the oxidation number of chlorine remains same on both sides of the equation. Therefore, zinc is reducing agent while HCl is oxidizing agent in reaction and the changes are shown as:

$$\overset{0}{Zn} + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Zn}\,\overset{-1}{Cl_2} + \overset{0}{H_2}$$

Step: 4 The increase and decrease in oxidation number per atom can be indicated as: O.N. increases by 2 per atom

$$\overset{0}{Zn} + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Zn}\,\overset{-1}{Cl_2} + \overset{0}{H_2}$$

Oxidation number decreased by 1 per atom

Step: 5 The increase in oxidation number of 2 per atom can be balanced with decrease in oxidation number of 1 per atom if Zn atoms are multiplied by 1 and HCl by 2. The equation will be:

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

Illustration 17: **Copper reacts with nitric acid. A brown gas is formed and the solution turns blue. The equation may be written as:** $Cu + NO_3^- \rightarrow NO_2 + Cu^{2+}$ **; Balance the equation by oxidation number method.**

Solution: **Step: 1** Skeleton equation

$$Cu + NO_3^- \longrightarrow NO_2 + Cu^{2+}$$

Step: 2 Writing oxidation numbers of each atom

$$\overset{0}{Cu} + \left[\overset{+5}{N}\overset{-2}{O_3}\right]^- \longrightarrow \overset{+4}{N}\overset{-2}{O_2} + \left[\overset{+2}{Cu}\right]^{+2}$$

Step: 3 The oxidation number of copper has increased from 0 to +2 while that of nitrogen has decreased from +5 to +4.

$$\overset{0}{Cu} + \left[\overset{+5}{N}\overset{-2}{O_3}\right]^- \longrightarrow \overset{+4}{N}\overset{-2}{O_2} + \left[\overset{+2}{Cu}\right]^{+2}$$

Step: 4 Oxidation number increases

Oxidation number increased by 1 per atom

$$\overset{0}{Cu} + \left[\overset{+5}{N}\overset{-2}{O_3}\right]^- \longrightarrow \overset{+4}{N}\overset{-2}{O_2} + \left[\overset{+2}{Cu}\right]^{+2}$$

Oxidation number increased by 1 per atom

Step: 5 Balance the increase/decrease in oxidation number by multiplying NO_3^- by 2 and Cu by 0.

$$Cu + 2NO_3^- \rightarrow NO_2 + Cu^{2+}$$

Step: 6 Balance other atoms except H and O as

$$Cu + 2NO_3^- \rightarrow 2NO_2 + Cu^{2+}$$

Step: 7 Reaction takes place in acidic medium, so add H^+ ions to the side deficient in H^+ and balance H and O atoms:

$$Cu + 2NO_3^- + 4H^+ \rightarrow 2NO_2 + Cu^{2+} + 2H_2O$$