STOICHIOMETRY

ATOMIC MASS

The *atomic mass* of an element is defined as the average relative mass of an atom of the element as compared to the mass of a carbon atom, which is taken as 12. Therefore, the atomic mass of an element shows the number of times an atom of the element is heavier than 1/12th of the mass of a carbon atom (C\text{12}). For example, the atomic mass of an oxygen atom is 16 a.m.u (atomic mass unit) and that of a hydrogen atom is 1.008 a.m.u.

**Atomic mass unit**—abbreviated as a.m.u—is defined as the quantity of mass of an atom equal to 1/12 of the mass of a carbon atom. By convention, the atomic mass of a carbon atom is 12 a.m.u. One mole of carbon signifies $6.023 \times 10^{23}$ atoms of carbon, and a mass of 12.000 g. Therefore, the mass of a carbon atom can be calculated as follows:

$$\frac{12.00}{6.023 \times 10^{23}} \text{ g or 1 a.m.u.} = \frac{1}{12} \times \frac{12}{6.023 \times 10^{23}} = \frac{1}{6.023 \times 10^{23}} = 1.66 \times 10^{-24} \text{ G}$$

**Gram-atomic mass** of an element is the atomic mass of the element expressed in grams. It is also known as *gram atom*. For example, 16 g of oxygen is equal to 1 gram-atom of oxygen or 14 g of nitrogen is equal to 1 gram-atom of nitrogen. Gram-atom can be calculated as shown below:

$$\text{Gram atom} = \frac{\text{Mass of the atom}}{\text{Atomic mass}}$$

**Molecular Mass and Gram-Molecule of a Substance**

*Molecular mass* of a compound is defined as the average mass per molecule of natural isotopic composition of the compound. It can be calculated as the sum of the atomic mass of all the atoms present in a molecule of a compound. For example, the molecular mass of H\text{2}O is

$$2 \times 1 + 16 = 18 \text{ a.m.u.}$$

**Gram-molecule or gram-mole** of a compound is the molecular mass of the compound expressed in grams.

**Examples:**

i) One gram-mole of H\text{2}SO\text{4} (molar mass = 98) is equal to 98 g.

ii) Half gram-mole of H\text{2}SO\text{4} is equal to 49 g.

iii) The molar mass of NaOH is 40 g. Therefore, 4 g of NaOH is equal to 0.1 mole.

**LAWS OF CHEMICAL COMBINATION:**

There are five important laws of chemical combination. There are:

(a) Law of conservation of mass
(b) Law of constant proportions
(c) Law of multiple proportions
(d) Law of Reciprocal proportions
(e) Law of Gaseous volume
The laws of chemical combination are the experimental laws which led to the idea of atoms being the smallest unit of matter. The laws of chemical combination played a significant role in the development of Dalton’s atomic theory of matter.

(a) **Law of Conservation of mass or matter:**

This law was given by Antoine Lavoisier. The law of conservation of mass means that in a chemical reaction, the total mass of products is equal to the total mass of the reactants. There is no change in mass during a chemical reaction. Suppose we carry out a chemical reaction between A and B. If the products formed are C and D then,

\[ A + B \rightarrow C + D \]

Example

When we burn a sample of metallic magnesium in the air, the magnesium combines with oxygen from the air to form magnesium oxide, a white powder. This chemical reaction is accompanied by the release of large amounts of heat energy and light energy. When we weigh the product of the reaction, magnesium oxide, we find that it is heavier than the original piece of magnesium. The increase in mass of the solid is due to the combination of oxygen with magnesium to form magnesium oxide. Many experiments have shown that the mass of the magnesium oxide is exactly the sum of the masses of magnesium and oxygen that combined to form it. Similar statements can be made of all chemical reactions.

(b) **Law of constant (definite) proportion:** Most elements can interact with other elements to form compounds. Hydrogen gas, for example, burns in oxygen gas to form water. Conversely, water can be decomposed into its component elements by passing an electrical current through it. Pure water, regardless of its source, consists of 11% hydrogen and 89% hydrogen atoms combined with one oxygen atom. The observation that the element composition of a pure compound is always the same is known as the law of constant composition (or the law of definite proportion). It was first put forth by the French chemist Joseph Louis Proust (1754-1826) in about 1800.

(c) **Law of multiple proportions:** Whenever two elements form more than one compound, the different masses of one element that combine with the same mass of the other element are in the ratio of small whole numbers. Strong support for Dalton’s theory came when Dalton and other scientists studied elements that are able to combine to give two (or more) compounds. For example, sulfur and oxygen form two different compounds which we call sulfur dioxide and sulfur trioxide. If we decompose a 2.00g sample of sulfur dioxide, we find it contains 1.00g of S and 1.00 g of O. If we compose a 2.50g sample of sulfur trioxide, we find it also contains 1.00g of S, but this the mass of O is 1.50g. This is summarized in the following table.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample size</th>
<th>Mass of sulfur</th>
<th>Mass of oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur dioxide</td>
<td>2.00g</td>
<td>1.00g</td>
<td>1.00g</td>
</tr>
<tr>
<td>Sulfur trioxide</td>
<td>2.50g</td>
<td>1.00g</td>
<td>1.50g</td>
</tr>
</tbody>
</table>

First, notice that sample sizes aren’t the same, they were chosen so that each has the same mass of sulfur. Second, the ratio of the masses of oxygen in the two samples is one of small whole numbers.
Similar observations are made when we study other elements that form more than one compound with each other, and these observations form the basis of the law of multiple proportions.

(d) The law of Reciprocal proportions: This law was given by “Richter” in 1792-94. Law states that “When two elements combine separately with third element and form different types of molecules, their combining ratio is directly reciprocated if they combine directly”

Example

\[
\begin{align*}
C + O_2 & \rightarrow CO_2, & C + 2H_2 & \rightarrow CH_4 \\
12 & & 32 & & 12 & & 4
\end{align*}
\]

C combines with O to form CO_2 and with H to form CH_4. In CO_2 12g of C reacts with 32g of O, whereas in CH_4 12g of C reacts with 4g of H. Therefore when O combines with H, they should combine in the ratio of 32:4 (i.e. 8:1) or in simple multiple of it. The same ratio is found to be true in H_2O molecules, the ratio of weight of H and O in H_2O is 1:8.

Other example is: NH_3, H_2O and N_2O_3

(e) The law of Gaseous volume: The law was given by “Gay lussac” in 1808. Law states that “Whenever gases react together, the volumes of the reacting gases as well as the products if they are gases, bear a simple whole number ratio, provided all the volumes are measured under similar conditions of Temperature & Pressure.

Example

\[
\begin{align*}
H_2(g) + Cl_2(g) & \rightarrow 2HCl(g) \\
1 \text{unit.vol.} & & 1 \text{ unit vol.} & & 2 \text{ unit vol.} \\
\text{ratio} = 1 : 1 : 2 \\
N_2(g) + 3H_2(g) & \rightarrow 2NH_3(g) \\
1 \text{unit.vol.} & & 3 \text{ unit vol.} & & 2 \text{ unit vol.} \\
\text{ratio} = 1:3:2
\end{align*}
\]

Ex.1 When 4.2g NaHCO_3 is added to a solution of CH_3COOH weighing 10.0 g, it is observed that 2.2g CO_2 is released into atmosphere. The residue is found to weigh 12.0g. Show that these observations are in agreement with the low of conservation of weight.

Sol. NaHCO_3 + CH_3COOH → CH_3COONa + H_2O + CO_2

Initial mass = 4.2 + 10 = 14.2

Final mass = 12 + 2.2 = 14.2
Thus, during the course of reaction law of conservation of mass is obeyed.

**Ex.1** 1.375g of pure cupric oxide was reduced by heating in a current of pure dry hydrogen and the mass of copper that remained 1.0980g. In another experiment, 1.179g of pure copper was dissolved in pure HNO₃ and the resulting copper nitrate converted into cupric oxide by ignition. The mass of copper oxide formed was 1.476g. Show that the results illustrate to law of constant composition with in the limits of experimental error.

**Sol.** 1.375g of pure cupric oxide gave 1.098g of Cu and hence,

Percentage of Cu in the oxide = \( \frac{1.098}{1.375} \times 100 = 79.85\% \)

in another experiment, 1.179g of pure copper gave 1.476g of the oxide and hence

percentage of Cu is the oxide = \( \frac{1.179}{1.476} \times 100 = 79.87\% \)

Since, both the oxides have almost the same percentage of Cu and hence, of oxygen, the result is obeying the law of constant composition.

**Ex.2** Hydrogen and oxygen combine in the ratio of 1:8 by mass of form water. What mass of oxygen gas would be required to react completely with 3g of hydrogen gas?

**Sol.** Here we have been given that hydrogen and oxygen always combine in the fixed ratio of 1:8 by mass. This means that 1g of hydrogen gas requires = 8g of oxygen gas

So, 3g of hydrogen gas requires = 8 \times 3g of oxygen gas = 24g of oxygen gas

Thus, 24 grams of oxygen was would be required to react completely with 3 grams of hydrogen gas.

**Ex.3** The following data were collected for several compounds of nitrogen and oxygen:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass of Nitrogen combining with 1g of Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.750g</td>
</tr>
<tr>
<td>II</td>
<td>0.875g</td>
</tr>
<tr>
<td>III</td>
<td>0.4375g</td>
</tr>
</tbody>
</table>

Show how these data illustrate the law of multiple proportions.

**Sol.** For the law of multiple proportions to hold, the ratios of the masses of nitrogen combining with 1 gram of oxygen in each pair of compounds should be small whole numbers. We write the ratios as follows:

\[ \frac{I}{II} = \frac{1.750}{0.875} = \frac{2}{1}, \frac{II}{III} = \frac{0.875}{0.4375} = \frac{2}{1}, \frac{I}{III} = \frac{1.750}{0.4375} = \frac{4}{1} \]

These results support the law of multiple proportions.
EXERCISE

1. 2.8g of calcium oxide prepared by heating limestone were found to contain 0.8g of oxygen. When one gram of oxygen was treated with calcium, 3.5g of calcium oxide were obtained. Show that the results illustrate the law of definite proportions.

2. 0.5g of the oxide of a metal gave 0.444g of the metal on reduction. 1g of another oxide of the same metal on reduction gave 0.798g of the metal. Show that these results are in agreement with the law of multiple proportions.

3. When AgNO₃ was treated with 5.08g of a sample of iron chloride, 11.48g of AgCl was formed. 6.51g of another iron chloride gave 17.22g of AgCl on treatment with AgNO₃. Show that these results illustrate the law of multiple proportions. [R.A.M. Ag = 108, Fe = 56 and Cl = 35.5]

4. Copper (II) sulphide contains 33.3% of sulphur, copper (II) oxide contains 20.1% of oxygen and oxide of sulphur contains 40% sulphur. Show that these data illustrate the law of reciprocal proportions.

Mole Concept

If you consider an amount equal to the molecular mass of CO₂, N₂, O₂, and H₂O—that is, 44g of carbon dioxide, 28g of nitrogen, 32g of oxygen, and 18g of water—you will find that each of them contains the same total number of molecules. This holds true for all molecules of different substances. Not only this, 1 gram-atom each of Na, K, Ag, and Mg contains the same total number of atoms. Is it not amazing? For convenience, this many number of molecules or atoms is called mole. In other words, one mole is the amount of a substance that contains Avogadro’s number of particles. The Avogadro’s number is denoted as N, No, or Na and is equal to 6.023 \times 10^{23} \text{ mol}^{-1}.

Examples:

i) 1 mole of oxygen contains 6.023 \times 10^{23} number of molecules. Also, 1 gram-atom of oxygen is equal to 6.023 \times 10^{23} atoms, or 1 mole of oxygen atom contains 6.023 \times 10^{23} atoms.

ii) 60 g of carbon is equal to 60/12 or 5 gram-atoms of carbon, and will have 5 \times 6.023 \times 10^{23} or 30.11 \times 10^{23} actual atoms of carbon.

iii) 64g of oxygen is equal to 64/32 or 2 moles of oxygen, and will have 2 \times 6.023 \times 10^{23} or 12.04 \times 10^{23} molecules.

No. of moles of molecules = \frac{\text{Wt. of substance in g}}{\text{Mol. wt. of substance}}; \text{No. of moles of atoms} = \frac{\text{Wt. of element in g}}{\text{At. wt. of the element}}

No. of moles of gas = \frac{\text{Volume of the gas at STP}}{\text{Standard molar volume (i.e. 22.4L)}}
**Relation of mole with gas volume:**

* Volume of one mole of a gas at NTP = 22.4 L

* Since 1 mole gas contains $6.023 \times 10^{23}$ molecules, so $6.023 \times 10^{23}$ ($N_A$) molecules have volume at NTP = 22.4 L

* Moles at NTP = \( \frac{\text{Volume (Litre)}}{22.4} \)

* Molecules Mass of gas = 2 × vapour density of gas

* Vapour density of gas = \( \frac{\text{Weight of a certain vol of gas at NTP}}{\text{Weight of the same vol of H}_2\text{ gas at NTP}} \)

* Weight of 1 ml of H$_2$ gas at NTP = \( \frac{\text{Weight of one mole of H}_2\text{ gas at NTP}}{\text{volume of one mole of H}_2\text{ gas at NTP}} = \frac{0.00009g}{22400\text{ml}} = 0.00009g \)

**Ex.1** What is the weight of $3.01 \times 10^{23}$ molecules of ammonia?

**Sol.** $6.023 \times 10^{23}$ molecules of NH$_3$ has weight = 17 g

\[ \therefore \quad 3.01 \times 10^{23} \text{ molecules of NH}_3 \text{ has weight} \]

\[ = \frac{17 \times 3.01 \times 10^{23}}{6.023 \times 10^{23}} = 8.50 \text{g} \]

**Ex.2** How many g of S are required to produce 10 moles and 10 g of H$_2$SO$_4$ respectively?

**Sol.** ∴ 1 mole of H$_2$SO$_4$ has = 32 g S

\[ \therefore \quad 10 \text{ mole of H}_2\text{SO}_4 = 32 \times 10 = 320 \text{g S} \]

Also, 98 g of H$_2$SO$_4$ has = 32 g S

\[ \therefore \quad 10\text{g of H}_2\text{SO}_4 \text{ has} = (32 \times 10)/98 = 3.265 \text{g S} \]

**Ex.3** P and Q are two elements which form $P_2Q_3$, $PQ_2$ molecules. If 0.15 mole of $P_2Q_2$ and $PQ_2$ weighs 15.9 g and 9.3 g, respectively, what are atomic weighs of P and Q?

