5. STOICHIOMETRY

Synopsis

LAWS OF CHEMICAL COMBINATION

- The mass relation between the reactants and products in a chemical reaction is called stoichiometry.
- There are four important laws of chemical combinations
- **THE LAW OF CONSERVATION OF MASS**:
- This law was proposed by Lavoisier in 1789 by carrying several experiments.
- The law states that matter can neither be created nor destroyed during a chemical change.
- The law may also be stated as the total mass of the products formed during a chemical change is exactly equal to the total mass of the reactants.
- Weighed amounts of solid and solid KI are dissolved in water separately and their solutions are mixed. The following reaction takes place
- Total mass of is equal to the total mass of .

- **LAW OF DEFINITE PROPORTIONS:**

- Proposed by Proust. Verified by Stress and Richards.
- It is also known as Law of constant proportions.
- A given compound always contains the same elements combined in a fixed proportions by weight.
- What ever the method a compound is prepared, it contains the same elements combined in a fixed ratio by weight
- **Eg:** CO_2 can be prepared by many ways i.e., by combining of carbon with oxygen or by heating lime stone etc., but what ever the method CO_2 is prepared; The ratio of carbon and oxygen by mass is 12 : 32 = 3 : 8

- **LAW OF MULTIPLE PROPORTIONS:**

- Proposed by Dalton. Verified by Berzelius.
- If two elements chemically combine to give two or more compounds, then the weight of one element which combines with the fixed weight of the other element in those compound bear a simple multiple ratio to one another.
- **Eg:** Nitrogen forms the oxides; N_2O, NO, N_2O_3, NO_2, N_2O_5
- In these compounds 28 gm of Nitrogen combines with 16, 32, 48, 64, 80 gm of oxygen respectively. The weight of oxygen in these compounds are in the ratio 16:32:48:64:80 or 1:2 : 3 : 4 : 5 a simple multiple ratio.

LAW OF RECIPROCAL PROPORTIONS:

- This law was proposed by Richter (1792) which states as "when two elements combine separately with a fixed mass of a third element, then the ratio of their masses in which they do so is either same or some whole number multiple of the ratio in which they combine with each other.

- **GAY-LUSSAC'S LAW OF COMBINING VOLUMES**

- According to this law gases combine in the simple whole number ratio of their volumes under similar conditions of temperature and pressure. If products are also gases, the simple whole number ratio also extends to the products.
- **Eg:**
- Under similar conditions, 2 lts of Hydrogen combines with 1lt of oxygen to give 2 lts of water vapour.
- It is applicable only to gaseous reaction.
- Law of combining volumes can be derived from Law of defininte proportions when expressed in terms of volumes.
- **AVOGADRO'S LAW:**

- At the same T, P equal volumes of all gases contain equal number of moles or molecules.
- No. of molecules = no. of moles × N
- The study of mass relation or quantity relation between reactants and products is called Stoichiometry.
- According to law of conservation of mass, proposed by Lavoisier, the mass of reactants should be equal to the mass of products.
- The balanced chemical equation which gives correct relation between reactants and products is called stoichiometric equation.
- The definite quantities which are involved in chemi-cal reaction and present in balanced stoichiometric equation are called stoichiometric quantities.

1) $H_2 + O_2 \rightarrow H_2O$

   $2g + 32g \rightarrow 18g$ (x)

2) $2H_2 + O_2 \rightarrow 2\ H_2O$

   $4g + 32g \rightarrow 36\ g$

Equation 1) is not stoichiometric equation and will not obey law of conservation of mass, because masses are not stoichiometric quantities

Equation 2) is stoichiometric equation and will obey law of conservation of mass, because masses are stoichiometric quantities.

Isotopic abundance:-

It is the percentage availability of an Isotope in the nature.

- The atomic wt of Cl is fractional i.e., 35.5 because it has two isotopes and both have significant abundance ^{35}Cl is available by 75% and ^{37}Cl is available by 25%

$\therefore$ Atomic weight of Cl (average) =

$$\frac{75 \times 35 + 25 \times 37}{100} = 35.5$$

Though many elements have isotopes, their atomic weights are whole numbers, because of negligible abundance of their isotopes.

Eg.: $^{1}_{1}H$ $^{2}_{1}H$ $^{3}_{1}H$

Protium deuterium tritium

Atomic weight = 1

Here, abundances of $^{2}_{1}H$ $^{3}_{1}H$ are negligible.

$\therefore$ Its atomic weight is 1.

Atomic weights:-

The relative atomic weights of elements are expressed in a.m.u.

1 amu = 1.66×10^{-24} g.

weight of one H-atom = 1 amu

weight of 1/16 of O-atom = 1 amu

weight of 1/12 of C-atom = 1 amu

The atomic weights are measured by C-12 scale.

The atomic weight of an element is the number of times heavier when compared to $1/12^{th}$ of C atom.

$$\text{Atomic weight} = \frac{\text{weight of atom of element}}{\text{1/12 of carbon atomic weight}}$$

Since, the atomic weight of an element is ratio, it has no units.

