PREFACE

Specific mass of a particular reactant gives how much of a product? How to determine the concentration of a solution? A number of such questions that the chemists want to answer require a knowledge of the quantitative relations that exist between the substances involved in chemical reactions. Quantitative calculations of chemical composition and reaction are referred to as stoichiometry.

A chemical reaction of any type always follows law of conservation of mass. This lesson acquaints us with the two most fundamental principles (mole and equivalent) required to do chemical calculations.

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STOICHIOMETRY & REDOX REACTIONS

1. THE CONCEPT OF ATOMS AND MOLECULES

1.1 THE ATOMS

The fact that all substances obeyed the laws of chemical combination by weight made the scientists to speculate about the ultimate particles of matter. The most famous of these speculations is due to John Dalton.

DALTON'S ATOMIC THEORY

The main postulates of this atomic theory are

- Matter is discrete (i.e., discontinuous) and is made up of atoms. *An atom is the smallest (chemically) indivisible particle of an element, which can take part in a chemical change*.

- Atoms of the same element are identical in all respects, size, shape, structure etc. and especially weight.

- Atoms of different elements have different properties and different weights.

- Atoms cannot be created or destroyed. So a chemical reaction is nothing but a rearrangement of atoms and the same number of atoms must be present before and after the reaction.

- A compound is formed by the union of atoms of one element with atoms of another in a fixed ratio of small whole numbers (1 : 1, 1 : 2, 2 : 3 etc).

All the postulates of Dalton's atomic theory have been proved to be incorrect.

An atom is divisible in the sense that it has a structure. Sub–atomic particles are known.

The existence of isotopes for most elements shows that atoms of the same element need not have the same mass. The atomic weight of an element is, in fact, a mean of the atomic masses of the different isotopes of the element.

Parts of atomic mass can be destroyed and an equivalent amount of energy is released during nuclear fission.

Atoms combine in fixed integral ratios; however, there are instances where atoms combine in non-integral ratios. e.g., in zinc oxide, zinc and oxygen have not combined in exactly an integral ratio. The atomic ratio of Zn: O = $(1 + x)$:1, where x is a very small fraction. Compounds of this kind are called *non–stoichiometric compounds or Berthollide compounds* as against compounds whose formulae are in accordance with atomic theory and Proust's law of definite proportions.

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1. 2 ATOMIC WEIGHTS

An atom is so minute that it cannot be detected even with the most powerful microscope, let alone placed on a balance pan and weighed. So there is no question of determining the absolute weight of an atom. So chemists decided to determine the relative masses of atoms (i.e., how many times one atom of an element is heavier than another). Hydrogen atom was first selected as standard. i.e.,

$$\text{Atomic weight of an element} = \frac{\text{Weight of 1 atom of the element}}{\text{Weight of 1 atom of hydrogen}}$$

When we state that the atomic weight of chlorine is 35.5, we mean that an atom of chlorine is 35.5 times heavier than an atom of hydrogen. It was later felt that the standard for reference for atomic weight may be oxygen, the advantage being that the atomic weights of most other elements became close to whole numbers.

$$\text{Atomic weight of an element} = \frac{\text{Weight of 1 atom of the element}}{\frac{1}{16} \times \text{weight of 1 atom of oxygen}}$$

The modern reference standard for atomic weights is carbon isotope of mass number 12.

$$\text{Atomic weight of an element} = \frac{\text{Weight of 1 atom of the element}}{\frac{1}{12} \times \text{weight of 1 atom of carbon} - 12}$$

On this basis, atomic weight of oxygen 16 was changed to 15.9994.

Nowadays atomic weight is called relative atomic mass and denoted by amu (atomic mass unit). The standard for atomic mass is C^{12}.

- Atomic weight is not a weight but a number.
- Atomic weight is not absolute but relative to the weight of the standard reference element (C^{12}).
- Gram atomic weight is atomic weight expressed in grams, but it has a special significance with reference to a mole.

Dulong and Petit measured the specific heats of a number of metals and found that the product of the specific heat and the atomic weight is a constant, having an approximate value of 6.4.

$$\text{Specific heat (cal/g–deg)} \times \text{atomic weight} \simeq 6.4$$

This correlation has been used to 'correct' the atomic weights of some elements in the periodic table. Dulong and Petit's law is applicable only to metals.

1. 3 THE MOLECULE

Avogadro (1811) suggested that the fundamental chemical unit is not an atom but a molecule, which may be a cluster of atoms held together in some manner causing them to exist as a unit. The term *molecule means the smallest particle of an element or a compound that can exist free and retain all its properties*.