**Sol.** Let at. wt. of P and Q be a and b respectively,

\[ \therefore \quad \text{Mol. wt. of } P_2Q_3 = 2a + 3b \]
and Mol. wt. of \( PQ_2 = a + 2b \)

\[
(2a + 3b) \times 0.15 = 15.9
\]

And \((a + 2b) \times 0.15 = 93\) \((\because \text{ wt. } = \text{ Mole } \times \text{ Mol. wt.})\)

Thus, \(a = 26, \quad b = 18\)

**Ex.4** Sugar reacts with oxygen as: \( C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O \). How many g of \(CO_2\) is produced per g of sucrose (sugar) used? How many mole of oxygen are needed to react with 1.0 g sugar?

**Sol.** \(\because\) 1 mole or 342g sugar produces 12 mole or \(44 \times 12\)g \(CO_2\)

\[
\therefore \text{1g sugar produces } \frac{44 \times 12}{342} = 1.54\text{g} \ CO_2
\]

Also 1 mole or 342g sugar requires 12 mole \(O_2\)

\[
\therefore \text{1g sugar requires } \frac{12}{342} = \text{mole} \ O_2 = 3.5 \times 10^{-2} \text{ mole}
\]

**Ex.5** The mass of one litre sample of ozonized oxygen at NTP was found to be 1.5g. When 100mL of this mixture at NTP were treated with turpentine oil, the volume was reduced to 90mL. Hence calculate the molecular mass of ozone.

(Terpenetine oil absorbs ozone)

**Sol.** Volume absorbed by turpentine oil = Volume of ozone = 10mL

\(\because\) turpentine oil absorbs only \(O_3\)

\[
\therefore \text{Volume of} \ O_2 = 100 - 10 = 90
\]

\[
\text{Volume of mole ratio of} \ O_2 \text{ and } O_3 \text{ is } 900 : 100
\]

\[
\therefore \text{Volume of mole ratio of} \ O_3 \text{ is } \frac{900 \times 32 + 100 \times a}{1000}
\]

Or \(33.62 = \frac{900 \times 32 + 100 \times a}{1000}\)

Or \(a = 48.2\)

\[
\therefore \text{Volume of mole ratio of} \ O_3 \text{ is } 48.2
\]

**Ex.6** A hydrate of iron (III) thiocyanate \(\text{Fe(SCN)}_3\), was found to contain 19% \(H_2O\). What is the formula of the hydrate?

**Sol.** Let the hydrate be \(\text{Fe(SCN)}_3\cdot mH_2O\)

Molecular weight of hydrate
\[
= 56 + 3 \times (32 + 12 + 14) + 18m = 230 + 18m
\]
\[\therefore \% \text{ of } H_2O = \frac{18m \times 100}{230 + 18m} = 19\]
or \[m = 3\]
\[\therefore \text{ Formula is Fe(SCN)}_3.3H_2O\]

**EXERCISE**

1. How many years it would take to spend Avogadro’s number of rupees at the rate of 1 million rupees in one second?

   Ans. \((19.098 \times 10^9 \text{ year})\)

2. Calculate the number of Cl\(^-\) and Ca\(^{2+}\) ions in 333g anhydrous CaCl\(_2\).

   Ans. \((3 N \text{ ion of Ca}^{2+}, 6 N \text{ ion of Cl}^-), \ N \to \text{avogadro’s constant}\)

3. Which of the following will weigh maximum amount?
   (a) 20g iron
   (b) 1.2 g atom of N,
   (c) 1 \times 10^{23} \text{ atoms of carbon}
   (d) 1.12 litre of O\(_2\) at STP.

   Ans. (a)

4. From 280mg of CO, \(10^{21}\) molecules are removed. How many g and mole of CO are left?

   Ans. \((233.5 \times 10^{-3} \text{ g, } 8.34 \times 10^{-3} \text{ mole})\)

5. Potassium chromate is isomorphous to potassium sulphate (K\(_2\)SO\(_4\)) and it is found to have 26.78% Cr. Calculate the at. wt. of Cr if at. wt. of potassium is 39.10.

   Ans. \((52.0)\)

**Empirical and Molecular Formula**

Every compound is represented by a formula. A formula represents a molecule of a substance by way of symbols of various elements present in the substance. The determination of the formula of a substance involves the chemical analysis of each constituent of the substance. The procedure given below is followed while calculating formula of a substance:

(a) The percentage analysis of each element is divided by the respective atomic mass of the element. In this way, the relative number of atoms of various elements present in a molecule is obtained.

(b) The various numbers obtained in *step (a)* are divided by the smallest value among them to obtain the simplest ratio of various other elements.
(c) The values obtained in step (b) are rounded up to the nearest whole number and, if necessary, multiplied with a suitable integer in order to convert them into whole numbers.

(d) The symbols of various elements are written side by side, whereas the numerical value is written at the right-hand lower corner of each symbol. This gives the empirical formula of the substance.

(e) The empirical formula mass is obtained. The ratio of actual molecular mass and empirical formula mass gives a factor with which the empirical formula is multiplied to obtain the molecular formula.

Ex. 1 An organic compound contains C—40.68%, H—5.085%, and O—54.228%. Its vapour density is 59. Calculate the molecular formula of the compound.

Sol. $C = \frac{40.68}{12} = 3.390$

$\frac{3.390}{3.389} = 1 = 2$

$H = \frac{5.085}{1} = 5.085$

$\frac{5.085}{3.389} = 1.5 = 3$

$O = \frac{54.228}{16} = 3.389$

$\frac{3.389}{3.389} = 1 = 2$

Therefore, the empirical formula of the compound is $C_2H_3O_2$.

Also, molecular mass of the compound = 59

And, vapour density = 59

Therefore, the actual molecular mass = 118

Actual molecular mass = (empirical formula mass) $\times$ n

Or, $118 = (59) \times n$

Or, $n = 2$

$\therefore$ The molecular formula of the compound is $C_4H_6O_2$.

Ex. 2 A salt containing water of crystallization gave the composition: Mg—9.76%, S—13.01%, O—26.02%, and $H_2O$—51.22%. What is the formula of the compound?

Sol. $Mg = \frac{9.76}{24} = 0.406/0.406 = 1$

$S = \frac{13.01}{32} = 0.406/0.406 = 1$

$O = \frac{26.02}{16} = 1.63/0.406 = 4.01$
H₂O = 51.22/18 = 2.84/0.406 = 7

Thus, the formula of the compound is MgSO₄·7H₂O.

SIGNIFICANCE OF CHEMICAL EQUATIONS:

Let us consider a balanced chemical equations.

PbS + 4H₂O₂ → PbSO₄ + 4H₂O

This equations will provide us various quantitative informations:

1. The molar ratio of reactants, i.e., PbS and H₂O₂ in which they react together is 1:4.
2. The molar ratio of the two products i.e., PbSO₄ and H₂O being formed in the reaction is also 1:4.
3. One can start the reaction with PbS and H₂O₂ in any molar ratio, but the ratio of PbS and H₂O₂ which are reacting will always be in the ratio of 1:4.
4. One mole of PbSO₄ and 4 moles of H₂O will be formed for each mole of PbS being consumed. The stoichiometric coefficients of a balanced chemical equation is the molar ratio and not the weight ratio.

One can use the balanced chemical equation for quantitative (gravimetrically or volumetrically) estimation of reactants consumed or products being formed.

Example: N₂ + 3H₂ ⇄ 2NH₃

Above balanced chemical equation gives idea that 1 mole of N₂ (28g) reacts with 3 mole of H₂ (6g) to give 2 mole of NH₃.

Example: 2N₂O₅ → 4NO₂ + O₂

Above balanced equation indicates that 2 mole of N₂O₅ (2 × 108g) will decompose to give 4 mole of NO₂ (4 × 46g) and 1 mole.

THE LIMITING REAGENT:

The reactions in which more than one reactants are reacting and if they are not present in the same molar ratio as the balanced equations requires, then one has to find out the limiting reagent i.e., the regent which is completely consumed in the reaction. All quantitative calculations are carried out with the help of limiting regent only. Now, how to decide the limiting reagent of a reaction? Consider the following example.

Example 1

Suppose you are given 5 moles of PbS and 18 moles of H₂O₂ and you have to calculate the maximum amount of PbSO₄ being produced.
Sol. The balance equations is:

\[ \text{PbS} + 4\text{H}_2\text{O}_2 \rightarrow \text{PbSO}_4 + 4\text{H}_2\text{O} \]

Initial moles 5 moles 18 moles

Now since 1 mol of PbS reacts completely with 4 moles of H\(_2\)O\(_2\) to produce 1 mol of PbSO\(_4\). Therefore, 5 moles of PbS will react with 20 moles of H\(_2\)O\(_2\). But since moles of H\(_2\)O\(_2\) is only 18. So, H\(_2\)O will be the reagent which will be consumed first, and hence H\(_2\)O\(_2\) is the limiting. As one can see from the balanced chemical equation that 1 mol of PbSO\(_4\) is produced from 4 moles of H\(_2\)O\(_2\). So 18 moles of H\(_2\)O\(_2\) will produce 4.5 moles of PbSO\(_4\).

Example 2

Suppose you are given 12g of C and 40gm of O\(_2\) and you have to calculate maximum amount of CO\(_2\) formed. The balanced chemical equations is:

Sol. 

\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]

1mole 1 mole 1 mole
12g 32g 44g

For complete reaction of 40g of O\(_2\) (1.25 mole) 15g of C (1.25 mole) is required but only 12g of C is present, therefore C is limiting reagent and 12g of C will gave 44g of CO\(_2\), O\(_2\) is excess reagent.

So, one can define limiting reagent in another way, The reagent producing the least number of moles of products is the limiting reagent.

Calculation of limiting reagent:

(a) By calculating the required amount by the equation and comparing it with given amount.
(b) By calculating amount of any one 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.
(d) The percentage yield of product = \( \frac{\text{actual yield}}{\text{the theoretical maximum yield}} \times 100 \)

(i) The actual amount of any limiting reagent consumed in such incomplete reactions is given by: [\% yield \times given moles of limiting reagent] [for reversible reactions]
(ii) For irreversible reaction with \% yield less than 100, the reactant is converted to product desired and waste.

SOLVED EXAMPLES

Ex.1 Calculate the moles of H\(_2\)O vapours formed if 1.57 mole of O\(_2\) are used in presence of excess of H\(_2\) for the given change, 2H\(_2\) + O\(_2\) \rightarrow 2H\(_2\)O

Sol. \( \therefore 2 \text{ mole } \text{H}_2 \approx 1 \text{ mole } \text{O}_2 \approx \text{ mole } \text{H}_2\text{O} \)

\( \therefore 1 \text{ mole } \text{O}_2 \approx 2 \text{ mole } \text{H}_2\text{O} \);
1.57 mole $O_2 = \frac{[1.57 \text{ mole of } O_2]}{1 \text{ mole } O_2} \times 2$

$= 1.57 \times \frac{2}{1} = 3.14 \text{ mole}$

**Ex.2** Potassium bromide $KBr$ contains $32.9\%$ by mass potassium. If $6.40g$ of bromine reacts with $3.60g$ of potassium, calculate the number of moles of potassium which combine with bromine to form $KBr$.

**Sol.** In $100g$ $KBr$, $K = 32.9g$, then $Br = 67.1g$ (at. wt. of $K$ and $Br$ are 39 and 80 respectively)

$$2K + Br_2 \rightarrow 2KBr$$

$$\frac{\text{Moles of } K}{\text{Moles of } Br_2} = \frac{\frac{32.9}{39}}{\frac{67.1}{80}} = \frac{1.0057}{1}$$

$$\therefore \frac{\text{Moles of } K}{\text{Moles of } Br_2} = \frac{1.0057 \times 2}{1} = \frac{2.0114}{1}$$

$$2K + Br_2 \rightarrow 2KBr$$

Given moles

$$\frac{3.60}{39} \quad \frac{6.40}{160}$$

$$= 0.092 \quad 0.04$$

The reaction ratio for moles of $K$ and $Br_2 = 2.0114$.

Thus, $Br_2$ will be completely used leaving $K$.

$\therefore$ Moles of $Br_2$ reacting $= 0.04$

$\therefore$ Moles of $K$ reacting $= 0.04 \times 2.0114 = 8.01 \times 10^{-2} \text{ mole}$

**Ex.3** For the reaction: $2Na_3PO_4(aq.) + 3Ba(NO_3)_2(aq.) \rightarrow Ba_3(PO_4)_2(s) + 6NaNO_3(aq.)$ Suppose that a solution containing $32.8g$ of $Na_3PO_4$ and $26.1g$ of $Ba(NO_3)_2$ is mixed. How many g of $Ba_3(PO_4)_2$ are formed?

**Sol.**

$$2Na_3PO_4 \quad + \quad 3Ba(NO_3)_2 \quad \rightarrow \quad Ba_3(PO_4)_2 \quad + \quad 6NaNO_3$$

Mole (32.8/164) 26.1/261 0 0

Before reaction

Reaction $= 0.2$

Mole[0.2−(0.1×2)/3] 0 0.1/3 (0.1×6)/3

After reaction

Mole ratio for $Na_3PO_4$:$Ba(NO_3)_2$:$Ba_3(PO_4)_2$:$NaNO_3$ : 2 : 3 : 1 : 6

Moles of $Ba_3(PO_4)_2$ formed $= 0.1/3$

$\therefore$ Weight of $Ba_3(PO_4)_2$ formed $= \frac{0.1}{3} \times 602 = 20.07g$
Ex.4
A mixture of Al and Zn weighing 1.67g was completely dissolved in acid and evolved 1.69 litre of H$_2$ at NTP. What was the weight of Al in original mixture?

Sol.
Let $a$ and $b$ g be weight of Al and Zn in mixture $a + b = 1.67$ (1)

\[ \begin{align*}
\text{Al} + 3\text{HCl} & \rightarrow \text{AlCl}_3 + (3/2) \text{H}_2; \\
\text{Zn} + 2\text{HCl} & \rightarrow \text{ZnCl}_2 + \text{H}_2
\end{align*} \]

\[ \therefore 27g \text{ Al gives } (3/2) \times 22.4 \text{ litre } \text{H}_2 \quad (\because \text{ at. wt. of Al} = 27) \]

\[ \therefore a \text{ g Al gives } \frac{3 \times 22.4 \times a}{2 \times 27} \text{ litre } \text{H}_2 \]

Similarly 65g Zn gives 22.4 litre H$_2$ \quad (\because \text{ at. wt. of Zn} = 65)

\[ \therefore b \text{ g Zn gives } \frac{22.4 \times b}{65} \text{ litre } \text{H}_2 \]

\[ \therefore \frac{3 \times 22.4 \times a}{2 \times 27} + \frac{22.4 \times b}{65} = 1.69 \] (2)

By eq. (1) and (2)
\[ a = 1.25 \text{g} \quad b = 0.42 \text{g} \]

Ex.5
A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38g carbon dioxide, 0.690g of water and no other products. A volume of 10.0 litre (Measured at STP) of this welding gas is found to weigh 11.6g. Calculate:

(i) empirical formula,
(ii) molar mass of the gas, and
(iii) molecular formula.