Molecular weights:- Even the molecular weights can be measured with the help of C-12 scale. The molecular weight of a substance is defined as the number of times when compared to $1/12^{th}$ of carbon atom.

$$\text{molecular weight} = \frac{\text{weight of one molecule}}{\text{weight of 1/12th of carbon}}$$

Thus, relative atomic weight and molecular weights are expressed in amu, but they don't have units.
Eg.:

1. Atomic weight of Hydrogen = 1 amu.

   Actual weight of Hydrogen = 1.66×10^{-24} g
   Actual weight of 10 H-atoms= $10 \times 1.66 \times 10^{-24}$ g
2. Atomic weight of oxygen = 16 amu
   Actual weight of oxygen = $16 \times 1.66 \times 10^{-24}$g
   Actual weight of 100 oxygen atoms=
   $100 \times 16 \times 1.66 \times 10^{-24}$g

Gram atom (Gram atomic weight):

If atomic weight is expressed in grams it is called gram atomic weight or gram atom.

1 gram atom of Hydrogen = 1 g
2 gram atom of Hydrogen = 2 g
1 gram atom of Oxygen = 16 g
2 gram atom of Oxygen = 32 g
4 gram atom of Oxygen = 64 g

Hydrogen : Atomic weight = 1
Gram Atomic weight = 1 g
Oxygen : Atomic weight = 16
Gram Atomic weight = 16 g

Gram molecule
(Gram molecular weight or Gram mole):

If molecular weight is expressed in grams, it is called gram molecule or gram molecular weight.

Ex.: Hydrogen : Molecular weight = 2
Gram Molecular weight = 2 g
Oxygen : Molecular weight = 32
Gram Molecular weight = 32 g
CO_2 : Molecular weight = 44
Gram Molecular weight = 44g
64g of Oxygen = 2 gram molecule of O_2
22g of CO_2 = 1/2 gram molecule of CO_2
360g of H_2O = 20 gram molecule of H_2O

Mole Concept:-

The amount of substance which contains Avagadro's number of particles is called mole. (or)
Mole is the amount of substance containing as many particles as the number of atoms in 12g of carbon.

1 mole of Hydrogen = 6.023×10^{23} molecules
1 gm molecule weight = 2 g.
1 mole of Carbon = 6.023×10^{23} atoms
1 gm atom weight = 12 g
1 mole of Carbondioxide = 6.023×10^{23} molecules

1 gm molecule weight = 44 g.
1 mole of Sodium = 6.023×10^{23} atoms
1 gm atom weight = 23 g.
1 mole of Sulphur dioxide = 6.023×10^{23} molecules
1 gm molecule weight = 64 g.
1 mole of Oxygen = 6.023×10^{23} molecules
1 gm molecule weight = 32 g.
1 mole of H_2SO_4 = 6.023×10^{23} molecules
1 gm molecule weight = 98 g.

Gram Molar volume (or)
Gram Molecular Volume (GMV):

It is the volume occupied by one mole of gas at STP
i.e. 22.4 lit.

44 g of CO_2 occupies 22.4 lit at STP
11 g of CO_2 occupies 5.6 lit at STP
8 g of CH_4 occupies 11.2 lit at STP
4 g of He occupies 22.4 lit at STP
142 g of Cl_2 occupies 2×22.4 lit at STP
Weight of 5.6 lit of Ethane at STP is 7.5 g
Weight of 44.8 lit of SO_2 at STP is 128 g.
22.4 lit of any gas at STP contains 6×10^{23} molecules
11.2 lit of Chlorine contains 3×10^{23} molecules
5.6 lit of Hydrogen contains 1.5×10^{23} molecules
3×10^{23} molecules of CO_2 will occupy 11.2 lit
6×10^{23} molecules of O_2 will occupy 22.4 lit
6×10^{24} atoms of O_2 will occupy 224 lit
3×10^{24} atoms of O_2 occupies a volume of 112 lit.

Empirical and Molecular formula:
Empirical formula:

It is the formula which gives the simplest ratio of atoms of various elements.

Molecular formula:

It is the formula which gives the actual number of atoms of various elements present in the molecule.

Name	Molecular formula	Empirical formula
Acetylene	C_2H_2	CH
Benzene	C_6H_6	CH
Methane	CH_4	CH_4
Glucose	$C_6H_{12}O_6$	CH_2O
Borazol	$B_3N_3H_6$	BNH_2
Sulphuric acid	H_2SO_4	H_2SO_4
Methyl alcohol	CH_3OH	CH_3OH

Ethylene	C_2H_4	CH_2
Ethane	C_2H_6	CH_3
Sugar	$C_{12}H_{22}O_{11}$	$C_{12}H_{22}O_{11}$
Acetic acid	CH_3COOH	CH_2O
Ethyl alcohol	$C_2H_5 - OH$	$C_2H_5 - OH$
Formic acid	HCOOH	HCOOH

Calculating Empirical formula:-

1) Divide the percentage weight of each element with its atomic weight.
2) Divide the above values with least of them.
3) Multiply with a suitable co-efficient to get whole number ratio. (If necessary)

Determining the molecular formula of gaseous hydrocarbon:

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

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

$$10 \text{ ml} + 10\left(x + \frac{y}{4}\right)\text{ml} \rightarrow 10x \text{ ml}$$

1. 10 ml of gaseous hydrocarbon is completely burnt in 80 ml of O_2 at STP. The gaseous residue occupied a volume of 70 ml. This when passed through caustic potash has become 50 ml. Calculate the empirical formula of the hydrocarbon.