Consider a molecule of sulphur dioxide. It has been established that it contains one atom of sulphur and two atoms of oxygen. This molecule can be split up into atoms of sulphur and oxygen. So the smallest particle of sulphur dioxide that can exist free and retain all its properties is the molecule of sulphur dioxide. A compound molecule should contain at least 2 different atoms.

The term molecule is also applied to describe the smallest particle of an element which can exist free. Thus a hydrogen molecule is proved to contain 2 atoms; when it is split up into atoms, there will be observed a change in properties (You may know that nascent hydrogen which may be thought of as atomic hydrogen is a more powerful reducing agent than ordinary hydrogen).

Molecules of elementary gases like hydrogen, oxygen, nitrogen, chlorine, etc., contain 2 atoms in a molecule; they are diatomic. Molecules of noble gases like helium, neon, argon, krypton and xenon are monoatomic. Molecules of phosphorus contain 4 atoms (tetratomic) while those of sulphur contain 8 atoms.

The number of atoms of an element in a molecule of the element is called its atomicity.

1. 4 MOLECULAR WEIGHT

It is the number of times a molecule is heavier than $\dfrac{1}{12}$ th of an atom of C−12.

$$\text{Molecular weight} = \frac{\text{Weight of 1 molecule}}{\dfrac{1}{12} \times \text{weight of 1 carbon} - 12 \text{ atom}}$$

- Molecular weight is not a weight but a number.
- Molecular weight is relative and not absolute.
- Molecular weight expressed in grams is called gram−molecular weight.
- Molecular weight is calculated by adding all the atomic weights of all the atoms in a molecule. Thus, the molecular weight of oxygen which contains 2 atoms in a molecule would be $(2 \times 16) = 32$. The molecular weight of carbon dioxide, which contains 1 atom of carbon and 2 atoms of oxygen would be $[12 + (2 \times 16)] = 44$. Molecular weight of sulphuric acid, which contains 2 atoms of hydrogen, 1 atom of sulphur and 4 atoms of oxygen is $[(2 \times 1) + (1 \times 32) + (4 \times 16)] = 98$.
- Molecular weight is now called relative molecular mass.

1. 5 AVOGADRO'S HYPOTHESIS

It states that equal volumes of gases at the same temperature and pressure contain equal number of molecules. It means that 1 ml of hydrogen, oxygen, ammonia, or a mixture of gases taken at the same temperature and pressure contains the same number of molecules.

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Application of Avogadro's hypothesis:

(a) **To prove that simple elementary gas molecules are diatomic.**

Consider the experimental result,

1 volume of hydrogen + 1 volume of chlorine $\longrightarrow$ 2 volumes of hydrogen chloride at the same temperature and pressure.

1 volume contains 'n' molecules. Then n molecules of hydrogen + n molecules of chlorine $\longrightarrow$ 2n molecules of hydrogen chloride.

Cancelling the common 'n', we have 1 molecule of hydrogen + 1 molecule of chlorine $\longrightarrow$ 2 molecules of hydrogen chloride.

A molecule of hydrogen chloride should contain at least 1 atom of hydrogen and 1 atom of chlorine. Two molecules of hydrogen chloride should contain at least 2 atoms of hydrogen and 2 atoms of chlorine and these should have come from 1 molecule of hydrogen and 1 molecule of chlorine respectively. Thus Avogadro's hypothesis enables us to establish that hydrogen and chlorine molecules must contain **at least 2 atoms** (Measurement of the ratio of specific heats of these gases at constant pressure and at constant volume, $C_P/C_V = 1.4$, establishes that these gases are diatomic).

(b) **To establish the relationship between molecular weight and vapour density of a gas.** *The absolute density of gas is the weight of 1 litre (dm^3) of the gas at S.T.P.* [Standard Temperature (0°C) and Pressure (1 atmosphere)].

The relative density or vapour density of a gas $= \dfrac{\text{Density of the gas}}{\text{Density of hydrogen}}$

Vapour density of a gas $= \dfrac{\text{Weight of 1 litre of gas at STP}}{\text{Weight of 1 litre of hydrogen at STP}}$

$= \dfrac{\text{Weight of a certain volume of the gas}}{\text{Weight of the same volume of hydrogen at the same temperature and pressure}}$

So the *vapour density of a gas is defined as the ratio of the weight of a certain volume of the gas to the weight of the same volume of hydrogen at the same temperature and pressure.*

$\therefore$ Vapour density (V.D.) of a gas

$= \dfrac{\text{Weight of 'V' litres of the gas}}{\text{Weight of 'V' litres of hydrogen at the same temperature and pressure}}$.