Sol.
Molecular mass of welding gas $= \frac{11.6 \times 22.4}{10} = 25.98$

CO$_2$ and H$_2$O are obtained from welding gas combustion in water.

\[ \therefore \text{ g-atoms of C in gas } = \frac{3.38}{44} = 0.077 \]

\[ \text{ g-atoms of H in gas } = \frac{0.690 \times 2}{18} = 0.077 \]

\[ \therefore \text{ Ratio of C and H atoms in gas is } 1 : 1 \]

Thus, empirical formula mass of welding gas is CH

Empirical formula mass of welding gas $= 13$

Molar mass $= (\text{empirical formula mass}) \times n$

\[ \therefore n = \frac{25.98}{13} \approx 2 \]

\[ \therefore \text{ Molecular formula } = 2 \times (\text{CH}) = \text{C}_2\text{H}_2 \]
Ex. 6 A plant virus was examined by the electron microscope and was found to consist of uniform cylindrical particles 150 Å in diameter and 5000 Å long. The virus has a specific volume of 0.75 cm³/g. Assuming virus particle as one molecule, calculate molecular weight of virus.

Sol. Given, length = 5000 × 10⁻⁸ cm,
\[ r = \frac{150}{2} \times 10^{-8} \text{ cm} \]
∴ Volume (cylindrical nature of virus) = \( \pi r^2 h \)
\[ = 3.14 \times \left(\frac{150}{2} \times 10^{-8}\right)^2 \times 5000 \times 10^{-8} \]
\[ = 8.83 \times 10^{-17} \text{ cm}^3 \]
Given that specific volume is 0.75 cm³/g
∴ 0.75 cm³ = 1 g
∴ \[ \frac{8.83 \times 10^{-17} \text{ cm}^3}{0.75} = 1.18 \times 10^{-16} \text{ g} \]
= weight of one virus
∴ Thus weight of \( N \) virus molecules
\[ = 1.18 \times 10^{-16} \times 6.023 \times 10^{23} \]
\[ = 7.10 \times 10^7 \text{ g/mol} \]
Or Mol. weight = 7.10 × 10⁷

Ex. 7 A natural gas sample contains 84% (by volume) of CH₄, 10% of C₂H₆, 3% of C₃H₈ and 3% N₂. If a series of catalytic reactions could be used for converting all the carbon atoms into butadiene (C₄H₆), with 100% efficiency, how much butadiene could be prepared from 100g of the natural gas?

Sol. \[ 4\text{CH}_4 \xrightarrow{\text{Catalyst}} \text{C}_4\text{H}_6 + 5\text{H}_2 \]
\[ 2\text{C}_2\text{H}_6 \xrightarrow{\text{Catalyst}} \text{C}_4\text{H}_6 + 3\text{H}_2 \]
\[ 4\text{C}_3\text{H}_8 \xrightarrow{\text{Catalyst}} 3\text{C}_4\text{H}_6 + 7\text{H}_2 \]
\[ m_{\text{mixture}} = \frac{\Sigma(\% \times \text{mol.mass})}{100} \]
\[ = \frac{84 \times 16 + 10 \times 30 + 3 \times 44 + 3 \times 28}{100} = 18.60 \]
\[ n_{\text{natural gas}} = \frac{100}{18.6} \]

\[ n_{\text{CH}_4} = \frac{100}{18.6} \times 0.84, \]

\[ n_{\text{C}_2\text{H}_6} = \frac{100}{18.6} \times 0.10, \]

\[ n_{\text{C}_3\text{H}_8} = \frac{100}{18.6} \times 0.03 \]

\[ n_{\text{C}_4\text{H}_6} = 1.52 \]

\[ \text{Amount of C}_4\text{H}_6 \text{ formed} = 1.52 \times 54 \quad (\because m = 54) \]

\[ = 82.08g \]

**Ex.8** A sample of coal gas contains 50% H\(_2\), 30% CH\(_4\), 14% CO and 6% C\(_2\)H\(_4\). 100ml of coal gas is mixed with 150 ml of O\(_2\) and the mixture is exploded. What will be the volume and composition of mixture when cooled to original conditions?

**Sol.** In 100ml of given coal gas contain H\(_2\) = 50ml, CH\(_4\) = 30ml, CO = 14ml, C\(_2\)H\(_4\) = 6ml

\[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O} (\ell) \]

50ml 25ml

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O} (\ell) \]

30ml 60ml 30ml

\[ \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) \]

14ml 7ml 14 ml

\[ \text{C}_2\text{H}_4(g) + 3\text{O}_2(g) = 2\text{CO}_2(g) + 2\text{H}_2\text{O}(1) \]

6 ml 18ml 12ml

\[ \therefore \text{Total volume of O}_2 \text{ consumed} = 25 + 60 + 7 + 18 = 110ml \]

\[ \therefore \text{volume of O}_2 \text{ remaining} = 150 - 110 = 40ml \]

\[ \therefore \text{total volume of CO}_2 \text{ produced} = 30 + 14 + 12 = 56ml \]

Hence % by volume of CO\(_2\) = \(\frac{56}{96}\times 100 = 58.334\)

Hence % by volume of O\(_2\) = \(\frac{40}{96}\times 100 = 41.666\)
\[ \text{total volume of product gas} = 40 + 56 = 96\text{ml} \text{ and it contains 58.334\% CO}_2 \text{ and 41.666\% O}_2 \text{ by volume.} \]

**Ex.9**  A mixture of 20mL of CO, CH\(_4\) and N\(_2\) was burnt in excess of O\(_2\) resulting in reduction of 13mL of volume. The residual gas was then treated with KOH solution to show a contraction of 14mL in volume. Calculate volume of CO, CH\(_4\) and N\(_2\) in mixture. All measurements are made at constant pressure and temperature.

**Sol.**  Let \(a\) mL CO, \(b\) mL CH\(_4\) and \(c\) mL N\(_2\) be present in mixture, then

\[ a + b + c = 20 \]

\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \]  

\[ \because \text{Volume of CO} = a; \quad \therefore \text{Volume of CO}_2 = a \]

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}(l) \]

\[ \therefore \text{Volume of CH}_4 = b; \quad \therefore \text{Volume of CO}_2 = b \]

\[ \text{N}_2 + \text{O}_2 \rightarrow \text{No reaction} \]

Volume of CO\(_2\) formed = Volume absorbed by KOH

\[ a + b = 14 \text{ mL} \]  

\[ \text{Now initial volume of CO} + \text{CH}_4 + \text{N}_2 + \text{vol. of O}_2 \text{ taken} - \text{volume of CO}_2 \text{ formed} - \text{volume of N}_2 - \text{volume of O}_2 \text{ left} = 13 \]  

\[ \therefore a + b + c + \text{vol. O}_2 \text{ taken} - \text{vol. O}_2 \text{ left} - (a + b) - c = 13 \]

\[ \therefore \text{Vol. of O}_2 \text{ used} = 13 \]

\[ \therefore \frac{a}{2} + 2b = 13 \quad \left( \because \text{volume of O}_2 \text{ used} = \frac{a}{2} + 2b \right) \]  

Solving Eqs. (1), (2), we get

\[ a = 10\text{mL}; \quad b = 4\text{mL}; \quad c = 6\text{mL} \]

**Ex.10**  \(n\)-butane is produced by the monobromination of ethane followed by Wurtz reaction. Calculate the volume of ethane at NTP to produce 55g \(n\)-butane if the bromination takes place with 90\% yield and the Wurtz reaction with 85\% yield.

**Sol.**

(i)  \[ 2\text{C}_2\text{H}_6 + 2\text{Br}_2 \rightarrow 2\text{C}_2\text{H}_5\text{Br} + 2\text{HBr} \]

(ii)  \[ 2\text{C}_2\text{H}_5\text{Br} + 2\text{Na} \rightarrow \text{C}_4\text{H}_{10} + 2\text{NaBr} \]
\[ \text{∵ Weight of butane formed} = 55\text{g} \]
\[ \therefore \text{Mole of butane formed} = \frac{55}{58} \text{mole} \]

\[ \therefore \text{Mole ratio in reaction} \]
\[ \text{C}_2\text{H}_6 : \text{C}_2\text{H}_5\text{Br} : \text{C}_4\text{H}_{10} : : 2 : 2 : 1 \]

\[ \therefore \text{Mole of C}_2\text{H}_5\text{Br required} = \frac{55}{58} \times 2 \]

Since efficiency of Wurtz reaction is 85%

\[ \therefore \text{Mole of C}_2\text{H}_5\text{Br actually required} = \frac{55}{58} \times 2 \times \frac{100}{85} \]

\[ \therefore \text{Mole of C}_2\text{H}_6 \text{required} = \frac{55}{58} \times 2 \times \frac{100}{85} \]

Since efficiency of bromination is 90%

\[ \therefore \text{Mole of C}_2\text{H}_6 \text{actually required} = \frac{55}{58} \times 2 \times \frac{100}{85} \times \frac{100}{90} = 2.479 \text{ mole} \]

\[ \therefore \text{Volume of C}_2\text{H}_6 \text{ at NTP actually required} = 22.4 \times 2.479 = 55.53 \text{ litre}. \]

**EXERCISE**

1. The vapour density of a mixture containing NO\(_2\) and N\(_2\)O\(_4\) is 38.3 at 27\(^{\circ}\)C. Calculate the mole of NO\(_2\) in 100 mole mixture.

Ans. (33.48 mole)

2. 23g sodium metal reacts with water. Calculate the:
   (a) volume of H\(_2\) liberated at NTP,
   (b) moles of H\(_2\) liberated,
   (c) weight of H\(_2\) liberated

Ans. (1/2 mole H\(_2\), 1g, 11200 mL)

3. Chemical absorbers can be used to remove exhaled CO\(_2\) of space travellers in short space flights. Li\(_2\)O is one of the most efficient in terms of absorbing capacity per unit weight. If the reaction is:

Ans. (746.67 litre CO\(_2\))

4. Zinc and hydrochloric acid according to the reaction:
   \[ \text{Zn(s) + 2HCl(aq.)} \rightarrow \text{ZnCl}_2(aq.) + \text{H}_2(g) \]
   If 0.30 mole of Zn are added to hydrochloric acid containing 0.52 mole HCl, how many moles of H\(_2\) are produced?

Ans. (0.26)
5. Calculate the weight of FeO produced from 2g VO and 5.75g of Fe$_2$O$_3$. Also report the limiting reagent. Given: VO + Fe$_2$O$_3$ → FeO + V$_2$O$_5$

Ans. (5.18g, Fe$_2$O$_3$)

6. Calculate the weight of line (CaO) obtained by heating 300kg of 90% pure limestone (CaCO$_3$)

Ans. (151.20 kg)

7. How much CO is produced by the reaction of 1.0 kg octane and 1.0 kg oxygen. Also report the limiting reagent for this reaction.

Ans. (823.48 kg, O$_2$)

8. A gaseous alkane on complete combustion gives CO$_2$ and H$_2$O. If the ratio of moles of O$_2$ needed for combustion and moles of CO$_2$ formed is 5:3 find out the formula of alkane.

Ans. (C$_3$H$_8$)

**EQUIVALENT WEIGHT:**

Equivalent weight of a substance (element or compound) is defined as “The number of parts by weight of it, that will combine with or displace directly or indirectly 1.008 parts by weight of hydrogen, 8 parts by weight of oxygen, 35.5 parts by weight of chlorine or the equivalent parts by weight of another element”

Equivalent weight of substance depends on the reaction in which it takes part. It is a relative quantity so it is unit less. When equivalent weight of substances are expressed in grams, they are called Gram equivalent weight (GEW).

**n Factor:** Equivalent weight is the ratio of atomic weight and a factor (say n-factor).

* Equivalent weight (E) = $\frac{\text{atomic or molecular weight}}{\text{n-factor}}$

In case acid/base the n-factor is basicity/acidity (i.e. number of dissociable H$^+$ ions/number of dissociable OH$^-$ ions) and in case of oxidizing agent/reducing agent, n-factor is number of moles of electrons gained/lost per mole of oxidizing agent/reducing agent. Therefore, in general, we can write.

* No. of equivalents of solute = $\frac{\text{wt}}{\text{eqwt}}$ = $\frac{W}{E}$ = $\frac{W}{M/n}$

* No. of equivalents of solute = No. of moles of solute × n-factor

* Normality = n-factor × molarity of solution
Equation of equivalent weight:

1. Equivalent weight of element = \( \frac{\text{Atomic weight of element}}{\text{Valency of element}} \)

2. Equivalent weight of salt = Equivalent weight of I part + Equivalent weight of II part

Or \( \frac{\text{Molecular weight of salt}}{\text{Total charge on cation}} \)

Example 1.

Find the equivalent weight of NaCl.

**Sol.**

Equivalent weight NaCl = \( E_{Na} + E_{Cl} = 23 + 35.5 \)
Equivalent weight NaCl = 58.5

Or Equivalent weight of NaCl = \( \frac{\text{Molecular weight of NaCl}}{\text{Total charge on Na}} \) = \( \frac{58.1}{1} \) = 58.5

Example 2.

Find the equivalent weight of AlCl\(_3\).

**Sol.**

Equivalent weight AlCl\(_3\) = \( E_{Al} + E_{Cl} = \frac{27}{3} = 35.5 \) = 9 + 35.5 = 44.5

Or \( E_{AlCl_3} = \frac{\text{Molecular weight of AlCl}_3}{\text{Total positive charge}} = \frac{133.5}{3} = 44.5 \)

**Equivalent weight of acid salt:**

Equivalent weight of acid salt = \( \frac{\text{Molecular weight of acid salt}}{\text{Replaceable } 'H' \text{ atom}} \)

Example 3.

Find the equivalent weight of NaHCO\(_3\).

**Sol.**

\( E_{NaHSO_4} = \frac{M_{NaHCO_3}}{\text{Replaceable } H \text{ atom}} = \frac{84}{1} = 84 \)

Example 4.

Find the equivalent wt. of CO\(_3\)^{2-}.

**Sol.**

\( E_{CO_3^{2-}} = \frac{60}{2} = 30 \)

**Equivalent weight of acid & base:**

(i) **Equivalent weight of acid:** Equivalent weight of an acid is the weight which contains one gram equivalent weight of replaceable hydrogen atoms.