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

$$10 \text{ ml} + 10\left(x + \frac{y}{4}\right)\text{ml} \rightarrow 10x \text{ ml}$$

Volume of CO_2 = contraction in volume by KOH = 20 ml.

$$\therefore 10x = 20 \Rightarrow x = 2.$$

At the end of the reaction, the residual gases will consist of volume of CO_2 produced and the volume of unreacted O_2 volume of CO_2 + volume of unreacted O_2 = 70 ml.

Volume of unreacted oxygen= 70–volume of CO_2

Volume of unreacted oxygen = 70 –20 = 50 ml

Volume of O_2 reacted = 80 – 50 = 30 ml.

$$\therefore 10 \text{ ml}\left(x + \frac{y}{4}\right) = 30 \text{ ml}.$$

$$x + \frac{y}{4} = 3;\ 2 + \frac{y}{4} = 3;\ y = 4$$

$\therefore$ Molecular formula is C_2H_4; Empirical formula is CH_2

Victor Meyer's method to determine Mol. Wt.:

2 x Vapour Density = Molecular

1. 0.2 g of a volatile organic compound on vapourisation gave 200 cc at STP it's mol.wt is

$2g \rightarrow 2000$ cc

$? \rightarrow 22{,}400$ cc

$\frac{2 \times 22400}{2000} = 22.4$ g

$\therefore$ mol. Wt is 22.4 g

Oxidation states (or) oxidation number:

The charge present on an atom is called oxidation state (or)

The charge that appears to have been present on the atom when electrons are counted according to some arbitary rules is called oxidation state.

- Oxidation state could be positive, negative, zero, whole number or fraction.
- More electronegative atom is assigned negative Oxidation State and less electronegative atom is assigned positive Oxidation State.
- The sum of Oxidation State's of all atoms in a molecule is equal to zero.
- The sum of oxidation state's of all atoms in an ion is equal to the charge present on the ion.
- IA group elements always exhibit +1 oxidation state
- IIA group elements always exhibit +2 oxidation state
- F always exhibits –1 oxidation state
- Common oxidation state of hydrogen is +1
- In metal hydride, hydrogen exhibits –1 oxidation state
- Common oxidation state of oxygen is –2.
- In perioxides, oxygen exhibits –1 oxidation state.
- In superoxides, oxygen exhibits –1/2 oxidation state.
- In O_2F_2 and OF_2 oxygen oxidation states are +1 and +2 respectively.
- Transition elements exhibit more than one oxidation state.
- Osmium and Ruthenium show the highest oxidation state i.e. +8.
- The oxidation state of any atom in its elementary state is zero.
- Nitrogen exhibits large number of oxidation state such as –3, –2, –1, 0, +1, +2, +3, +4, +5 and even –1/3.
- Oxidation state of an element will not exceed it's group number. Thus, maximum oxidation state of an element may be equal to its group number.
- Maximum oxidation state of sulphur is +6
  (VIA group)
- Maximum oxidation state of chlorine is +7
  (VIIA group)
- Maximum oxidation state of nitrogen is +5
  (VA group)