Let 'V' litres of the gas contains 'n' molecules.

V.D. of a gas $= \dfrac{\text{Weight of 'n' molecules of the gas}}{\text{Weight of 'n' molecules of hydrogen}} = \dfrac{\text{Weight of 1 molecule of the gas}}{\text{Weight of 1 molecule of hydrogen}}$

V.D. of a gas $= \dfrac{\text{Weight of 1 molecule of the gas}}{\text{Weight of 2 atoms of hydrogen}} = \dfrac{1}{2} \times \dfrac{\text{Weight of 1 molecule of the gas}}{\text{Weight of 1 atom of hydrogen}}$

V.D. of a gas $= \dfrac{1}{2} \times$ Molecular weight of the gas

$\therefore$ *Molecular weight of the gas = 2 × Vapour density of the gas*

(c)   Gram–Molecular volume or Molar Volume

Molecular weight of a gas $= 2 \times \dfrac{\text{Weight of 1L of the gas at STP}}{\text{Weight of 1L of hydrogen at STP}}$

Molecular weight of a gas $= 2 \times \dfrac{\text{Weight of 1 L of the gas at STP}}{0.089 \text{ g}}$

Gram–Molecular weight of a gas $= \dfrac{2}{0.089} \times$ weight of 1 L of the gas at STP

Gram–Molecular weight of a gas $= 22.4 \times$ Weight of 1 L of the gas at STP

$\qquad\qquad\qquad\qquad = $ Weight of 22.4 L of the gas at STP

This establishes that gram–molecular weight of any gas (or vapour) occupies the same volume of 22.4 L at S.T.P. The volume occupied by a gram–molecular weight of any gas is called a molar volume and its value is 22.4 L at STP.

2. STOICHIOMETRY

Chemical stoichiometry deals with the determination of quantities of reactants or products of a chemical reaction. The word "stoichiometry" is derived from greek work "*stoichion*" means element and "*metry*" means measure. Stoichiometry is divided into two subsections.

(a) Gravimetric analysis and

(b) Volumetric analysis.

The problems on gravimetric and volumetric analysis can be solved using two well known concepts i.e. mole concept and equivalent concept. But generally, the problems on gravimetric analysis are solved using mole concept since mole concept is easier to apply in such cases while problems on volumetric analysis are solved making use of equivalent concept since it does not require the use of balanced chemical reaction. However, there is no hard and fast rule that these guidelines should be followed strictly. We can make use of equivalent concept for gravimetric problems and mole concept for volumetric problems. Let us first understand the mole concept and its use in chemical reactions and then we will learn about equivalent concept.

2. 1   THE MOLE

The concept of amount of substance is confined to the chemical measurements. The amount of substance of a system is proportional to the number of elementary entities (which may be atoms or molecules or ions or specified group of such particles) of that substance present in the system.

Let us take elements Ag, Mg and Hg with masses equal to their atomic masses in grams, and then to our surprise, each element contains equal number of atoms. This is not only limited to atoms but also applicable to molecules. For example, if we have molecules like CO_2, NO_2 and SO_2 with masses equal to their molecular

masses in grams, then they would also contain equal number of molecules. This specified number of atoms or molecules is referred as a "mole".

Thus a system containing a specified number (6.023×10^{23}) of elementary entities is said to contain 1 mole of the entities. Thus 1 mole of an iron sample mean that the sample contain 6.023×10^{23} atoms of iron. Similarly, 1 mole of NaCl crystal contains 6.023×10^{23} ion paris (Na^+Cl^-).

This specific number 6.023×10^{23} elementary entities is called Avogadro number or constant (N_{AV}). The SI unit for amount of substance is the mole. The mole is defined as the amount of substance in exactly 12 g of carbon−12. One mole of any substance contains the same number of elementary entities as there are carbon atoms in exactly 12 g of carbon−12.

The mass of specific number (6.023×10^{23}) of elementary entities is equal to atomic mass for atoms and molecular mass for molecules.

Let M g/mole be the molecular mass of a species. Thus M g be the mass of 1 mole (equal to the mass of 6.023×10^{23} molecules) of the species. Then, x g of the species contain $\left(\dfrac{1}{M} \times x\right)$ mole.