[The number of maximum replaceable hydrogen atoms present in a molecule is called the basicity of the acid.]
* Equivalent weight of an acid = \( \frac{\text{Molecular weight of the acid}}{\text{Basicity of the acid}} \)

<table>
<thead>
<tr>
<th>Acid</th>
<th>HCl</th>
<th>H₂SO₄</th>
<th>H₃PO₄</th>
<th>H₃PO₃</th>
<th>H₃PO₂</th>
<th>HClO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basicity</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>E.W.</td>
<td>( \frac{M}{1} = 36.5 )</td>
<td>( \frac{M}{2} = 49 )</td>
<td>( \frac{M}{3} = 32.66 )</td>
<td>( \frac{M}{2} = 41 )</td>
<td>( \frac{M}{1} = 66 )</td>
<td>( \frac{M}{1} = 100.5 )</td>
</tr>
</tbody>
</table>

(ii) Equivalent weight of base: Equivalent weight of base is the weight which contains one gram equivalent weight of replaceable hydroxyl radicals. [The number of maximum replaceable hydroxyl (OH) groups present in the molecule of a base is called the acidity of the base]

* Equivalent weight of Base = \( \frac{\text{Molecular weight of the base}}{\text{Acidity of the base}} \)

<table>
<thead>
<tr>
<th>Base</th>
<th>NaOH</th>
<th>Ca(OH)₂</th>
<th>Al(OH)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.W.</td>
<td>( \frac{M}{1} = 40 )</td>
<td>( \frac{M}{2} = 37 )</td>
<td>( \frac{M}{3} = 26 )</td>
</tr>
</tbody>
</table>

Method of determination of equivalent weight:

1. **By hydrogen displacement**: Equivalent weight of metals like Ca, Zn, Sn, Mg etc. which react with dilute acids to produce hydrogen can be determined by this method.

   \[ \text{Equivalent weight of metal} = \frac{\text{Weight of metal taken}}{\text{Weight of displaced } H_2} \times 1.008 = \frac{\text{Weight of metal}}{\text{Volume of displaced } H_2 \text{ at STP}(L)} \times 11.2 \]

2. **By oxide formation**: Equivalent weight of metals like copper, magnesium, mercury, zinc etc. which form their oxides relatively easily, can be determined by this method.

   \[ \text{Equivalent weight of metal} = \frac{\text{Weight of metal taken}}{\text{Weight of oxygen combined } (w_2 - w_1)} \times 8 \]

   \( (w_2 = \text{weight of metal oxide}, w_1 = \text{weight of pure metal}) \)

3. **By metal chloride formation**: Equivalent weight of metals like Na, K, Ag, Au etc. which form their chlorides easily can be determine by this method.

   \[ \text{Equivalent weight of metal} = \frac{\text{Weight of metal taken}}{\text{Weight of chlorine combined}} \times 35.5 \]

4. **By metal displacement**: More active metal can displace less active metal from their salt solution. This displacement is based on the law of equivalent.

   \[ \frac{\text{Weight of } A \text{ deposited}}{\text{Weight of } B \text{ deposited}} = \frac{\text{Equivalent weight of metal } A}{\text{Equivalent weight of metal } B} \]

5. **By Electrolysis**: This method based on Faraday’s second law of electrolysis. The law state – “When same quantity of electricity is passed through the solutions of different electrolytes, the weight of different substances liberated as a result of electrolysis, are in the ratio of their equivalent weights”.
Example 1.

0.4g of metal when heated in air gives 0.72g of the metal oxide. Find the equivalent weight of the metal.

Sol.  Weight of the metal = 0.4g

Weight of the oxide = 0.72g

\[ \text{Weight of oxygen which combines with 0.4g of the metal} = 0.72 - 0.40 = 0.32g \]

Now 0.32g of oxygen combines with metal = 0.40g

1g of oxygen combines with metal = \( \frac{0.40}{0.32} \) g

8g of oxygen combines with metal = \( \frac{0.40}{0.32} \times 8 = 10g \)

Thus eq. weight of the metal is 10g.

Example 2.

In a Victor Meyer determination of the relative molecular mass of benzene, the heating vessel was maintained at 120°C. A mass of 0.1528g of benzene was used and the volume of displaced air collected over water at 15°C, was 48 cm³. The barometric pressure was 743 mm mercury. Calculate the relative molecular mass of benzene. The vapour pressure of water at 15°C = 13 mm Hg.

Sol.  Actual pressure of displaced dry air = 743 – 13 = 730 mm = \( \frac{730}{760} \) atm

15°C = 15 + 273 = 288K

\[ V = 48 \text{ cm}^3 = 48 \times 10^{-3} \text{ lit.} \]

W = 0.1528

\[ M = \frac{WRT}{PV} = \frac{0.1528 \times 0.082 \times 288}{\frac{730}{760} \times 0.048} = 78.26. \text{ Hence, the molecular weight of benzene} = 78.26 \]

Example 3.

1.296g of sliver metal was displaced when 0.382g of copper was added to the solution of silver sulphate. If the eq. wt. of silver metal is 108, find that the copper.

Sol.  Wt. of copper = 0.382g., Wt. of silver = 1.296g

Applying the law of equivalents we have
EXPRESSION OF STRENGTH / CONCENTRATION OF SOLUTION:

The amount of solute which dissolved in unit volume of solution is called concentration of solution.

Concentration = \( \frac{\text{amount of solute}}{\text{volume of solution}} \)

**Weight – weight percent (w/W):** Weight of solute present in 100gm of the solution.

\[
\text{Weight percent} = \frac{\text{Weight of solute (g)}}{\text{weight of solution (g)}} \times 100
\]

% by weight = \( \frac{W}{W} \times 100 \)

**Volume – volume percent (v/V) : (In liquid – liquid solution)**

Volume of solute in ml present in 100ml of the solution is called volume – volume percent.

\[
\text{Volume – Volume percent} = \frac{\text{Volume of solute (ml)}}{\text{Volume of solution (ml)}} \times 100
\]

% by volume = \( \frac{V}{V} \times 100 \)

**Weight – volume percent (w/V) :-**

Weight of solute in gm present in 100ml of the solution is called weight – volume percent.

\[
\text{weight – Volume percent} = \frac{\text{weight of solute (g)}}{\text{Volume of solution (ml)}} \times 100
\]

% by strength = \( \frac{W}{V} \times 100 \)

**Normality:** The number of gram equivalents of the solute dissolved per litre of the solution. It is denoted by ‘N’:

Normality = \( \frac{\text{number of gram equivalents of solute}}{\text{Volume of solution (lit.)}} \)

\[
\therefore \quad \text{Gram equivalents of solute} = \frac{\text{weight of solute (g)}}{\text{equivalent weight of solute}}
\]

\[
\therefore \quad \text{Normality} = \frac{\text{weight of solute (g)}}{\text{equivalent weight of solute}} \times \frac{1}{\text{volume of solution (lit.)}}
\]

**Formula:**

\[
N = \frac{w}{E} \times \frac{1}{V(\text{lit.})} \quad (1)
\]

\[
N = \frac{w}{E} \times \frac{1000}{V(\text{ml})} \quad (2)
\]
\[
N = n_E \times \frac{1}{V(lit)} \quad (3)
\]
\[
n_E = N \times V \quad (4)
\]

\(w\) = weight of solute (g), \(E\) = Equivalent weight of solute (To calculate equivalent weight see the section after gravimetric analysis), \(V\) = volume of solution, \(n_E\) = number of gram equivalent of solute.

Number of Gram equivalents = Normality of solution \(\times\) volume of solution (lit.)

Milli gram equivalents = Normality of solution \(\times\) volume of solution (ml)

1 gram equivalent = 1000 milli equivalent.

<table>
<thead>
<tr>
<th>(N/2)</th>
<th>(N/5)</th>
<th>(N/10)</th>
<th>(N/100)</th>
<th>(N/1000)</th>
<th>Normal</th>
<th>Normal</th>
<th>Normal</th>
<th>Normal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semi</td>
<td>Penti</td>
<td>Deci</td>
<td>Centi</td>
<td>milli</td>
<td>normal</td>
<td>Penta</td>
<td>Deca</td>
<td></td>
</tr>
<tr>
<td>normal</td>
<td>normal</td>
<td>normal</td>
<td>normal</td>
<td>normal</td>
<td>normal</td>
<td>normal</td>
<td>normal</td>
<td></td>
</tr>
</tbody>
</table>

**gm Equivalent**

per litre. →

<table>
<thead>
<tr>
<th>(\frac{1}{2})</th>
<th>(\frac{1}{5})</th>
<th>(\frac{1}{10})</th>
<th>(\frac{1}{100})</th>
<th>(\frac{1}{1000})</th>
<th>1</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
</table>

If density (gm ml\(^{-1}\)) and weight (gm) of the solution is given, then

Normality \(N\) = \(\frac{w}{E} \times \frac{d}{W} \times 1000\) \quad (5) \quad (where \(d\) = density solution)

\[
N = \frac{10 \times d}{E} \quad (W = \text{Weight of solution})
\]

\[x = \frac{w}{W} \times 100 = \text{weight-weight percentage}\]

**Molarity:** The number of gram moles of the solute dissolved per litre of the solution. It is denoted by \(’M’\).

\[
\text{Molarity} = \frac{\text{Number of gram moles of solute}}{\text{volume of solution (lit.)}}
\]

\[
\therefore \quad \text{Gram moles} = \frac{\text{weight of solute (g)}}{\text{Molecular weight of solute}}
\]

\[
\therefore \quad \text{Molarity} = \frac{\text{weight of solute (g)}}{\text{Molecular weight of solute}} \times \frac{1}{\text{volume of solution (lit.)}}
\]

**Formula:**

\[
M = \frac{w}{M'} \times \frac{1}{V(lit)} \quad (1)
\]

\[
M = \frac{w}{M'} \times \frac{1000}{V(lit)} \quad (2)
\]

\[
M = n_M \times \frac{1}{V(lit)} \quad (3)
\]

\[
n_M = M \times V(lit.) \quad (4)
\]
Where, \( w \) = weight of solute, \( M' \) = Molecular weight of solute, \( V \) = volume of solution, \( n_M \) = number of gram moles.

Gram moles = Molarity of solution \( \times \) volume of solution (litre)
Milli moles = Molarity of solution \( \times \) volume of solution (ml)
1 Gram mole = 1000 milli moles

<table>
<thead>
<tr>
<th>( M )</th>
<th>( M )</th>
<th>( M )</th>
<th>( M )</th>
<th>( M )</th>
<th>( M )</th>
<th>( M )</th>
<th>( M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5</td>
<td>10</td>
<td>100</td>
<td>1000</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Semi molar</td>
<td>Pentimolar</td>
<td>Decimolar</td>
<td>Centimolar</td>
<td>millimolar</td>
<td>molar</td>
<td>Penta molar</td>
<td>Decimolar</td>
</tr>
<tr>
<td>( \text{sol}^n )</td>
<td>( \text{sol}^n )</td>
<td>( \text{sol}^n )</td>
<td>( \text{sol}^n )</td>
<td>( \text{sol}^n )</td>
<td>( \text{sol}^n )</td>
<td>( \text{sol}^n )</td>
<td>( \text{sol}^n )</td>
</tr>
</tbody>
</table>

No. of \( \rightarrow \) gm moles per lit.

| \( \frac{1}{2} \) | \( 1 \) | \( 1 \) | \( 1 \) | \( 1 \) | \( 1 \) | \( 5 \) | \( 10 \) |

If density and weight of the solution is given, then

Molarity = \( M = \frac{w}{M'} \times \frac{d}{W} \times 1000 \) (5)

\[
M = \frac{10 \times d}{M'}
\] (6)

Where, \( d \) = density of \( \text{sol}^n \), \( W \) = weight of \( \text{sol}^n \). Then volume of \( \text{sol}^n \) = \( V = \frac{W}{d} \)

\[
x = \frac{w}{W} \times 100 = \text{weight} - \text{weight percentage}
\]

Molarity of dilution:

Before dilution \( M_1V_1 \) = After dilution \( M_2V_2 \)

Molarity of mixing:

\[
M_1V_1 + M_2V_2 + M_3V_3 = M_R (V_1 + V_2 + V_3)
\]

\( M_R = \) resultant molarity

Specific gravity of solution:

\[
\text{Specific gravity} = \frac{\text{weight of solution}}{\text{volume of solution}} \text{ i.e., weight of 1mL solution.}
\]

Molarity: The number of gram moles of solute dissolved in 1000gm of 1kg of the solvent. It is denoted by 'm'

\[
\text{Molarity} = \frac{\text{Gram moles of solute}}{\text{weight of solvent (kg)}}
\]

\[
\therefore \text{Gram moles of solute} = \frac{\text{weight of solute (g)}}{\text{Molecular weight of solute}}
\]
Molarity = \frac{\text{weight of solute (g)}}{\text{Molecular weight of solute} \times \text{weight of solvent}}

**Formula:**

\[ m = \frac{w}{M} \times \frac{1}{W(kg)} \] \hspace{1cm} (1)

\[ m = \frac{w}{M} \times \frac{1000}{W(g)} \] \hspace{1cm} (2)

\[ m = n_M \times \frac{1}{W(kg)} \] \hspace{1cm} (3)

where \( w \) = weight of solute, \( M \) = molecular weight of solute, \( W \) = weight of solvent, \( n_M \) = no. of moles of solute

Molarity is the most convenient method to express the concentration because it involves the mass of liquids rather than their volumes. It is also independent of variation of temperature.

**Formality:** The no. of gram formula weight of a solute dissolved per litre of the solution is called formality of the solution. It is denoted by 'F'.

**Formula:**

\[ F = \frac{w}{f} \times \frac{1}{V(\text{litre})} \] \hspace{1cm} (1)

\[ F = \frac{w}{F} \times \frac{1000}{V(\text{mL})} \] \hspace{1cm} (2)

\[ F = n_f \times \frac{1}{V(\text{litre})} \] \hspace{1cm} (3)

Where, \( w \) = weight of solute, \( f \) = formula weight of solute, \( V \) = volume of solution, \( n_f \) = no. of gram formula weight.

**Mole fraction:** The mole fraction of a component in a solution is the ratio of the number of moles of that components to the total number of moles present in the solution.

Suppose \( A \rightarrow \text{Solute} \) \( B \rightarrow \text{Solvent} \) Solution; \( n_A \) = No. of moles of solute, \( n_B \) = No. of moles of solvent

Then mole fraction of solute \( X_A = \frac{n_A}{n_A + n_B} \)

Mole fraction of solvent \( X_B = \frac{n_B}{n_A + n_B} \); \( X_A + X_B = 1 \)

**For gaseous mixture:**

A binary system of two gases A & B

\( P_A \) = Partial pressure of A

\( P_B \) = partial pressure of B

\( P = P_A + P_B \) = Total pressure of gaseous mixture

Mole fraction of gas A: \( X_A = \frac{P_A}{P_A + P_B} = \frac{P_A}{P} \)
Mole fraction of gas B: \( X_B = \frac{P_B}{P_A + P_B} = \frac{P_B}{P} \)

Mole percentage:

Mole percentage = Mole fraction \times 100
Mole percent of A = \( X_A \times 100 \)
Mole percent of B = \( X_B \times 100 \)

ppm. (Parts per million): The parts of the component per million (10\(^6\)) parts of the solution.

\[ ppm = \frac{w}{W+w} \times 10^6; \quad \text{Where, } w = \text{weight of solute, } W = \text{weight of solvent.} \]

SOLVED EXAMPLE

Ex.1 Calculate the percentage composition in terms of mass of a solution obtained by mixing 300g of a 25% and 400g of a 40% solution by mass.