(1) $\mathbf{H_2\underline{S}O_4}$

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

$2 + x - 8 = 0$

$x = 6$

(2) $\mathbf{\underline{P}Cl_3}$

$x+3(-1) = 0$

$x = 3\ x - 6 = 0$

(3) $\mathbf{\underline{S}O_2}$

$x+2(-2) = 0$

$x = 4$

(4) $\mathbf{\underline{N_2}O_5}$

$2(x)+5(-2) = 0$

$x = +5$

(5) $\underline{N}_2H_4$
$2(x)+4(1) = 0$
$2x = 4$
$x = +2$

(6) $H\underline{Cl}O_4$
$1+x+4(-2) = 0$
$x = +7$

(7) $\underline{Co}(NH_3)_6Cl_3$
$x + 6(0) + 3(-1) = 0$
$x = 3.$

(8) $[\underline{Fe}(H_2O)_6]^{3+}$
$x + 0 = 3$
$x = 3$

(9) $\underline{S}O_3^{2-}$
$x + (-6) = -2$
$x = +4$

(10) $H_3\underline{N}$
$3 + x = 0$
$x = -3$

(11) $\underline{S}O_4^{2-}$
$x + (-8) = -2$
$x = +6$

(12) $OC\underline{l}^-$
$-2 + x = -1$
$x = +1$

(13) $\underline{N}_3H$
$3x = -1$
$x = -1/3$

(14) $\underline{Cl}O_2^-$
$x + 2(-2) = -1$
$x - 4 = -1;\ x = 3$

(15) $\underline{Cl}_2O_3^-$
$2x + (-6) = -1$
$2x = 5$
$x = 5/2$

(15) $\underline{Cl}O_4^-$
$x + (-8) = -1$
$x = 8 - 1$
$x = 7$

(17) $\underline{N}O_2^-$
$x + 2(-2) = -1$
$x - 4 = -1$
$x = +3$

(18) $\underline{N}O_3^-$
$x + 3(-2) = -1$
$x - 6 = -1$
$x = 6 - 1$
$x = +5$

Sum of oxidation states of all C-atoms in glucose molecule is

$C_6H_{12}O_6$
$6x + 12 + (-12) = 0$
$6x = 0$

The oxidation state of N-atom in hydrazoic acid is

N_3H
$3x + 1 = 0$
$3x = -1$
$x = -1/3$

The sum of oxidation states of all C-atoms in benzaldehyde is

C_6H_5CHO
$7x + 6 - 2 = 0$
$7x = -4$
$x = -4/7$

The sum of oxidation states of all carbon atoms in nitrobenzene is

$C_6H_5NO_2$
$6x + 5 + 2(-2) + 3 = 0$
$6x + 8 - 4 = 0$

$6x = -4 \Rightarrow x = -4/6$

Sum of oxidation states of all carbon atoms in aniline (aminobenzene) is

$C_6H_5NH_2$

$6x + 7 - 3 = 0$

$6x = -4 \Rightarrow x = -4/6$

Calculate the oxidation states of underlined atoms in the following?

1) $H_2\underline{S}_2O_3$ **2) $Cu\underline{S}O_4 . 5H_2O$**

3) $K_3[\underline{Fe}(CN)_6]$ **4) $K_4[\underline{Fe}(CN)_6]$**

5) $Na_2\underline{S}_4O_6$ **6) $[\underline{Cu}(NH_3)_4]SO_4$**

7) $(NH_4)_2\underline{C}O_3$ **8) $Na_2\underline{S}_2O_3$**

9) $H_2\underline{S}_2O_7$ **10) $\underline{P}Cl_5$**

Ans:

1) +2 **2) +6**

3) +3 **4) +2**

5) +2.5 **6) +2**

7) +4 **8) +2**

9) +6 **10) +5**

Redox reactions:

Based on the involvement of electrons, chemical reactions are classified into two types.

(i) **Reactions which donot involve electron transfer:**

Precipitation ionic reactions and neutralisation reactions do not involve electron transfer

a) $AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3(aq)$

b) $BaCl_2 + Na_2SO_4 \rightarrow 2NaCl + BaSO_4\downarrow$

Spectator ions:

These ions do not undergo any change in a chemical reaction. These ions are present commonly on both sides of the equation.

Spectator ions:

a) Na^+, NO_3^-

b) Na^+, Cl^-

$NaOH + HCl \rightarrow NaCl + H_2O$

Spectator ions: Na^+, Cl^-

$2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O$

Spectator ions: K^+, SO_4^{2-}

Reactions which involve electron transfer:

The reactions which involve e^- transfer are commonly known as Redox reactons.

$Na + \frac{1}{2}Cl_2 \rightarrow NaCl$

$Zn + CuSO_4 \rightarrow Cu + ZnSO_4$

$H_2 + Cl_2 \rightarrow 2HCl$

Oxidation: It is the process in which

1) electrons are removed
2) de-electronation occurs.
3) addition of oxygen.
4) removal of hydrogen
5) increase in the oxidation state

Ex: $Na \rightarrow Na^+ + e^-$

$Zn \rightarrow Zn^{2+} + 2e^-$

$Ca + \frac{1}{2} O_2 \rightarrow CaO$

$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2$

Reduction: It is process in which

1) electrons are added
2) electronation occurs
3) oxygen is removed
4) hydrogen is added
5) decrease in the oxidation state

$Cl_2 + 2e^- \rightarrow 2Cl^-$

$F_2 + H_2O \rightarrow 2HF + \frac{1}{2} O_2$

$CO_2 + C \rightarrow 2CO$

$CuO + H_2 \rightarrow Cu + H_2O$

Disproportionantion Reactions:

If same substance undergoes both oxidation and reduction, it is called disproportionation. Thus, disproportionation reactions are also redox reactions.

$Cl_2 + NaOH \rightarrow NaCl + NaOCl + H_2O$

$P + NaOH \rightarrow PH_3 + NaH_2PO_2$

Oxidising agent (Oxidant): It is the substance

1) Which gains electrons
2) Which undergoes reduction
3) Which oxidises other substances.

Reducing agent: It is the substance

1) Which loses electrons.
2) Which undergoes oxidation
3) Which reduces other substances.