Hence, Number of moles of a species $= \dfrac{\text{weight (grams)}}{\text{Atomic or molecular mass (g/mole)}} = \dfrac{w}{M}$

It is also known that one mole of a gas at STP occupies a volume of 22.4 litres. Thus, if a gas occupies x L at STP, then the number of moles of the gas can be calculated by dividing the actual volume occupied by the gas at STP with the volume occupied by 1 mole of the gas at STP.

Thus, number of moles of a gas $= \dfrac{\text{Volume occupied by gas at STP}}{\text{Volume occupied by 1 mole of the gas at STP}}$.

The volume of gas and the number of moles of gas at temperature and pressure other than the STP can be related by ideal gas equation, $PV = nRT$.

2.2   CHEMICAL EQUATIONS AND STOICHIOMETRY

Let the balanced chemical equation we have is

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$
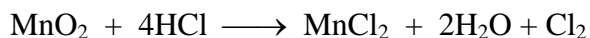
The quantitative information drawn from this balanced chemical equation is

(a)   The molar ratio in which two reactants (MnO_2 and HCl) reacting is 1 : 4.

(b)   The molar ratio between two products can also be known i.e. moles of H_2O produced would be double the moles of $MnCl_2$ produced.

(c)   The initial moles of MnO_2 and HCl (to be taken in vessel) for the reaction to occur not necessarily be 1 and 4 respectively or also should not be in the molar ratio of 1 : 4.

(d) We can start reaction with MnO_2 and HCl taken in any molar ratio, but the moles of two reacting will always be in the molar ratio of 1 : 4.

(e) The balanced chemical equation should follow the law of conservation of mass.

Let us consider the same chemical system with initial composition (in terms of mole) as $n^{\circ}_{MnO_2}$, n°_{HCl}, $n^{\circ}_{MnCl_2}$, $n^{\circ}_{H_2O}$, and $n^{\circ}_{Cl_2}$. The n°_{HCl} is four times of $n^{\circ}_{MnO_2}$. When the reaction occurs, these mole numbers change as the reaction progresses. The mole numbers of the various species do not change independently but the changes are related by the stoichiometric coefficients in the chemical equation. Let after time 't' from the commencement of reaction, the moles of MnO_2 reacting be x, then the moles of HCl reacting in the same time interval be $4x$ since MnO_2 and HCl react in the molar ratio of 1 : 4.

Thus, after time t, the composition of the system would be

$$n_{MnO_2} = n^{\circ}_{MnO_2} - x$$

$$n_{HCl} = n^{\circ}_{HCl} - 4x$$

$$n_{MnCl_2} = n^{\circ}_{MnCl_2} + x$$

$$n_{H_2O} = n^{\circ}_{MnO_2} + 2x$$

$$n_{Cl_2} = n^{\circ}_{Cl_2} + x$$

The algebraic signs, $+$ and $-$ indicates that the reactants are consumed and products are produced.

In general, mole numbers of various species at any time would be given as

$$n_i = n^{\circ}_i + v^{\circ}_i x$$

where n°_i is the initial amount, x is the degree of advancement and v_i is the stoichiometric coefficient which will be given a negative sign for reactants and a positive sign for products.

After long time interval from the commencement of reaction i.e. after ∞ time, the composition of the system would be

$$n_{MnO_2} = 0, \ n_{HCl} = 0$$

$$n_{MnCl_2} = n^{\circ}_{MnCl_2} + n^{\circ}_{MnO_2} = n^{\circ}_{MnCl_2} + \frac{n^{\circ}_{HCl}}{4}$$

$$n_{H_2O} = n^{\circ}_{H_2O} + 2n^{\circ}_{MnO_2} = n^{\circ}_{H_2O} + \frac{n^{\circ}_{HCl}}{2}$$

$$n_{Cl_2} = n^{\circ}_{Cl_2} + n^{\circ}_{MnO_2} = n^{\circ}_{Cl_2} + \frac{n^{\circ}_{HCl}}{4}$$

2.3 THE LIMITING REAGENT

Let the initial moles of MnO_2 and HCl be $n^{\circ}_{MnO_2}$ and n°_{HCl} respectively and $n^{\circ}_{HCl} \neq 4n^{\circ}_{MnO_2}$. Thus, in the given chemical reaction, after ∞ time, one of the reactant will be completely consumed while the other would be left in excess. Thus, the reactant which is completely consumed when a reaction goes to completion and which decides the yield of the product is called limiting reagent.