Sol. 25% sol. means 25g solute in 100g solution 40% solution means 40g solute in 100g solution

Mass of solute in 300g solution = \( \frac{25 \times 300}{100} = 75g \)

Mass of solute in 400g solution = \( \frac{40 \times 300}{100} = 160g \)

\( \therefore \) Total mass of solute = 75 + 160 = 235g

\( \therefore \) Mass % in mixture = \( \frac{235}{700} \times 100 = 33.57\% \)

Ex.2 A sample of NaNO\(_3\) weighing 0.38g is placed in a 50.0mL volumetric flask. The flask is then filled with water to the mark on the neck. What is the molarity of the solution.

Sol. Molarity \( \times \) Volume in mL = Milli-mole

\[ = \frac{w}{M} \times 1000 \]

\( \therefore \) Molarity \( \times \) 50 = \( \frac{0.38}{85} \times 1000 \)

[ Mol. wt. of NaNO\(_3\) = 85 ]

\( \therefore \) Molarity = 8.94 \times 10^{-2}

Ex.3 Chemical absorbers can be used to remove exhaled CO\(_2\) of space travellers in short space flights. Li\(_2\)O is one of the most efficient in terms of absorbing capacity per unit weight. If the reaction is:

Sol. Li\(_2\)O + CO\(_2\) \rightarrow Li\(_2\)CO\(_3\)
∵ 30g Li$_2$O absorbs $= 22.4$ litre CO$_2$

∴ 100g Li$_2$O absorbs $\frac{22.4 \times 1000}{30} = 746.67$ litre CO$_2$

**Ex.4** A solution of specific gravity 1.6 g mL$^{-1}$ is 67% by mass. What will be the % by mass of the solutions of same acid if it is diluted to specific gravity 1.2 g mL$^{-1}$?

**Sol.** Let the volume of Solution is 100 mL, then

Mass of Solution $= 100 \times 1.6 = 160g$

Mass of solute $= \frac{67 \times 160}{100} = 107.2g$ (∵ 67% by mass)

Suppose $x$ g H$_2$O (or $x$ mL H$_2$O) is added in it (∵ $d_{H_2O} = 1g/mL$)

Mass of new Solution $= (100 + x)g$

∴ Volume of new Solution $= (100 + x)$ mL

∴ Mass of new Solution $= (100 + x) \times 1.2g$ (∵ $d_{sol.} = 1.2$ g/mL)

∴ $160 + x = (120 + 1.2x)g$

$x = 200$ mL or 200 g

∴ Conc. of new Sol. (% by mass)

$$= \frac{107.2}{(160 + 200)} \times 100 = 29.78\%$$

**Ex.5** 250mL of $xM$ solution and 500mL of $yM$ solution of a solute A are mixed and diluted to 2 litre to produce a final concentration of 1.6 $M$. If $x:y = 5:4$, calculate $x$ and $y$.

**Sol.**

m-mole of solute A $= 250 \times x$ (Solution I)

m-mole of solute A $= 500 \times x$ (Solution II)

∴ Total m-mole of solute $= 250x + 500y$

Because final concentration is 1.6 $M$ and therefore,

m-mole of solute A is resultant Solution

$$= 1.6 \times 2000$$ (∵ $V = 2L$)

∴ $250x + 500y = 1.6 \times 2000$ (1)

And

$$\frac{x}{y} = \frac{5}{4}$$

∴ $4x = 5y$
Solving eq. (10 and 2),
\[ x = 4.92; \quad y = 3.94 \]

**Ex.6** A sea water sample has density of 1.03 g/cm\(^3\) and 2.8\% NaCl by mass. A saturated solution of NaCl in water is 5.45 \(M\) NaCl. How much water would have to be evaporated from 10\(^6\) litre of sea water before NaCl would precipitate?

**Sol.** From the data
\[ M_{\text{sea water}} = \frac{2.8 \times 100}{5.85 \times \frac{100}{1000}} = 0.493 \]

Now on heating water is evaporated and suppose VL solution is left with molarity 5.45 \(M\).

\[ 5.45 \times V = 0.493 \times 10^6 \]

\[ V = 9.1 \times 10^4 \text{L} \]

Thus,

Volume of water evaporated = 100 \times 10^4 − 9.1 \times 10^4

\[ = 90.9 \times 10^4 \text{L} \]

**EXERCISE**

1. 1g charcoal is placed in 100mL of 0.5 \(M\) CH\(_3\)COOH to form an absorbed mono-layer of acetic acid molecule and there by the molarity of CH\(_3\)COOH reduces to 0.49. Calculate the surface area of charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal = 3.01 \times 10^2 m\(^2\)/g.

Ans. \((5 \times 10^{-19} \text{ m}^2)\)

2. A sample of NaCl contains NaNO\(_3\) as an impurity, 250 ml of its solution were prepared by dissolving 1.25g of the sample. 25ml of this solution required 17.75 ml. of (M/10) AgNO\(_3\) solution. Calculate the composition of the solution in g/litre.

Ans. \((0.8464 \text{ g/lit.})\)

3. How much CaCl\(_2\). 6H\(_2\)O and water must be weighed to prepare 100g of a solution that is 5.0\% CaCl\(_2\)?

Ans. \((9.9 \text{g CaCl}_2 \cdot 6\text{H}_2\text{O}, 90.1 \text{g water})\)
4. What will be the final concentration of solution when 2.0 litre of 3.0 \( M \) sugar solution and 3.0 litre of 2.5 \( M \) sugar solutions are mixed? If the solution is now diluted to 10 litre what molarity will it have?

Ans. (2.7 \( M \), 1.35 \( M \))

5. An antifreeze solution is prepared from 222.6g of ethylene glycol \([\text{C}_2\text{H}_4\text{(OH)}_2]\) and 200g of water. Calculate the molality of the solution. If the density of the solution is 1.072g mL\(^{-1}\) then what shall be the molarity of the solution?

Ans. (17.95 \( m \), 9.11M.)

6. Calculate the amount of oxalic acid \((\text{H}_2\text{C}_2\text{O}_4\cdot\text{2H}_2\text{O})\) required to obtain 250 mL of decimolar solution.

Ans. (3.15 g)

7. How many gram of \( \text{Al}_2(\text{SO}_4)_3 \) are present in 100 mL of 0.15 \( m \) solution of \( \text{Al}_2(\text{SO}_4)_3 \)? The density of solution is 1.4 g/mL.

Ans. (6.83g \( \text{Al}_2(\text{SO}_4)_3 \).)

8. How much 1.0 \( M \) HCl should be mixed with what volume of 0.250 \( M \) HCl in order to prepare 2.0 litre of 0.50 \( M \) HCl?

Ans. (666 mL, 1334mL)

OXIDATION NUMBER (OXIDATION STATE):

Oxidation state of an element in a particular species (atoms, molecules or ions) is the number of electrons gained or lost by that element during its change from free state into that species. For example, the oxidation state of Na in NaCl is +1, of calcium in \( \text{Ca}_3(\text{PO}_4)_2 \) is +2, of chlorine in Cl\(_2\) is zero.

(1) Oxidation no. is given positive sign if electrons are lost, oxidation no. is given negative sign if electrons are gained.

(2) Oxidation no. represents real charge 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 decided oxidation no. of elements on the basis of their periodic properties.

1. In uncombined state or free state, oxidation number of an element is zero.

2. In combined state oxidation no. of
   (a) F is always −1.
   (b) O is −2, In peroxides it is −1, in superoxides it is −1/2. However in \( \text{F}_2\text{O} \) it is +2.
   (c) H is +1. In ionic hydrides it is −1 (i.e., IA, IIA and IIIA metals hydrides).
   (d) halogens as halide is always −1.
(e) sulphur as sulphide is always $-2$.
(f) metals is always $+ve$.
(g) alkali metals (i.e., IA group – Li, Na, K, Rb, Cs, Fr) is always $+1$.
(h) alkaline earth metals (i.e., IIA group – Be, Mg, Ca, Sr, Ba, Ra) is always $+2$.

3. The algebraic sum of the oxidation no. of all the atoms in a compound is equal to zero, e.g. KMnO$_4$. Oxidation no. of K + Ox. no. of Mn + (Ox. no. of O) $\times 4 = 0$

\[ (+1) + (+7) + 4 \times (-2) = 0 \]

4. 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 + $3 \times$ (Oxidation no. of 3O) = $-2$

\[ (+4) + 3 \times (-2) = -2 \]

5. Oxidation number can be zero, +ve, −ve (integer or fraction)

6. Maximum oxidation no. of an element is = Group number (Except O and F)
Minimum oxidation no. of an element is = Group number $-8$ (Except metals)

Example

Find the oxidation number of

(a) S in SO$_4^{2-}$ ion
(b) S in HSO$_3^-$ ion
(c) Pt in (PtCl$_6$)$^{2-}$
(d) Mn in (MnO$_4$)$^-$_ion

Sol.

(a) Let the oxidation number of S be x.
We know that Ox. no. of O = $-2$
So Ox. no S + 4 (Ox. no. O) = $-2$ \( \Rightarrow x + 4(-2) = -2 \)
or \( x - 8 = -2 \Rightarrow x = +8 - 2 = +6. \)

(b) Let the oxidation number of S be x in HSO$_3^-$ ion.
We know that Ox. no. of H = $+1$ and that of O = $-2$
So, Ox. no. H + Ox. no. S + 3 (Ox. no. O) = $-1$
\[ +1 + x + 3 (-2) = -1 \Rightarrow +1 + x - 6 = -1 \Rightarrow x - 5 = -1 \]
or \( x = +5 - 1 = +4 \Rightarrow \) The oxidation number of S in HSO$_3^-$ ion is $+4$.

(c) Let oxidation number of Pt be x. We know that Ox. no. of Cl = $-1$
So Ox. no. Pt + 6 (Ox. no. Cl) = $-2$ \( \Rightarrow x + 6 (-1) = -2 \)
or \( x - 6 = -2 \Rightarrow \) The oxidation number of Pt in [Pt(Cl)$_6$]$^{2-}$ ion is $+4$.

(d) Let oxidation number of Mn be x. We know that Ox. no. of O = $-2$
So Ox. no. Mn + 4 (Ox. no. O) = $-1$ \( \Rightarrow x + 4(-2) = -1 \Rightarrow x - 8 = -1 \)
or \( x = +8 - 1 = +7 \Rightarrow \) The oxidation number of Mn in [MnO$_4$]$^-$ ion is $+7$
INTRODUCTION TO REDOX REACTION:

Oxidation: It is a process in which electrons are lost by an atom, ion or molecule.

\[
\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \\
2\text{Cl} \rightarrow \text{Cl}_2 + 2e^- \\
\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^-
\]

Reduction: Reduction is a process in which electrons are gained by an atom, ion or molecule.

\[
\text{Na}^+ + e^- \rightarrow \text{Na} \\
\text{I}_2 + 2e^- \rightarrow 2\text{I}^- \\
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-
\]

Redox Reactions: Those reactions in which electrons are transferred from one substance to another are called Redox Reactions.

\[
\text{Zn} + \text{Fe}^{2+} \rightarrow \text{Zn}^{2+} + \text{Fe} \\
\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}
\]

Example 4.

5 moles of \( \text{K}_2\text{Cr}_2\text{O}_7 \) gains 30 moles of \( e^- \). Determine the final oxidation state of Cr?

Sol.

5 moles \( \rightarrow \) 30 moles of \( e^- \)
1 mole \( \rightarrow \) 6 moles of \( e^- \)
2 atoms = 6/2 moles of \( e^- \)
3\( e^- \) + Cr\( ^{6+} \) \( \rightarrow \) Cr\( ^{3+} \)

Example 5.

What will be the final oxidation state of an ion \( A^{+3} \) if it gains 7\( e^- \)?

Sol.

7\( e^- \) + \( A^{+3} \) \( \rightarrow \) \( A^{-4} \)

OXIDISING AGENTS AND REDUCING AGENTS (OXIDANTS AND REDUCTANTS):

Those species (atoms, molecules and ions) which have the tendency to accept the electrons are known as oxidizing agents or oxidants, whereas those species (atoms, molecules and ions) which release the electrons are called reducing agents or reductants. In other words, oxidizing agents are reduced and reducing agents are oxidized.