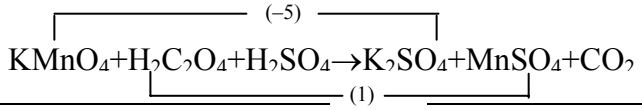
Reaction	Half-oxidation reaction	Half-reduction reaction	Oxidising agent	Reducing agent
1) $KMnO_4+H_2C_2O_4+H_2SO_4 \rightarrow K_2SO_4+MnSO_4+H_2O+CO_2$	$H_2C_2O_4 \rightarrow CO_2$	$KMnO_4 \rightarrow MnSO_4$	$KMnO_4$	$H_2C_2O_4$
2) $K_2Cr_2O_7+FeSO_4+H_2SO_4 \rightarrow K_2SO_4+ Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + H_2O$	$FeSO_4 \rightarrow Fe_2(SO_4)_3$ (or) $Fe^{2+} \rightarrow Fe^{3+}$	$K_2Cr_2O_7 \rightarrow Cr_2[SO_4]_3$ $2Cr^{+6} \rightarrow 2Cr^{3+}$	$K_2Cr_2O_7$	$FeSO_4$
3) $KMnO_4+FeSO_4+H_2SO_4 \rightarrow K_2SO_4+ Fe_2(SO_4)_3 + MnSO_4 + H_2O$	$KMnO_4 \rightarrow MnSO_4$ $Mn^{+7} \rightarrow Mn^{2+}$	$FeSO_4 \rightarrow Fe_2(SO_4)_3$ $Fe^{2+} \rightarrow Fe^{3+}$	$KMnO_4$	$FeSO_4$
4) $K_2Cr_2O_7 + NaNO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + NaNO_3 + H_2O$	$NO_2^- \rightarrow NO_3^-$	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	$K_2Cr_2O_7$	$NaNO_2$
5) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$	$Cu \rightarrow Cu(NO_3)_2$ $Cu \rightarrow Cu^{2+}$	$HNO_3 \rightarrow NO_2$ $NO_3^- \rightarrow NO_2$	HNO_3	Cu
6) $C + HNO_3 \rightarrow CO_2 + NO_2 + H_2O$	$C \rightarrow CO_2$	$HNO_3 \rightarrow NO_2$ $NO_3^- \rightarrow NO_2$	HNO_3	C
7) $P + HNO_3 \rightarrow H_3PO_4 + NO_2 + H_2O$	$P^0 \rightarrow P^{+5}$	$HNO_3 \rightarrow NO_2$	HNO_3	P
8) $F_2Cl_2 \rightarrow 2ClF$	$F_2 \rightarrow ClF$ $F^0 \rightarrow F^-$	$Cl_2 \rightarrow ClF$ $Cl_2 \rightarrow 2Cl^+$	F_2	Cl_2
9) $2Na + Cl_2 \rightarrow 2NaCl$	$Na \rightarrow NaCl$ $Na \rightarrow Na^+$	$Cl_2 \rightarrow NaCl$ $Cl_2 \rightarrow 2Cl^-$	Cl_2	Na
10) $SO_2 + H_2S \rightarrow S + H_2O$	$H_2S \rightarrow S$	$SO_2 \rightarrow S$	SO_2	H_2S
11) $Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl + S$	$Na_2S_2O_3 \rightarrow Na_2SO_4$ $S^{+2} \rightarrow S^{+6}$	$Cl_2 \rightarrow 2HCl$ $Cl_2^0 \rightarrow 2Cl^-$	Cl_2	$Na_2S_2O_3$
12) $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$	$Na_2S_2O_3 \rightarrow Na_2S_4O_6$ $S^{+2} \rightarrow S^{+5/2}$	$I_2 \rightarrow 2NaI$ $I^0 \rightarrow I^-$	I_2	$Na_2S_2O_3$

Balancing of redox reactions:

There are two methods of balancing an equation

(i) Oxidation number method:

1) Write the skeleton equation
   Skeleton equation:
   $KMnO_4 + H_2C_2O_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$
2) Identify the elements for which oxidation states are changing
   $KMn^{+7}O_4 + H_2C_2^{+3}O_4 + H_2SO_4 \rightarrow K_2SO_4 + Mn^{+2}SO_4 + C^{+4}O_2 + H_2O$
3) Locate the change in oxidation states



4) Interchange the coefficient so that total decrease in the oxidation state becomes equal to total increase in the oxidation state.

$2KMnO_4 + 5H_2C_2O_4 + H_2SO_4 \rightarrow$

$K_2SO_4 + MnSO_4 + CO_2 + H_2O$

5) Balance elements other than oxygen and hydrogen by inspection (hit and trail) method.

$2KMnO_4 + 5H_2C_2O_4 + H_2SO_4 \rightarrow$

$K_2SO_4 + 2MnSO_4 + 10CO_2 + H_2O$

6) Balance oxygen and hydrogen

$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow$

$K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$

Half-reaction method: (Ion electron method)

This method is for balancing of ionic form of equations.

Molecular form or ionic form of equations can be balanced by this method.

Balancing of Redox reaction equations by the half reaction method or ion-electron method is as follows:

Represent first the ionic equation.

a) Indicate the oxidation half-reaction and reduction half-reaction separately.
b) Balance the half reactions separately. While balancing the half reactions, balance the atoms other than oxygen and hydrogen first.
c) In acid medium include enough number of water molecules where there is a deficiency of oxygen and include enough number of H^+ ions on the side where there is a deficiency of Hydrogen.
d) In alkaline medium include enough number of OH^- ions on the side where there is a deficiency of oxygen and enough number of water molecules where there is a deficiency of hydrogen. After balancing the atoms, balance the charge.
e) To balance the charge include enough number of electrons wherever necessary.
f) Multiply the reduction half reaction with the number of electrons lost in oxidation and multiply the oxidation half reaction with the number of electrons gained in reduction.
g) Add the two half reactions after canceling the electrons.
In the final balanced equation not only the atoms but the net charge also should be balanced.