For example, if in the given case $n^{\circ}_{HCl} > 4n^{\circ}_{MnO_2}$, and there is no $MnCl_2$ and H_2O in the beginning, then

$$MnO_2 \quad + \quad 4HCl \quad \longrightarrow \quad MnCl_2 \quad + \quad Cl_2 \quad + \quad 2H_2O$$

Initially $\quad n^{\circ}_{MnO_2} \qquad n^{\circ}_{HCl} \qquad\qquad 0 \qquad\qquad 0 \qquad\qquad 0$

After ∞ time $\quad 0 \qquad n^{\circ}_{HCl} - 4n^{\circ}_{MnO_2} \qquad n^{\circ}_{MnO_2} \qquad n^{\circ}_{MnO_2} \qquad 2n^{\circ}_{MnO_2}.$
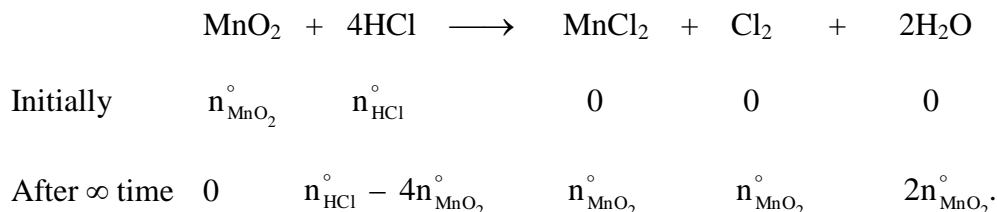
Thus, MnO_2 is the limiting reagent and the yield of all the products is governed by the amount of MnO_2 taken initially.

Similarly, if in the given case $n^{\circ}_{HCl} < 4n^{\circ}_{MnO_2}$ and no $MnCl_2$, Cl_2 & H_2O are present initially, then

$$MnO_2 \quad + \quad 4HCl \quad \longrightarrow \quad MnCl_2 \quad + \quad Cl_2 \quad + \quad 2H_2O$$

Initially $\qquad n^{\circ}_{MnO_2} \qquad n^{\circ}_{HCl} \qquad\qquad 0 \qquad\qquad 0 \qquad\qquad 0$

After ∞ time $\quad n^{\circ}_{MnO_2} - \dfrac{n^{\circ}_{HCl}}{4} \qquad 0 \qquad\qquad \dfrac{n^{\circ}_{HCl}}{4} \qquad \dfrac{n^{\circ}_{HCl}}{4} \qquad \dfrac{n^{\circ}_{HCl}}{2}$
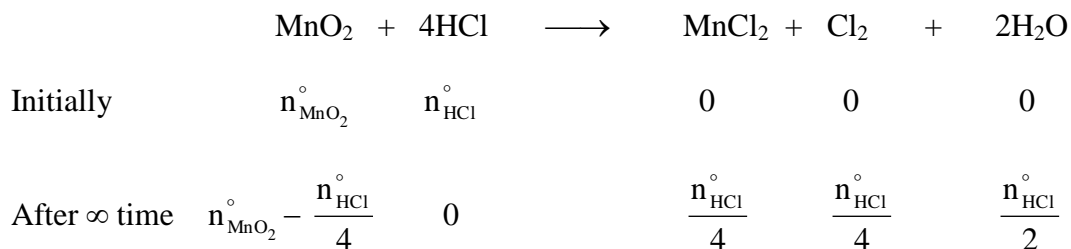
Here, HCl would become limiting reagent & the product's yield is decided by the amount of HCl taken initially.

2.4 THE YIELD OF PRODUCT

Let us suppose that the amount of $MnCl_2$ produced in the last case actually be less than $\dfrac{n^{\circ}_{HCl}}{4}$ while the theoretical yield should be $\dfrac{n^{\circ}_{HCl}}{4}$. This means that the yield of the product is not 100%. Thus, percentage yield of the product is given as ratio of actual yield by theoretical maximum yield multiplied by 100.

$\therefore$ % yield of the product $= \dfrac{\text{Actual yield}}{\text{Theoretical max imum yield}} \times 100.$

STOICHIOMETRY & REDOX REACTIONS

3. GRAVIMETRIC ANALYSIS

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

The gravimetric analysis is broadly classified into three heads.