(1) Oxidants are substances which:

(a) oxidize other
(b) are reduced themselves
(c) show electronation
(d) show a decrease in oxidation number during a redox change
(e) has higher oxidation no. in a conjugate pair of redox.
(2) **Reductant are substances which:**

(a) reduce other  
(b) are oxidized themselves  
(c) show de-electronation  
(d) show an increase in oxidation no. during a redox change  
(e) has lower oxidation no. in a conjugate pair of redox

(3) **A redox change is one in which a reductant is oxidized to liberate electrons, which are then used up by an oxidant to get itself reduced.**

\[
M_1 \rightarrow M_1^{+n} + \text{ne} \quad \text{oxidation} \\
M_2^{+n} + \text{ne} \rightarrow M_2 \quad \text{reduction} \\
M_1 + M_2^{+n} \rightarrow M_1^{+n} + M_2 \quad \text{Redox reaction}
\]

(4) **A redox change occurs simultaneously. For example,**

\[
2\text{KMnO}_4 + 10\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{Fe}_2(\text{SO})_3 + 8\text{H}_2\text{O}
\]

One can see the above the equation in the ionic form,

\[
\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}
\]

(As MnO$_4^-$ is accepting 5e$^-$, so it is being reduced and hence it is an oxidant)

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-
\]

As Fe$^{2+}$ is losing 1e$^-$, so it is being reduced and hence it is a reducing agent Similarly,

\[
\text{PbS} + 4\text{H}_2\text{O}_2 \rightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}
\]

Reductant Oxidant

\[
\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}
\]

Oxidant Reductant

\[
\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}
\]

Oxidant Reductant
### COMMON OXIDISING AND REDUCING AGENTS

<table>
<thead>
<tr>
<th>Oxidising agent</th>
<th>Effective Change</th>
<th>Decrease in Oxidation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMnO$_4$ in acid solution</td>
<td>MnO$_4^-$ → Mn$^{2+}$</td>
<td>5</td>
</tr>
<tr>
<td>KMnO$_4$ in neutral solution</td>
<td>MnO$_4^-$ → MnO$_2$</td>
<td>3</td>
</tr>
<tr>
<td>K$_2$Cr$_2$O$_7$ in acid solution</td>
<td>Cr$_2$O$_7^{2-}$ → Cr$^{3+}$</td>
<td>3</td>
</tr>
<tr>
<td>dilute HNO$_3$</td>
<td>NO$_3^-$ → NO</td>
<td>3</td>
</tr>
<tr>
<td>concentrated HNO$_3$</td>
<td>NO$_3^-$ → NO$_2$</td>
<td>1</td>
</tr>
<tr>
<td>concentrated H$_2$SO$_4$</td>
<td>SO$_4^{2-}$ → SO$_2$</td>
<td>2</td>
</tr>
<tr>
<td>manganese (IV) oxide</td>
<td>MnO$_2$ → Mn$^{2+}$</td>
<td>2</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl$_2$ → Cl$^-$</td>
<td>1</td>
</tr>
<tr>
<td>Chloric (I) acid</td>
<td>ClO$^-$ → Cl$^-$</td>
<td>2</td>
</tr>
<tr>
<td>KIO$_3$ in dilute acid</td>
<td>IO$_3^-$ → I$_2$</td>
<td>5</td>
</tr>
<tr>
<td>KIO$_3$ in concentrated acid</td>
<td>IO$_3^-$ → I$^+$</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reducing agent</th>
<th>Effective Change</th>
<th>Increase in Oxidation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (II) salts (acid)</td>
<td>Fe$^{2+}$ → Fe$^{3+}$</td>
<td>1</td>
</tr>
<tr>
<td>tin (II) salts (acid)</td>
<td>Sn$^{2+}$ → Sn$^{4+}$</td>
<td>2</td>
</tr>
<tr>
<td>oxalate (acid)</td>
<td>C$_2$O$_4^{2-}$ → CO$_2$</td>
<td>1</td>
</tr>
<tr>
<td>sulphites (acid)</td>
<td>SO$_3^{2-}$ → SO$_4^{2-}$</td>
<td>2</td>
</tr>
<tr>
<td>sulphide</td>
<td>S$^{2-}$ → S</td>
<td>2</td>
</tr>
<tr>
<td>iodides (dilute acid)</td>
<td>I$^-$ → I$_2$</td>
<td>1</td>
</tr>
<tr>
<td>iodides (concentrated acid)</td>
<td>I$^-$ → I$^+$</td>
<td>2</td>
</tr>
<tr>
<td>metals, e.g. Zn</td>
<td>Zn → Zn$^{2+}$</td>
<td>2</td>
</tr>
<tr>
<td>hydrogen</td>
<td>H$_2$ → H$^+$</td>
<td>1</td>
</tr>
</tbody>
</table>
TITRATION:

Titration is a procedure of determination of concentration of unknown solution with the help of solution of known concentration.

In this procedure for determining the concentration of solution A, to its known volume is added by a carefully measured volume of a solution with known concentration of B until the reaction of A & B is just complete.

The fundamental basis of titration is the “Law of equivalence” which states that at end point of a titration volumes of the two titrants reacted have the same number of equivalents or milli equivalents.

**Acid-base titration:** Titrations are often used for acid-base reactions. Prior to the start of an acid-base titration, a drop or two of an indicator solution is added to the solution in the receiving flask. An acid-base indicator is a dye that has one color in an acidic solution and a different color in a basic solution. Phenolphthalein, is more commonly used in acid-base titrations. It is colorless in acid and pink in base.

During an acid-base titration, the analyst adds titrant slowly, watching for a change in the indicator color, which would signal that the solution has changed from acidic to basic (or basic to acidic, depending on the nature of the reactants in the buret and flask). Usually this color change is very abrupt, and occurs with the addition of only one final drop of the titrant just as the end of the reaction is reached. When the color change is observed, the end point has been reached. At this time the addition of titrant is stopped and the total volume of the titrant that’s been added to the receiving flask is recorded.

One gm equivalent of acid is neutralized by one gm equivalent of base.

It means – equivalents of acid = equivalents of base

\[
\text{Acid } [N_1V_1] = \text{Base } [N_2V_2] \quad \text{[}\because\text{ gm equivalent } = \text{Normality } \times \text{ volume}]\]

**Back titration:** Back titration is used in volumetric analysis to find out excess of reagent added by titrating it with suitable reagent. It is also used to find out percentage purity of sample. For example in acid-base titration suppose we have added excess base in acid mixture. To find excess base we can titrate the solution with another acid of known strength.

Let us assume that we are given a solid substance Na$_2$CO$_3$ (C) and two solutions HCl (A) and NaOH (B)

Therefore, out of x equivalent of HCl (excess equivalent of HCl w.r.t. Na$_2$CO$_3$) reacts with NaOH.

Let no. of equivalents of HCl is x and NaOH is y such that x > y

\[\because\text{ Equivalents of HCl reacted with Na}_2\text{CO}_3 = x - y\]

\[\therefore\text{ Equivalents of Na}_2\text{CO}_3 = x - y\]

For the reaction, Na$_2$CO$_3$ + 2HCl \rightarrow 2NaCl + CO$_2$ + H$_2$O

N factor of Na$_2$CO$_3$ = 2

Moles Na$_2$CO$_3$ = \(\frac{x-y}{n}\) = \(\frac{x-y}{2}\)

Weight of pure Na$_2$CO$_3$ = \(\left(\frac{x-y}{2}\right) \times 106g\)
Let, the weight of sample of Na$_2$CO$_3$ = wg

% purity of Na$_2$CO$_3$ = \( \left( \frac{x-y}{2} \right) \times \frac{106}{w} \times 100 \)

**Precipitation titration:** In ionic reaction we can know the strength of unknown solution of a salt by titrating it against a reagent with which it can form precipitate. For example NaCl strength can be known by titrating it against AgNO$_3$ solution with which it forms white ppt. of AgCl. So meq. of NaCl at equivalence point = meq of AgNO$_3$ used = meq of AgCl formed

**Double indicator acid-base titration:** In the acid-base titration the equivalence point is known with the help of indicator which changes its colour at the end point. In the titration of polyacidic base of or polybasic acid there are more than one end point. One indicator is not able to give colour change at every end point. So to find out each end point we have to use more than one indicator is not able to give colour change at every end point. So to find out each end point we have to use more than one indicator. For example in the titration of Na$_2$CO$_3$ against HCl there are two end points.

\[
\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{NaCl}
\]

\[
\text{NaHCO}_3 + \text{HCl} \rightarrow \text{H}_2\text{CO}_3 + \text{NaCl}
\]

When we use phenolphthalein in the above titration it changes its colour at first end point when NaHCO$_3$ is formed and with it we can not know second end point. Similarly with methyl orange it changes its colour at second end point only and we can not know first end point. It is because all indicators change colour on the basis of pH of medium. So in the titration of NaHCO$_3$, KHCO$_3$ against acid phenolphthalein can not be used.

**SOLVED EXAMPLES**

**Ex.1** A 1.2g of a mixture containing H$_2$C$_2$O$_4$.2H$_2$O and KHC$_2$O$_4$.H$_2$O and impurities of a neutral salt, consumed 18.9ml of 0.5N NaOH for complete neutralization. On titration with KMnO$_4$ solution 0.4g of the same substance needed 21.55mol of 0.25N KMnO$_4$. Calculate the percentage composition of the substance.

**Sol.** Let the mass of H$_2$C$_2$O$_4$.2H$_2$O and KHC$_2$O$_4$.H$_2$O be x and y g respectively.

\[
\frac{x}{126} \times 2 + \frac{y}{146} \times 1 = \frac{0.5 \times 18.9}{1000} ; \quad \frac{x}{126} \times 2 + \frac{y}{146} \times 2 = \frac{21.55 \times 0.25 \times 3}{1000}
\]

\[
\therefore x = 0.1764\text{g}, \; y = 0.9709\text{g}
\]

% H$_2$C$_2$O$_4$.H$_2$O = \( \frac{0.1764}{1.2} \times 100 = 14.7% \); % KHC$_2$O$_4$.H$_2$O = \( \frac{0.9709}{1.2} \times 100 = 80.9% \)

**Ex.2** Determine which reagent is in excess and by how much amount if 100g P$_4$O$_6$ is treated with 100g of KMnO$_4$ in HCl solution to form H$_3$PO$_4$ and MnCl$_2$.

**Sol.** P$_4^{+3}$ → 4P$_5^{+5}$ + 8e

Mn$^{+7}$ + 5e → Mn$^{2+}$ (acid medium)
Meq. of KMnO$_4$ = $\frac{100 \times 5 \times 1000}{158} = 3164.56$

Meq. of P$_4$O$_6$ = $\frac{100 \times 8 \times 1000}{219.9} = 3638.02$

Meq. of P$_4$O$_6$ in excess = 473.46

\[ \therefore \frac{W_{P_4O_6(excess)}}{219.9} \times 8 \times 1000 = 473.46 \]

\[ W_{P_4O_6} \text{(in excess)} = 13.01 \]

**Ex.3**

1g mixture containing equal number of moles of carbonates of two alkali metals required 44.4 ml of 0.5 N HCl for complete neutralization. The atomic weight of one metal is 7, find the atomic weight of other metal. Also calculate the amount of sulphate formed on quantitative conversion of 1.0g of the mixture into sulphates.

**Sol.**

Let two carbonates are $M'_2CO_3$ and $M''_2CO_3$ since alkali metals are monovalent

Also $M'_2CO_3 = a \text{ g}$, $M''_2CO_3 = b \text{ g}$

\[ A + b = 1 \quad (1) \]

\[ M_{M'_2CO_3} = 2 \times 7 + 60 = 74, \quad M_{M''_2CO_3} = 2m + 60 \]

\[ \therefore \frac{a}{74} = \frac{b}{2m+60} \quad (2) \]

Meq. of carbonate 1 + Meq. of carbonate (2) = Meq. of HCl

\[ \therefore \frac{a}{74/2} \times 1000 + \frac{b}{(2m+60)/2} \times 1000 = 44.4 \times 0.5 \quad (3) \]

Solving equation (1), (2) and (3) : $m = 23$, $a = 0.41 \text{ g}$, $b = 0.59 \text{ g}$

Meq. of sulphates ($M'_2SO_4$) = Meq. of $M'_2CO_3 = \frac{0.41}{74/2} \times 1000 = 11.08$

\[ = \frac{W}{142/2} \times 1000 = 11.08, \quad \therefore W_{M'_2SO_4} = 0.609 \text{ g} \]

Meq. of sulphate ($M'_2SO_4$) = Meq. of $M''_2CO_3$

\[ = \frac{W}{142/2} \times 1000 = \frac{0.59}{106/2} \times 1000 \quad \therefore W_{M''_2SO_4} = 0.7902 \text{ g} \]

\[ \therefore \text{Weight of sulphates} = 0.6094 + 0.7902 = 1.3996 \text{ g} \]

**Ex.4**

7.68g of a mixture of Na$_2$CO$_3$ and NaHCO$_3$ was dissolved in water and made up to a litre. 20ml of the made up solution required 24ml of 0.1 N HCl for neutralisation using methyl orange as indicator. Calculate the volume of the same acid required to neutralise 20ml of the solution to phenolphthalein end point.

**Sol.**

\[
\begin{align*}
\text{Na}_2\text{CO}_3 & \xrightarrow{\text{Phenolphthalein}} \text{NaHCO}_3 \xrightarrow{\text{NaCl}} \text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} \\
\text{NaHCO}_3 \xrightarrow{\text{methyl orange}} \text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]
**Na₂CO₃** : Na₂CO₃ + 2HCl → 2NaCl + CO₂ + H₂O

Volume of HCl required to completely neturalise Na₂CO₃ = 2x ml

Amount of Na₂CO₃ present in a litre of solution = \( \frac{2x \times 0.1}{20} \times 53 = 0.53x \text{ g} \)

**NaHCO₃** : NaHCO₃ + HCl → NaCl + H₂O + CO₂

Volume of HCl required to neturalise NaHCO₃ in the mixture = (24 – 2x) ml

Amount of NaHCO₃ present in a litre of solution = \( \frac{(24-2x) \times 0.1}{20} \times 84 \)

= 10.08 – 0.84x g

Total amount of Na₂CO₃ and NaHCO₃ present in a litre of solution = 0.53x + 10.08 – 0.84x = 7.68

0.31x = 2.4

\( x = \frac{2.4}{0.31} = 7.74 \text{ ml} \)

**Ex. 5** 3.10 g of a mixture of CaO and MCO₃ was heated strongly. The residue weighed 2.66g. It was dissolved in 200ml of 0.5 N HCl. The excess required 32ml of 1.25 NaOH for neutralization. Identify the metal M. (Atomic weight of calcium = 40)

**Sol.** Weight of CaO + MCO₃ = 3.10g

Weight of residue i.e, CaO + MO = 2.66g

Weight of CO₂ evolved = 0.44g = \( \frac{0.44}{44} \) mole = 0.01 mole

MCO₃ = 0.01 mole (MCO₃ → MO + CO₂)

and MO = 0.01 mole

The mixture of oxides was treated with 0.5 \( \times \) 56g = 1.12g

But CaO + MO = 2.66g

MO = 2.66 – 1.12 = 1.54g

MO = 0.01 mole i.e, 0.01 mole = 1.54g

1 mole of MO = 154g, i.e. Mole weight = 154.

\( \therefore \) atomic weight of M = 154 – 16 = 138, which corresponds to barium (roughly)
Ex. 6 12.53 mL of 0.509 M SeO₂ reacted with 25.52 mL 0.1 M CrSO₄ solution. In the reaction Cr²⁺ was oxidized to Cr³⁺. To what oxidations state selenium was converted in the reaction? Write the redox change for SeO₂.

**Sol.** Se⁴⁺ + (a − 4)e → Seᵃ⁺  

\[ n = a - 4 \] 

(where \( n \) is valence factor)  

or  

\[ \text{Cr}^{2+} \rightarrow \text{Cr}^{3+} + e \]  

Meq. of SeO₂ = Meq. of CrSO₄  

\[ 0.0509 \times n \times 12.53 = 0.1 \times 1 \times 25.52 \]  

:\. \[ n = 4 \]  

\[ a - 4 = 4 \]  

or \[ a = 0 \]  

Thus redox change is: Se⁴⁺ + 4e → Se⁰

Ex. 7 Mn²⁺ (aq) can be determined by titration with MnO₄⁻ (aq) 3 Mn²⁺ + 2 MnO₄⁻ → 6 MnO₂ + 2 H₂O  

A 25.00 mL sample of Mn²⁺ (aq) requires 34.77 mL of 0.05876 M KMnO₄ (aq) for its titration. What is the molarity of the Mn²⁺ (aq)?