How many electrons and on which side are to be added in the following half-reaction

i) $CH_4 \rightarrow CH_2O$; $CH_4 \rightarrow CH_2O + 4e^-$
ii) $Na_4S_2^{+2}O_3 \rightarrow Na_2S_4^{+2.5}O_6$
$Na_4S_2O_3 \rightarrow Na_2S_4O_6 + 1e^-$
iii) $CH_3OH \rightarrow HCOOH$; $CH_3OH \rightarrow HCOOH + 4e^-$
iv) $MnO_4^- \rightarrow Mn^{2+}$; $MnO_4^- + 5e^- \rightarrow Mn^{2+}$
v) $S_2O_3^{2-} \rightarrow S^0$; $S_2O_3^{2-} + 4e^- \rightarrow S$

- If an element is in higher oxidation state, it acts as oxidising agent.
- If an element is in its lowest oxidation state, it acts as reducing agent.
- If the element is in intermediate oxidation state, it acts as both O.A and R.A.

Eg:

i) Na_2S (R.A.); Na_2SO_3 (Both);

$Na_2S_2O_3$(both); Na_2SO_4(O.A.)

ii) SO_2 (R.A.) SO_3(O.A.)

iii) $KMnO_4$(O.A.); K_2MnO_4 (both); MnO_2 $MnSO_4$ (R.A)

iv) HNO_2; HNO_3(O.A.); N_3H; NH_3(R.A); N_2H_4 (O.A)

v) N_2O; NO; N_2O_3; NO_2; N_2O_4; N_2O_5 (O.A.)

vi) $K_2Cr_2O_7$(OA); H_2CrO_4(O.A)

vii) O_2(OA); H_2O(RA); H_2O_2(both)

Equivalent weight of an element:

- It may be defined as the number of parts by weight of that element which combines with (or) displaces directly (or) indirectly 1.008 parts by weight of hydrogen (or) 8 parts by weight of oxygen (or) 35.45 parts by weight of chlorine.

  Eq. wt of an element = $\frac{\text{At.wt. of an element}}{\text{Valency}}$

- The valency of an element may vary though the atomic weight of the element is constant.
- One element may possess more than one equivalent weight.

  Eq. wt. of Fe^{+2} (Ferrous ion) = $\frac{55.84}{2} = 27.92$

  Eq. wt of Fe^{+3} (Ferric ion) = $\frac{55.84}{3} = 18.613$

- Radicals (ions) also possess equivalent weights.
- A radical behaves like an d element.

  Eq. wt. of radical = $\frac{\text{Molecular weight of radical}}{\text{Valency}}$

  Eq. wt. of $SO_4^{-2} = \frac{96}{2} = 48$

- If the equivalent weight of an element (or) radical expressed in grams is called gram equivalent weight.
- Ex. Gram equivalent weight of oxygen = 8 g.

  Gram equivalent weight of carbonate ion = $\frac{60}{2}$ =30 g

- Equivalent weight of substance depends on whether one needs to calculate the equivalent weight of an element (or) acid (or) base (or) oxidant (or) a reductant.
- Equivalent weight of substances may have different values.
- Eq. wt. of $KMnO_4$ acidic medium = 31.6
- Eq. wt. of $KMnO_4$ in Alkaline medium = 52.6
- Eq. wt. of $KMnO_4$ in neutral medium = 158

Equivalent weights of Acids :

- Equivalent weight of an acid is the number of parts by weight of it that contains 1.008 parts by weight of replaceable hydrogen. Alternately it is the quantity by weight that supplies one mole of H^+.
- The number of hydrogen atoms that get displaced from a molecule of acid is equal to the number of equivalent per molecular weight of the acid.
- Eq.wt. of an acid = $\frac{\text{Mol.wt (or) Formula wt.of acid}}{\text{Basicity of the acid}}$
- Basicity of an acid is the number of replaceable hydrogen atoms present in one molecule of the acid.

- Eq.wt of $HCl = \frac{M}{1} = \frac{36.5}{1} = 36.5$
- Eq.wt of $HNO_3 = \frac{M}{1} = \frac{63}{1} = 63$
- Eq.wt of $H_2SO_4 = \frac{M}{2} = \frac{98}{2} = 49$
- Eq.wt of $H_3PO_4 = \frac{M}{3} = \frac{98}{3} = 32.6$
- Eq.wt of $H_3PO_2 = \frac{M}{2} = \frac{82}{2} = 41$
- Eq.wt of $H_2C_2O_4.2H_2O = \frac{M}{2} = \frac{126}{2} = 63$
- Eq.wt of $H_2C_2O_4 = \frac{M}{2} = \frac{90}{2} = 45$

Equivalent weight of Bases :

- Equivalent weight of a base is the number of parts by weight of it that completely neutralises one gram equivalent of an acid. Alternately it is the quantity of weight that reacts with one mole of H^+.
- Eq. wt. of base

$$= \frac{\text{Mol.wt.(or)Formula wt. of the base}}{\text{Acidity}}$$

- The number of hydroxyl groups present in a molecule of the base is known as its acidity.
- Eq. wt. of $NaOH = \frac{M}{1} = \frac{40}{1} = 40$
- Eq. wt of $KOH = \frac{M}{1} = \frac{56}{1} = 56$
- Eq. wt. of $Ca(OH)_2 = \frac{M}{2} = \frac{74}{2} = 37$
- Eq. wt. of $Ba(OH)_2 = \frac{M}{2} = \frac{171}{2} = 85.5$
- Eq. wt. of $Fe(OH)_3 = \frac{M}{3} = \frac{107}{3} = 35.7$