(a) Mass–mass relationship

(b) Mass–volume relationship and

(c) Volume–volume relationship

3.1 MASS – MASS RELATIONSHIP

This relates the mass of a species (reactant or product) with the mass of another species (reactant or product) involved in a chemical reaction. Let us consider a chemical reaction,

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g).$$
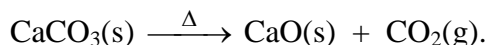
Let the mass of $CaCO_3$ taken be x g and we want to calculate the mass of CaO obtained by heating x g $CaCO_3$. Then the moles of $CaCO_3$ taken would be $\dfrac{x}{M_1}$ (where M_1 represents the molar mass of $CaCO_3$).

According to the balanced reaction, the molar ratio of $CaCO_3$ and CaO is 1 : 1, so same number of moles $\left(\dfrac{x}{M_1}\right)$ of CaO would be formed. Now for converting the moles of CaO into mass of CaO obtained, we need to multiply the moles of CaO with the molar mass of CaO. Let the molar mass of CaO be M_2, so the mass of CaO obtained by heating x g of $CaCO_3$ would be $\left(\dfrac{x}{M_1} \times M_2\right)$ g.

3.2 MASS – VOLUME RELATIONSHIP

This establishes the relationship between the mass of a species (reactant or product) and the volume of a gaseous species (reactant or product) involved in a chemical reaction.

Let us take x g of $CaCO_3$ in a vessel of capacity V L and the vessel is heated so that $CaCO_3$ decomposes as

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$
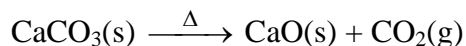
We want to find out the volume of CO_2 evolved at STP by heating x g of $CaCO_3$. Then

Moles of $CaCO_3 = \dfrac{x}{M_1}$

Moles of CO_2 evolved $= \dfrac{x}{M_1}$ (since molar ratio of $CaCO_3$ and CO_2 is 1 : 1)

$\therefore$ Volume of CO_2 evolved at STP $= \left(\dfrac{x}{M_1} \times 22.4 \right) L$

But, if the volume of CO_2 evolved is to be calculated at pressure P atm and temperature TK. Then, moles of CO_2 evolved $= \dfrac{x}{M_1}$.

Volume of CO_2 evolved at pressure P and temperature T $= \dfrac{x}{M_1} \times \dfrac{RT}{P}$ (Using PV = nRT)

3.3 VOLUME – VOLUME RELATIONSHIP

This relationship deals with the volume of a gaseous species (reactant or product) with the volume of another gaseous species (reactant or product) involved in a chemical reaction.

Let us consider the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. We are given x L of N_2 at pressure P atm and temperature TK and we want to know the volume of H_2 required to react with it at the same pressure and temperature.

Moles of $N_2 = \dfrac{P \times x}{RT}$

Moles of H_2 required $= \dfrac{3 \times P \times x}{RT}$ (since molar ratio of N_2 & H_2 is 1 : 3)

$\therefore$ Volume of H_2 required at same pressure & temperature $= \dfrac{3 \times P \times x \times RT}{RT \times P} = 3\,x\,L$

This result could also have been obtained by knowing that for a gaseous relation, at the same pressure and temperature, the moles of gas is directly proportional to volume of the gas (V α n since P & T are constant) or molar ratio and volume ratio are same.

Thus, when x L of N_2 is taken at Pressure P atm and temperature TK, then at the same pressure and temperature, the volume of H_2 required would be 3 x L (since the volume ratio of N_2 & H_2 would be same as molar ratio i.e. 1 : 3). But if the volume of H_2 required is to be calculated at another pressure P' atm and temperature T'K, then

Moles of H_2 required $= \dfrac{3 \times P \times x}{RT}$

$\therefore$ Volume of H_2 required at pressure P' atm & temperature T'K

$$= \dfrac{3 \times P \times x \times RT'}{RT \times P'} = \left(\dfrac{3x \times PT'}{P'T} \right) L$$

STOICHIOMETRY & REDOX REACTIONS

Illustration 1

Question: **How much zinc should be added to 0.01 mol AgNO₃ solution to displace all the silver in the solution?**

Solution: The involved balanced reaction would be

$$Zn + 2AgNO_3 \longrightarrow Zn(NO_3)_2 + 2Ag$$
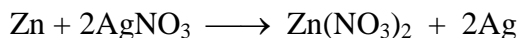
Moles of $AgNO_3$ in the solution = 0.01

Moles of Zn to be added to solution = 0.005

(since $AgNO_3$ and Zn are reacting in the molar ratio of 2 : 1)

∴ Mass of Zn to be added to solution = 0.005 × 65.4 = **0.327 g**

Illustration 2

Question: **NaCl of 95% purity is used to prepare salt cake (Na₂SO₄) by the reaction,**

$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$
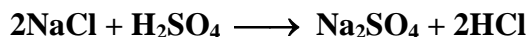
If the product (Na₂SO₄) is only 85% pure, what weight of NaCl is used up in producing 1 kg of the impure salt cake?