**Sol.** Mn²⁺ → Mn⁴⁺ + 2e  

Mn⁷⁺ + 3e → Mn⁴⁺  

Also, Meq. of MnO₄⁻ = Meq. of Mn²⁺  

\[ 0.05876 \times 3 \times 34.77 = M \times 2 \times 25 \]  

\[ M_{Mn²⁺} = 0.1226 \ M \]

Ex. 8 What mass of K₂Cr₂O₇ is required to produce 5.0 litre CO₂ at 75⁰C and 1.07 atm pressure on treating with excess of H₂C₂O₄ in acidic medium.

**Sol.** Mole of CO₂ = \( \frac{PV}{RT} = \frac{1.07 \times 5}{0.0821 \times 348} = 0.187 \)  

\[ (C³⁺)₂ → 2C⁴⁺ + 2e \]  

\[ (C³⁺)₂ → 2C⁴⁺ + 2e \]  

\[ 6e + (Cr⁶⁺)₂ → 2Cr³⁺ \]  

:\. Meq. of K₂Cr₂O₇ = Meq. of H₂C₂O₄ = Meq. of CO₂ = Mole of CO₂ × 1000  

(Valence factor of CO₂ = 1)
\[ \frac{w}{M/6} \times 1000 = 0.187 \times 1000 \]

Or
\[ \frac{w}{M/6} \times 1000 = 0.187 \times 1000 \quad (M_{K_2Cr_2O_7} = 294.2) \]

\[ \therefore \quad w_{K_2Cr_2O_7} = \frac{0.187 \times 294.2}{6} = 9.17 \text{ g} \]

**Ex. 9** Calculate the mass of oxalic acid \((H_2C_2O_4)\) which can be oxidized to \(CO_2\) by 100.0 mL of \(MnO_4^-\) solution, 10 mL of which is capable of oxidising 50.0 mL of 1.0 \(N\) \(-I^-\) to \(I_2\).

**Sol.**
\[ Mn^{7+} + 5e \rightarrow Mn^{2+} \]
\[ 2I^- \rightarrow I_2 + 2e \]

Meq. of \(-I^-\) = Meq. of \(MnO_4^-\)
\[ 50 \times 1.0 = 10 \times N \]
\[ N_{MnO_4^-} = 5 \]

Now \(Mn^{7+} + 5e \rightarrow Mn^{2+}\)
\[ C_2^{3+} \rightarrow 2C^{4+} + 2e \]

Meq. of \(H_2C_2O_4\) = Meq. of \(MnO_4^-\)
\[ \frac{w}{90/2} \times 1000 = 5 \times 100 \]
\[ w = 22.5 \text{ g} \]

**Ex. 10** A \(KMnO_4\) solution can be standardised by titration against \(As_2O_3\) (s). A 0.1156g sample of \(As_2O_3\) requires 27.08 mL of the \(KMnO_4\)(aq) for its titration. What is the molarity of the \(KMnO_4\)(aq) \([As = 75]\).

\[ 5As_2O_3 + 4MnO_4^- + 9H_2O + 12H^+ \rightarrow 10H_2AsO_4 + 4Mn^{2+} \]

**Sol.** Meq. of \(As_2O_3\) = Meq. of \(KMnO_4\)
\[ (As_2^{3+} \rightarrow 2As^{5+} + 4e) \]
\[ \frac{0.1156}{198/4} \times 1000 = M \times 5 \times 27.08 \]
\[ (Mn^{7+} + 5e \rightarrow Mn^{2+}) \]
\[ \therefore \quad M = 0.0172 \]
\[ \therefore \quad M_{MnO_4^-} = 0.0172 \times M \]
Ex.11 25 mL of 0.017 \( M \) \( \text{H}_2\text{SO}_3 \) is strongly acidic medium required 16.9 mL of 0.01 \( M \) \( \text{KMnO}_4 \) and in neutral medium required 28.6 mL of 0.01 \( M \) \( \text{KMnO}_4 \) for complete conversion of \( \text{SO}_3^{2-} \) to \( \text{SO}_4^{2-} \). Assign the oxidation no. of Mn the product formed in each case.

Sol. 
\[ \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} \]
\[ S^{4+} \rightarrow S^{6+} + 2e \]

\( \therefore \) Valence factor of \( \text{SO}_3 \) = 2

In acid medium:

Meq. of \( \text{SO}_3^{2-} \) = Meq. of \( \text{MnO}_4^- \)
\[ 25 \times 0.017 \times 2 = 16.9 \times 0.01 \times n_1 \]
\( \therefore \) \( n_1 = 5 \)
\( \therefore \) \( \text{Mn}^{7+} + 5e \rightarrow \text{Mn}^{2+} \)

In neutral medium:

Meq. of \( \text{SO}_3^{2-} \) = Meq. of \( \text{MnO}_3^- \)
\[ 25 \times 0.017 \times 2 = 28.6 \times 0.01 \times n_2 \]
\( \therefore \) \( n_2 = 3 \)
\( \therefore \) \( \text{Mn}^{7+} + 3e \rightarrow \text{Mn}^{4+} \)

**EXERCISE**

1. What mass of \( \text{Na}_2\text{S}_2\text{O}_3\cdot\text{H}_2\text{O} \) is needed to make 500 cm\(^3\) of 0.200 \( N \) solution for the reaction: \( 2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^- \)

Ans. \((w = 24.8 \text{g})\)

2. In a reaction, \( \text{Cr}_2\text{O}_7^{2-} \) is reduced to \( \text{Cr}^{3+} \). What is concentration of 0.1 \( M \) \( \text{K}_2\text{Cr}_2\text{O}_7 \) in equivalent per litre? \( \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \)

Ans. \((0.6 \text{ \( N \)})\)

3. What is molarity and normality of a \( \text{MnO}_4^- \) solution if 32.00 mL of the solution is required to titrate 40.00 mL of 0.400 \( N \text{ Fe}^{2+} \)?

\[ \text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \]

Ans. \((0.1 \text{ \( M \)})\)

4. 40 mL of an acidified solution of 0.40 \( M \) iron (II) is completely oxidized by 32 mL \( \text{KMnO}_4 \) solution. What is molarity of \( \text{KMnO}_4 \) solution.
Ans. \((0.1 \text{ } M)\)

5. A 1.100g sample of copper ore is dissolved and the \(\text{Cu}^{2+} (aq)\) is treated with excess KI. The liberated \(\text{I}_2\) requires 12.12 mL of 0.10 \(M\) \(\text{Na}_2\text{S}_2\text{O}_3\) solution for titration. What is % copper by mass in the ore?

Ans. \(7.00\%\)

6. What mass of \(\text{N}_2\text{H}_4\) can be oxidized to \(\text{N}_2\) by 24.0g \(\text{K}_2\text{CrO}_4\), Which is reduced to \(\text{Cr(OH)}_4^-\)?

Ans. \(2.97\text{g}\)

7. It requires 40.0 mL of 0.50 \(M\) \(\text{Ce}^{4+}\) to titrate 10.0 mL of 1.0 \(M\) \(\text{Sn}^{2+}\) to \(\text{Sn}^{4+}\). What is the oxidation state of cerium in the reduced product?

Ans. \(+3\)

8. A particular acid-rain water has \(\text{SO}_3^{2-}\). If a 25.00 mL sample of this water requires 34.08 mL of 0.01964 \(M\) \(\text{KMnO}_4\) for its titration, what is the molarity of \(\text{SO}_3^{2-}\) in acid-rain?

\[
2\text{MnO}_4^- + 5\text{SO}_3^{2-} + 6\text{H}^+ \rightarrow 5 \text{SO}_4^{2-} + 2\text{Mn}^2+ 3\text{H}_2\text{O}
\]

Ans. \(0.0669 \text{ } M\)

9. Hydroxylamine reduces iron III according to the equation

\[
4\text{Fe}^{3+} + 2\text{NH}_2\text{OH} \rightarrow \text{N}_2\text{O} + \text{O}_2 + 4\text{Fe}^{2+} + 4\text{H}^+
\]

Iron II thus produced is estimated by titration with standard \(\text{KMnO}_4\) solution. The reaction is \(\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}\)

A 10mL of hydroxylamine solutions was diluted to one litre. 50mL of this diluted solution was boiled with an excess of \(\text{Fe}^{3+}\) solution. The resulting solution required 12mL of 0.02 \(M\) \(\text{KMnO}_4\) solution for complete oxidation of \(\text{Fe}^{2+}\). Calculate the mass of \(\text{NH}_2\text{OH}\) in one litre of original solution.

Ans. \(39.6 \text{ } \text{g/L}\)

10. How many mole of \(\text{FeCl}_3\) can be prepared by the reaction of 10g of \(\text{KMnO}_4\). 10.07 mole of \(\text{FeCl}_2\) and 500 mL of 3\(M\) \(\text{HCl}\) following the reaction:

\[
5\text{FeCl}_2 + \text{KMnO}_4 + 8\text{HCl} \rightarrow 5\text{FeCl}_3 + \text{KCl} + \text{MnCl}_2 + 4\text{H}_2\text{O}
\]

Ans. \(0.315 \text{ } \text{mole}\)
QUESTION BANK

OBJECTIVE TYPE QUESTIONS

1. One litre of \(N/2\) HCl solutions was heated in a beaker. When volume was reduced to 600 mL, 3.25g of HCl was given out. The new normality of solution is:
   (a) 6.85  
   (b) 0.685  
   (c) 0.1043  
   (d) 6.50

2. Molarity of \(H_2SO_4\) (density 1.8g/mL) is 18\(M\). The molarity of this \(H_2SO_4\) is:
   (a) 36  
   (b) 200  
   (c) 500  
   (d) 18

3. Volume of 2\(M\) HCl required to neutralize the solution containing 1 mole of \(NH_4Cl\) and 1 mole of NaOH is:
   (a) 1 litre  
   (b) 2 litre  
   (c) 3 litre  
   (d) 1/2 litre

4. The molality of 1\(M\) solution of \(NaCl\) (specific gravity 1.0585 g/mL) is:
   (a) 1.0585  
   (b) 1.0  
   (c) 0.10  
   (d) 0.0585

5. Two elements \(A\) (at. wt. 75) and \(B\) (at. wt. 16) combine to yield a compound. The % by weight of \(A\) in the compound was found to be 75.08. The formula of the compound is:
   (a) \(A_2B\)  
   (b) \(A_2B_3\)  
   (c) \(AB\)  
   (d) \(AB_2\)

6. 4.4g of \(CO_2\) and 2.24 litre of \(H_2\) at STP are mixed in a container. The total number of molecules present in the container will be:
   (a) \(6.022 \times 10^{23}\)  
   (b) \(1.2044 \times 10^{23}\)  
   (c) 2 mole  
   (d) \(6.023 \times 10^{24}\)

7. The hydrated salt, \(Na_2SO_4.nH_2O\) undergoes 55.9% loss in weight on heating and becomes anhydrous. The value of \(n\) will be:
   (a) 5  
   (b) 3  
   (c) 7  
   (d) 10

8. The hemoglobin from the red blood corpuscles of most mammals contains approximately 0.33% of iron by weight. The molecular weight of hemoglobin as 67,200. The number of iron atoms in each molecule of hemoglobin is (atomic weight of iron = 56):
   (a) 2  
   (b) 3  
   (c) 4  
   (d) 5

9. 3.0 molal \(NaOH\) solution has a density of 1.110 g/mL. The molarity of the solutions is:
   (a) 2.9732  
   (b) 3.05  
   (c) 3.64  
   (d) 3.0504

10. Insulin contains 3.4% sulphur. The minimum mol. weight of insulin is:
   (a) 941.176  
   (b) 944  
   (c) 945.27  
   (d) None of these

11. Number of mole of 1 m\(^3\) gas at NTP are:
   (a) 44.6  
   (b) 40.6  
   (c) 42.6  
   (d) 48.6

12. The weight of 350 mL of a diatomic gas at 0\(^0\)C and 2 atm pressure is 1g. The weight of one atom is: (\(N\) is the Av.no.)
   (a) \(16/N\)  
   (b) \(32/N\)  
   (c) \(16N\)  
   (d) \(32N\)

13. A partially dried clay mineral contains 8% water. The original sample contained 12% water and 45% silica. The % of silica in the partially dried sample is nearly:
   (a) 50%  
   (b) 49%  
   (c) 55%  
   (d) 47%
14. If half mole of oxygen combine with Al to form Al₂O₃, the weight of Al used in the reaction is:
   (a) 27g  (b) 40.5g  (c) 54g  (d) 18g

15. A compound has the molecular formula X₄O₆. If 10g of X₄O₆ has 5.72g X, atomic mass of X is:
   (a) 32 amu  (b) 37 amu  (c) 42 amu  (d) 98 amu

16. The molality of 1 litre solution with X% by weight H₂SO₄ is equal to 9. The weight of the solvent present in the solution is 910g. The value of X:
   (a) 90  (b) 80.3  (c) 40.13  (d) 9

17. The isotopic abundance of C-12 and C-14 is 98% and 2% respectively. What would be the number of C-14 isotope in 12g carbon sample.
   (a) 1.032 × 10²²  (b) 3.01 × 10²³  (c) 5.88 × 10²³  (d) 6.02 × 10²³

18. The dehydration yield of cyclohexanol to cyclohexene is 75%. What would be the yield if 100g of cyclohexanol is dehydrated:
   (a) 61.7g  (b) 16.5g  (c) 6.15g  (d) 615g

19. 10 mole of SO₂ and 15 mole of O₂. Were passed over catalyst to produce 8 mole of SO₃. The ratio of SO₂ and SO₃ moles in mixture is:
   (a) 5/4  (b) 1/4  (c) 1/2  (d) 3/4

20. Mole friction of I₂ in C₆H₆ is 0.2. The molality of I₂ in C₆H₆ is:
   (a) 3.2  (b) 6.40  (c) 1.6  (d) 2.30

21. Equal masses of O₂, H₂ and CH₄ are taken in a container. The respective mole ratio of these gases in container is:
   (a) 1:16:2  (b) 16:1:2  (c) 1:2:16  (d) 16:2:1

22. The mole fraction of the solute in one molal aqueous solution is:
   (a) 0.009  (b) 0.018  (c) 0.027  (d) 0.036

23. After equal volumes of 0.10 M solutions of (NH₄)₂SO₄ and Ba(OH)₂ have been mixed, which of the following species is present in greatest concentration in solution:
   (a) NH₄⁺(aq.)  (b) Ba²⁺(aq.)  (c) NH₃(aq.)  (d) BaSO₄(aq.)