Equivalent weight of oxidising and reducing agents:

- Equivalent weight of an oxidising agent is that weight of the compound which can supply 8 parts by weight of oxygen (or) can react with 1.008 g parts by weight of hydrogen similarly.
- Equivalent weight of a reducing agent is that weight of the compound which can supply 1.008 parts by weight of hydrogen (or) can be oxidised by 8 parts by weight of oxygen.
- In redox reaction electrons are transfered from the reducing agent to the oxidising agent.
- In a stoichiometric equation if the number of electrons (n) transferred from one mole of reducing agent (reductant) to one mole of oxidising agent (oxidant).
- Eq. wt. of oxidant = $\frac{\text{Formula wt. of oxidant}}{\text{No.of electrons gained by oxidant}}$
- Eq. wt. of reductant = $\frac{\text{Formula wt. of reductant}}{\text{No.of electrons lost by reductant}}$

Example 1:

- $FeSO_4$ is reducing agent. It is oxidised to $e_2(SO_4)_3$. The reaction can be written as $Fe^{2+} \rightarrow Fe^{3+} + 1e^-$.

- One mole of Ferrous ion loses one mole of electrons.
- Eq. wt. of Ferrous ion = $\frac{\text{wt. of Ferrous ion}}{\text{No.of } e^- \text{ involved in the reaction}} = \frac{55.84}{1} = 55.84$

Example 2:

- Oxalate ion ($C_2O_4^{-2}$) is another reducing agent. When it is oxidised the reaction written as $C_2O_4^{-2} \rightarrow 2CO_2 + 2e^-$
- One mole of oxalate ion loses two moles of electrons.
- Eq. wt. of $C_2O_4^{-2}$ ion = $\frac{\text{Formula wt. of } C_2O_4^{-2}}{\text{No.of } e^- \text{ involved in the reaction}} = \frac{88}{2} = 44$
- Eq.wt of $Na_2C_2O_4 \,.\, 2H_2O$ = $\frac{\text{Molecular wt. of } Na_2C_2O_4.2H_2O}{2} = \frac{170}{2} = 85$

Example 3:

- In acid medium $KMnO_4$ is a strong oxidising agent.
  $KMnO_4 + 8\ H^+ + 5e^- \rightarrow K^+ + Mn^{+2} + 4H_2O$
  One mole of $KMnO_4$ takes five moles of electrons.
- Eq. wt. of $KMnO_4$ =
  $$\frac{\text{Molecular weight of } KMnO_4}{\text{No.of } e^- \text{ involved in the reaction per mole of } KMnO_4}$$
  $$= \frac{\text{Molecular weight of } KMnO_4}{5} = \frac{158}{5} = 31.6$$
  (or) Eq. wt. of $MnO_4^- = \frac{\text{wt.of } MnO_4^-}{5} = \frac{119}{5} = 23.8$.

Example 4 :

- $KMnO_4$ in function as oxidising agent in neutral as well as basic medium.
- In Alkaline medium the reaction is
  $KMnO_4 + 2H_2O + 3e^- \rightarrow K^+ + 4OH^- + MnO_2$
  Eq. wt. of $KMnO_4$ = = $\frac{\text{Molecular weight of } KMnO_4}{\text{No.of.} e^- \text{ involved in the reaction per mole of } KMnO_4}$
  $= \frac{158}{3} = 52.6$
- In neutral medium the reaction is $KMnO_4 + e^- \rightarrow K^+ + MnO_4^{2-}$
- Eq. wt of $KMnO_4 = \frac{\text{Mol.wt.of } KMnO_4}{1} = 158$
- Equivalent weight of the substances changes with chemical reaction.

Example 5 :

- $K_2Cr_2O_7$ functions as oxidising agent in acidic medium $Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$.
- Change in oxidation number for one Cr atom = 3.
- Change in oxidation number for two Cr atoms = 6.
- No. of electrons gained = 6.
- Eq. wt. of $K_2Cr_2O_7$ = $\frac{\text{Molecular weight of } K_2Cr_2O_7}{6} = \frac{294}{6} = 49$

Equivalent weight of salts :

- Salts consist of cations and anions.
- Salts are neutral substances.

- For a salt total positive charge is equal to total negative charge.
- Eq. wt. of salt = $\frac{\text{Formula weight of salt}}{\text{Total charge of the cation (or) anion of the salt}}$
- Eq. wt. of $NaCl = \frac{F}{1} = \frac{58.5}{1} = 58.5$
- Eq. wt. of $Na_2CO_3 = \frac{F}{2} = \frac{106}{2} = 53$
- Eq. wt. of $CaCO_3 = \frac{F}{2} = \frac{100}{2} = 50$.

TYPES OF REDOX REACTIONS

Chemical combination reactions: The redox reactions in which the compounds are formed by combining two or more elements with eath other or with a compound $A + B \rightarrow AB$.