Solution: Let the weight of NaCl used up in producing 1 kg of impure product be x g.

Mass of pure NaCl = $\dfrac{x \times 95}{100}$

Moles of pure NaCl = $\dfrac{x \times 95}{100 \times 58.5}$

Moles of pure Na_2SO_4 = $\dfrac{x \times 95}{100 \times 58.5} \times \dfrac{1}{2}$

Mass of pure Na_2SO_4 = $\dfrac{x \times 95}{100 \times 58.5} \times \dfrac{1}{2} \times 142 = \dfrac{1000 \times 85}{100}$

∴ $x =$ **737.2 g**

Illustration 3

Question: **KClO₃ decomposes on heating in two possible ways as**

$KClO_3 \xrightarrow{\Delta} KCl + 3/2\ O_2$

$4KClO_3 \xrightarrow{\Delta} KCl + 3KClO_4$
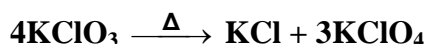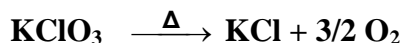
when 15 g of KClO₃ were heated in an experiment, analysis of the product showed that 5.21 g of KCl and 4.59 g of KClO₄ were formed. What was the weight of KClO₃ remaining undecomposed? What fraction of the KClO₃ decomposed yielded KClO₄?

Solution: In order to calculate the weight of KClO₃ remaining undecomposed, we need to find out the total weight of KClO₃ that decomposes. The weight of KClO₃ that decomposes in second reaction would be known using the KClO₄ data. Using KClO₄ data, we would also calculate the weight of KCl obtained in second reaction. Since, total weight of KCl obtained is known to us, so the weight

of KCl obtained in first reaction would also be known, using this we will find out the weight of $KClO_3$ decomposed in first reaction.

Moles of $KClO_4$ obtained $= \dfrac{4.59}{138.5}$

Moles of KCl obtained in IInd reaction $= \dfrac{4.59}{138.5} \times \dfrac{1}{3} = 0.011$ (since molar ratio of $KClO_4$ and KCl in IInd reaction is 3 : 1).

Moles of $KClO_3$ that decomposes in IInd reaction $= \dfrac{4.59}{138.5} \times \dfrac{4}{3}$ (since molar ratio of $KClO_4$ and $KClO_3$ in IInd reaction is 3 : 4)

$\therefore$ Mass of $KClO_3$ that decomposes in IInd reaction $= \dfrac{4.59}{138.5} \times \dfrac{4}{3} \times 122.5 = 5.41$ g

Moles of KCl obtained in Ist reaction $= \left(\dfrac{5.21}{74.5} - 0.011 \right) = 0.07 - 0.011 = 0.059$

Moles of $KClO_3$ that decomposes in Ist reaction $= 0.059$

(since molar ratio of KCl and $KClO_3$ in Ist reaction is 1 : 1)

Mass of $KClO_3$ that decomposes in Ist reaction $= 0.059 \times 122.5 = 7.23$ g

Total mass of $KClO_3$ that decomposes in both the reactions $= (5.41 + 7.23) = 12.64$ g

$\therefore$ Mass of $KClO_3$ that remain undecomposed $= 15 - 12.64 = \textbf{2.36 g}$

Moles of O_2 evolved in Ist reaction $= 0.059 \times \dfrac{3}{2}$

Volume of O_2 evolved at STP in Ist reaction $= 0.059 \times \dfrac{3}{2} \times 22.4 = \textbf{1.98 L}$

Fraction of $KClO_3$ decomposed yielding $KClO_4 = \dfrac{5.41}{15} = \textbf{0.36}$

4. BALANCING OF REDOX REACTIONS

Oxidation−reduction or redox reactions involves electron transfer either between the atoms of same molecule or between atoms of different molecules. Redox reactions can take place in solution or in the gas phase, or they may be heterogeneous reactions (involving more than one phase). Redox reactions take place between both inorganic and organic compounds.