24. Chlorophyll, a green colouring matter contains 2.68% Mg. The number of atoms of Mg present in 1g chlorophyll are:
   (a) 6.72 × 10²⁰  (b) 6.72 × 10²¹  (c) 6.72 × 10²²  (d) 6.72 × 10²³

25. 16g of SO₄ occupies 5.6 litre at STP. Assuming ideal gas nature, the value of x is:
   (a) 1  (b) 2  (c) 3  (d) None of these

26. Equal moles of H₂O and NaCl are present in a solution. The molality of NaCl solution is:
   (a) 55.6  (b) 5.56  (c) 1  (d) 0.5

27. A compound contains 10⁻²% of phosphorus. If atomic mass of phosphorus is 31, the molar mass of the compound having one phosphorus per molecule is:
   (a) 31  (b) 31 × 10²  (c) 31 × 10⁴  (d) 31 × 10³
28. \( \text{Al}_2(\text{SO}_4)_3 \cdot \text{XH}_2\text{O} \) has 8.1% aluminum by mass. The value of \( X \) is:
(a) 4  (b) 10  (c) 16  (d) 18

29. One litre of \( \text{N}_2 \) and 7/8 litre of \( \text{O}_2 \) under identical conditions of \( P \) and \( T \) are mixed. The amount of gases present in mixture show:
(a) \( w_{\text{N}_2} = 3w_{\text{O}_2} \)  (b) \( w_{\text{N}_2} = 8w_{\text{O}_2} \)  (c) \( w_{\text{N}_2} = w_{\text{O}_2} \)  (d) \( w_{\text{N}_2} = 16w_{\text{O}_2} \)

30. The atomic weight of a triatomic gas is \( a \). The correct formula for the number of moles of gas in its \( \text{w g} \) is:
(a) \( \frac{3w}{a} \)  (b) \( \frac{w}{3a} \)  (c) \( 3wa \)  (d) \( \frac{a}{3w} \)

31. 100 mL each of 0.5 \( \text{N}_2\text{OH} \), \( \text{N}/5 \) \( \text{HCl} \) and \( \text{N}/10 \) \( \text{H}_2\text{SO}_4 \) are mixed together. The resulting solution will be:
(a) Acidic  (b) Neutral  (c) Alkaline  (d) None of these

32. The equivalent weight of iron in \( \text{Fe}_2\text{O}_3 \) would be:
(a) 18.6  (b) 26.66  (c) 56  (d) 112

33. 25mL of 3.0 \( M \) \( \text{HNO}_3 \) are mixed with 75mL of 4.0 \( M \text{HNO}_3 \). If the volumes are additive, the molarity of the final mixture would be:
(a) 3.25 \( M \)  (b) 4.0 \( M \)  (c) 3.75 \( M \)  (d) 3.50 \( M \)

34. An oxide of metal have 20% oxygen. The eq. wt. of oxide is:
(a) 32  (b) 40  (c) 48  (d) 52

35. If 250 mL of a solution contains 24.5g \( \text{H}_2\text{SO}_4 \) the molarity and normality respectively are:
(a) 1\( M \), 2\( N \)  (b) 1\( M \), 0.5\( N \)  (c) 0.5\( M \), 1\( N \)  (d) 2\( M \), 1\( N \)

36. 0.5 mole of \( \text{H}_2\text{SO}_4 \) is mixed with 0.2 mole of \( \text{Ca(OH)}_2 \). The maximum number of mole of \( \text{CaSO}_4 \) formed is:
(a) 0.2  (b) 0.5  (c) 0.4  (d) 1.5

37. A metal oxide has 40% oxygen. The equivalent weight of the metal is:
(a) 12  (b) 16  (c) 24  (d) 48

38. A solution contains \( \text{Na}_2\text{CO}_3 \) and \( \text{NaHCO}_3 \). 10 mL of the solution required 2.5 mL of 0.1\( M \) \( \text{H}_2\text{SO}_4 \) for neutralization using phenolphthalein as indicator. Methyl orange is then added when a further 2.5 mL of 0.2\( M \) \( \text{H}_2\text{SO}_4 \) was required. The amount of \( \text{Na}_2\text{CO}_3 \) and \( \text{NaHCO}_3 \) in 1 litre of the solution is:
(a) 5.3g and 4.2g  (b) 3.3g and 6.2g  (c) 4.2g and 5.3g  (d) 6.2g and 3.3g

39. 0.7g of \( \text{Na}_2\text{CO}_3 \cdot \text{xH}_2\text{O} \) were dissolved in water and the volume was made to 100mL, 20mL of this solution required 19.8 mL of \( \text{N}/10 \) \( \text{HCl} \) for complete neutralization. The value of \( x \) is:
(a) 7  (b) 3  (c) 2  (d) 5

40. When a metal is burnt, its weight is increased by 24%. The equivalent weight of the metal will be:
(a) 25  (b) 24  (c) 33.3  (d) 76
41. 0.71g of chlorine combines with certain weight of a metal giving 1.11g of its chloride. The eq. wt. of the metal is:
   (a) 40   (b) 20   (c) 80   (d) None of these

42. Amount of phosphoric acid needed to neutralize 100g of magnesium hydroxide is:
   (a) 66.7g   (b) 252g   (c) 112g   (d) 168g

43. 0.078g Al(OH)₃ is dehydrated to Al₂O₃. The Al₂O₃ so obtained reacted with 6 milli equivalent of HCl. The equivalent of AlCl₃ produced during the reaction are:
   (a) 10⁻³   (b) 3 × 10⁻³   (c) 4 × 10⁻³   (d) \( \frac{10⁻³}{2} \)

44. Vapour density of a metal chloride is 66. Its oxide contains 53% metal. The atomic weight of metal is:
   (a) 21   (b) 54   (c) 26.72   (d) 2.086

45. Volume strength of H₂O₂ labelled is 10 vol. What is normality of H₂O₂:
   (a) 1.79   (b) 2.79   (c) 0.79   (d) 5.6

46. How many milli litre of 0.5M H₂SO₄ are needed to dissolve 0.5g of copper (II) carbonate:
   (a) 8.10 mL   (b) 16.20 mL   (c) 4.05 mL   (d) 12.05 mL

47. 1g of Ca was burnt in excess of O₂ and the oxide formed was dissolved to make up one litre solution. The normality and molarity of solution respectively are:
   (a) 0.05, 0.025   (b) 0.1, 0.05   (c) 0.1, 0.2   (d) 0.01, 0.02

48. \( V_1 \) mL of NaOH of normality \( X \) and \( V_2 \) mL of Ba(OH)₂ of normality \( Y \) are mixed together. The mixture is completely neutralized by 100 mL of 0.1N HCl. If \( V_1/V_2 = \frac{1}{4} \) and \( \frac{x}{y} = 4 \), what fraction of the acid is neutralized by Ba(OH)₂:
   (a) 0.5   (b) 0.25   (c) 0.33   (d) 0.67

49. An aqueous solution of 6.3g of oxalic acid dehydrate is made upto 250mL. The volume of 0.1N NaOH required to completely neutralize 10mL of this solution is:
   (a) 20mL   (b) 40mL   (c) 10mL   (d) 15mL

50. 0.63g of diabasic acid was dissolved in water. The volume of the solution was made 100mL. 20mL of this acid solution required 10mL of N/5 NaOH solution. The molecular mass of acid is:
   (a) 63   (b) 126   (c) 252   (d) 128

51. In the reaction
   \[ \text{Na}_2\text{S}_2\text{O}_3 + 4\text{Cl}_2 + 5\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 8\text{HCl} \]

   The equivalent weight of \( \text{Na}_2\text{S}_2\text{O}_3 \) will be
   (a) M/4   (b) M/8   (c) M/1   (d) M/2
52. 25mL of a solution containing HCl and H₂SO₄ required 10mL of a 1N NaOH solution for neutralization. 20mL of the same acid mixture on being treated with an excess of AgNO₃ gives 0.1435g of AgCl. The normality of the HCl and the normality of the H₂SO₄ are respectively (a) 0.40N and 0.05N (b) 0.05N and 0.35N (c) 0.50N and 0.25 N (d) 0.40N and 0.5 N

SUBJECTIVE TYPE QUESTIONS

LEVEL – 1

1. 8 litre of H₂ and 6 litre of Cl₂ are allowed to react to maximum possible extent. Find out the final volume of reaction mixture. Suppose P and T remains constant throughout the course of reaction.

2. What is the molecular weight of a substance, each molecule of which contains 9 carbon atoms, 13 hydrogen atoms and 2.33 × 10⁻³ g of other component?

3. What is the total molar concentration of ions in 0.350M solution of Na₂SO₄ assuming its complete ionization?

4. In a reaction vessel 0.184g of NaOH is required to be added for completing the reaction. How many milliliter of 0.150 M NaOH solution should be added for this requirement?

5. Find the molality of H₂SO₄ solution whose specific gravity is 1.98g mL⁻¹ and 90% (w/v) of H₂SO₄.

6. The vapour density of a mixture containing NO₂ and N₂O₄ is 38.3 at 27⁰C. Calculate the mole of NO₂ in 100g mixture.

7. Chlorine is prepared in the laboratory by treating manganese dioxide (MnO₂) with aqueous hydrochloric acid according to the reaction:

   \[ 4\text{HCl}(aq.) + \text{MnO}_2(s) \rightarrow 2\text{H}_2\text{O}(l) + \text{MnCl}_2(aq.) + \text{Cl}_2(g) \]

   How many gram of HCl react with 5.0g of manganese dioxide?

8. The concentration of Fe²⁺ ion in aqueous solution can be determined by redox titration with bromate ion, according to reaction:

   \[ 6\text{Fe}^{2+}(aq.) + 3\text{BrO}_3^-(aq.) + 6\text{H}^+(aq.) \rightarrow 6\text{Fe}^{3+}(aq.) + 3\text{Br}^-(aq.) + 3\text{H}_2\text{O}(l) \]

   What is molar concentration of Fe²⁺ if 31.50mL of 0.105 M KBrO₃ is required for complete neutralization of 10.0mL of Fe²⁺ solution.

9. The vapour density of a metal chloride is 85. If equivalent weight of metal is 7.01, calculate the at. wt. of metal.

10. 1.12g impure sample of calcium oxide was dissolved in water and the solution was completely neutralized by 21mL of 0.8 N acid. What is the purity of CaO?
11. 30mL of 0.1M BaCl₂ is mixed with 40mL of 0.2M Al₂(SO₄)₃. What is the weight of BaSO₄ formed?

\[ \text{BaCl}_2 + \text{Al}_2(\text{SO}_4)_3 \rightarrow \text{BaSO}_4 + \text{AlCl}_3 \]

12. Calculate the percentage of BaO in 29.0g mixture of BaO and CaO which just reacts with 100.8mL of 6.0M HCl.

13. A mixture of Xe and F₂ was heated and the white solid so formed reacted with H₂ to give 81 mL of Xe at STP and HF. The HF formed required 68.43mL of 0.3172M NaOH for complete neutralization. Determine empirical formula of white solid.

**LEVEL – 2**

1. A mixture of C₃H₈, CH₄ and CO contains 36.5% C₃H₈ (by volume). When 100mL of this mixture is burnt, find out the volume (in mL) of CO₂ liberated.

2. The cupric salt (i.e., Cu²⁺) of a monobasic acid contains 3 molecules of water of hydration per atom of Cu. One g of hydrated salt yielding on strong heating 0.3306g of CuO. What is the equivalent mass of anhydrous acid?

3. 3.150g of oxalic acid [(COOH)₂, xH₂O] were dissolved in 500mL water. 28mL of this solution required 35mL of 0.08 N NaOH solution for complete neutralization. Find out the number of molecules of water of crystallization in the acid.

4. 0.50g mixture of K₂CO₃ and Li₂CO₃ required 30mL of 0.25N HCl for complete neutralization. Calculate percentage composition of mixture.

5. 250mL solution of NaCl and Na₂CO₃ was prepared by dissolving 4g of their mixture in water. 25mL of this solution was completely neutralized by using 50mL of N/10 HCl. Calculate the percent composition of mixture of NaCl and Na₂CO₃.

6. 5g of CuSO₄.5H₂O is intended to be prepared by using CuO and four times the stoichiometric amount of H₂SO₄. Assuming that 10% of the material is lost in crystallization, what mass of oxide should be taken and how many litre or mL of a 5M H₂SO₄?

7. A mixture contains 20g of caustic soda, 20g of sodium carbonate and 20g of sodium bicarbonate in one litre. What will be the litre value if 55mL of this mixture is used for titration against 1N HCl if:
   (a) First titrated with phenolphthalein.
   (b) Methyl orange added after first end point.
   (c) Methyl orang added from the very beginning.

8. The formula weight of an acid is 820. 100cm³ of a solution of this acid containing 39.0g of the acid per litre were completely neutralized by 95.0 cm³ of aqueous NaOH containing 40.0g of NaOH per litre. What is the basicity of the acid?

9. 1.20g sample of Na₂CO₃ and K₂CO₃ was dissolved in water to form 100mL of a solution. 20mL of this solution required 40mL of 0.1N HCl for complete neutralization. Calculate the weight of Na₂CO₃ in mixture. If another 20mL of this solutions is treated with excess of BaCl₂, what will be the weight of precipitate?
10. 5mL of 8N HNO₃, 4.8mL of 5N HCl and a certain volume of 17M H₂SO₄ are mixed together and made upto 2 litre. 30mL of this acid mixture exactly neutralizes 42.9mL of Na₂CO₃ solution containing 1g Na₂CO₃.10H₂O in 100mL of water. Calculate the amount of sulphate ions in g present in solution.

ANSWERS

OBJECTIVE TYPE QUESTIONS

1. b  2. c  3. d  4. b  5. b  6. b  7. d
15. a  16. b  17. a  18. a  19. b  20. a  21. a
22. b  23. c  24. a  25. b  26. a  27. c  28. d
29. c  30. b  31. c  32. a  33. c  34. b  35. a
36. a  37. a  38. a  39. c  40. c  41. b  42. c
43. b  44. c  45. a  46. a  47. a  48. a  49. b
50. b  51. b  52. b

SUBJECTIVE TYPE QUESTIONS

LEVEL – 1

1. 14 litre  2. 135.04  3. 1.05M  4. 30.67 ml
5. 8.50  6. 0.437  7. 8.39g  8. 1.9849
9. 28.04  10. 42% CaO  11. 0.699g  12. 65.62%
13. XeF₆

LEVEL – 2

1. 173 ml  2. 62.58  3. 2  4. 96%, 4%
5. 33.75%, 66.25%  6. 1.753g, 4.41ml  7. 31.34ml, 16.93ml, 48.26ml
8. Basicity = 2  9. 0.5962g, 0.934g  10. 6.528g