1) $C^{0}_{(s)} + O^{0}_{2(g)} \rightarrow \overset{+4}{C}O^{-2}_{2(g)}$

2) $S^{0}_{(s)} + O^{0}_{2(g)} \rightarrow \overset{+4}{S}O^{-2}_{2(g)}$

3) $\overset{-4\ +1}{C}H_{4(g)} + O^{0}_{2(g)} \rightarrow \overset{+4}{C}O^{-2}_{2(g)} + \overset{+1}{H}_2O^{-2}_{(l)}$

Decomposition reactions: The redox reactions in which the chemical compounds chemically split into two or more simple substances. $AB \rightarrow A + B$

Eg: 1) $2\overset{+1}{K}\overset{+5}{Cl}O^{-2}_{3} \rightarrow 2\overset{+1}{K}\overset{-1}{Cl} + 3O^{0}_{2}$

2) $H^{+1}_{2}O^{-2} \rightarrow H^{0}_{2} + O^{0}_{2}$

Displacement reactions: The redox reactions in which the place of one species in it's compound is taken up by other species

Eg: $A + BC \rightarrow AC + B$

$$Zn^{0}_{(s)} + Cu^{+2}SO^{-2}_{4(aq)} \rightarrow Zn^{+2}SO^{-2}_{4(aq)} + Cu^{0}_{(s)}$$

l In non metal displacement redox reactions, generally hydrogen gets displaced and rarely oxygen.

Eg: $Na^{0}_{(s)} + 2H^{+1}_{2}O^{-2}_{(l)} \rightarrow 2Na^{+1}O^{-2}H^{+1}_{(aq)} + H^{0}_{2(g)}$

$$Zn^{0}_{(s)} + 2H^{+1}Cl^{-1}_{(aq)} \rightarrow \overset{+2}{Zn}Cl^{-1}_{2(aq)} + H^{0}_{2(g)}$$

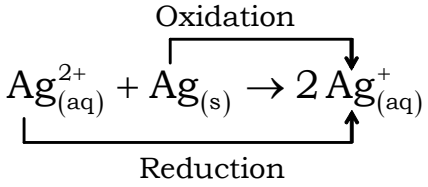
$$3Cl^{0}_{2(g)} + 6OH^{-}_{(aq)} \rightarrow \left[\overset{+5}{Cl}O_3\right]^{-}_{aq} + 5Cl^{-1}_{(aq)} + 3H_2O_{(l)}$$

$$Cl_{2(g)} + 2OH^{-}_{(aq)} \rightarrow \left[Cl^{+}O\right]^{-}_{aq} + Cl^{-1}_{(aq)} + H_2O$$

Comproportionation reactions:

In these reactions, two species with the same element in two different oxidation states form a single product in which the element is in an intermediate oxidation state. It is reverse of disproportionation.

Eg:



APPLICATIONS OF REDOX REACTIONS IN QUANTITATIVE ANALYSIS AND ELECTRODE PROCESS

In titrimetric quantitative analysis:

- The solutions of accurately known concentration is called standard solution.
- In titrimetric analysis, the substance of known concentration is called titrant.
- Substance being titrated is called titrand.
- The process of adding the standard solution until the reaction gets completed is called titration.
- The point at which the titrand just completely reacts is called equivalence point or theoretical point or Stoichiometric end point.
- Completion of titration is detected by
  - o Observing physical change
  - o By using an Indicator.
- In $Cr_2O_7^{2-}$ (dichromate) titrations, diphenyl amine is used as a reagent. End point is intense blue colour due to oxidation of $Cr_2O_7^{2-}$.
- In titration of Cu^{2+} and I^- to I_2 it gives deep blue Colour with starch solution.
- $Cu^{2+}_{(aq)} + 4I^-_{(aq)} \rightarrow Cu_2I_2(s) + I_{2(aq)}$
- In the titration of I_2 with thiosulphate, blue colour disappears due to the conversion of I_2 to I^-.
- $I_{2_{(aq)}} + 2S_2O^{2-}_{3_{(aq)}} \rightarrow 2I^-_{(aq)} + S_4O^{2-}_{6_{(aq)}}$
- Br_2 and I_2 dissolve in CCl_4 solvent to give reddish brown and purple colour respectively. They are detected by extracting into CCl_4 layer and the test is called 'Layer test'.
- **Electrode process:**
- Galvanic, Daniel cells were constructed based on redox reactions. They convert chemical energy to electrical energy.
- In Galvanic cell Cu acts as cathode, Zn acts as anode.
- It is represented as: $Zn\left|Zn^{2+}_{(aq)} \,||\, Cu^{2+}_{(aq)}\right|Cu$.
- Daniel cell is represented as $Zn,\ Zn^{2+}_{(aq)} \,||\, Cu^{2+}_{(aq)},\ Cu$.
- Salt Bridge is an inverted U shaped rubber tube containing an inert electrolyte solutions like KCl or KNO_3 or NH_4NO_3 made in the form of semi solid in agar agar. It is denoted by in galvanic and in Danielcell.
- When the concentration of the electrolyte is 1M at 298 K, the potential obtained for the electrode is called standard electrode potential
- Standard electrode potential for hydrogen electrode is assumed as zero.
- The series in which the electrods are arranged in ascending or descending order of reduction potential values is known as electro chemical series.