A redox reaction is the sum of two half−reactions, one of which involves loss of electrons and the other gain of electrons. For example, reaction of Li with oxygen to form Li_2O.

$$2Li(s) + \frac{1}{2} O_2(g) \longrightarrow Li_2O(s).$$
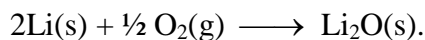
In crystalline Li_2O, lithium exists as Li^+ ions and oxygen as oxide ions (O^{2-}), so the two half−reactions are

Oxidation half−reaction: $2Li(s) \longrightarrow 2Li^+ + 2e^-$ ……..(i)

Reduction half−reaction: $2e^- + \frac{1}{2} O_2(g) \longrightarrow O^{2-}$ ……..(ii)
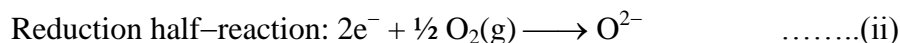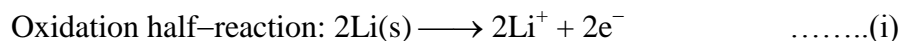
The two half−reactions on summing algebrically gives overall reaction. In reaction (i), metallic lithium loses electrons & becomes lithium ions. This process is known as *oxidation* and the lithium is said to be *oxidized*. In reaction (ii), the oxygen gains electrons to become oxide ions and is said to be *reduced*. This process is known as *reduction*.

Thus, oxidation is defined as the loss of electrons and reduction as the gain of electrons.

The species which gets oxidized & reduces others is called *reducing agent* or *reductant* and the species getting reduced but oxidizes others is called *oxidizing agent* or *oxidant*.

4.1 THE OXIDATION STATE OF AN ELEMENT

To describe the changes that occur in oxidation−reduction reactions and to write the correctly balanced equations for such reactions, it is helpful to know the concept of the oxidation state (or oxidation number) of an atom.

For monoatomic ions, the oxidation state is simply the charge on the ion. For example, oxidation states of Na^+, Mg^{2+}, Cl^- and N^{3-} are +1, +2, −1 and −3 respectively. For covalently bonded substances, the charge on an atom would be so small that it is impossible to calculate the exact charge on each atom in the molecule. Thus, oxidation state for covalently bonded molecule is defined as "the charge an atom would possess if all the bonds associated with that atom are broken heterolytically considering them to be completely ionic". For example, in NH_3 there are three N−H bonds. If we consider all three N−H bonds to be ionic, then each H will possess a charge of +1 while N has the charge −3 (because N is more electronegative than H). In H_2O_2, there are two O−H bonds and one O−O bond as evident from the structural formula H−O−O−H. Assuming each O−H bond to be ionic, each H atom would possess +1 charge while each O possess −1 charge. The O−O bond is not ionic as the bond is between atoms of similar electronegativity.

It is not necessary to know the structure of a molecule in order to calculate the oxidation state of an atom in a molecule. The following set of bookkeeping rules are used to assign oxidation states to atoms in ions or molecules.

1. Each pure element has an oxidation state of zero. This is true whether the element is a monoatomic gas, a metallic solid or a polyatomic molecule. Thus, $Fe(s)$, $N_2(g)$, $P_4(s)$ and $S_8(s)$ are all in the zero oxidation state.

2. In monoatomic ions, the oxidation state of the element is equal to the charge on the ion. Thus, oxidation state of all alkali metals is +1 and that of alkaline earth metals is +2 in all their compounds. In ionic solid K_2S, the oxidation state's of potassium and sulfur are +1 and −2 respectively. In AgCl, the oxidation state of silver and chlorine are +1 and −1 respectively.

3. The oxidation state of hydrogen in any molecule in which it is combined with another element is +1, except in the metallic hydrides such as LiH or CaH_2, where the oxidation state of hydrogen is −1.

4. The oxidation state of oxygen in any molecule or ion in which it is combined with another element is −2, except in the peroxides, the superoxides and in OF_2. The peroxides (H_2O_2, Na_2O_2, BaO_2 etc.) are compounds in which there is an O−O covalent bond and the peroxide ion is O_2^{2-}. The oxidation state of oxygen in peroxides is −1. The superoxides (like KO_2, CsO_2 etc.) are ionic compounds involving the superoxide ion, O_2^-. The oxidation state of oxygen is − ½ in superoxide ion. In OF_2, the oxidation state of oxygen is +2 since fluorine is more electronegative than oxygen.

5. The oxidation state of all the halogens is −1 in all their compounds except where they are combined with an element of higher electronegativity or in interhalogen compounds.. Oxidation state of fluorine is always −1, since it is the most electronegative element.

6. In covalent compounds not involving hydrogen or oxygen, the more electronegative element is assigned negative oxidation state while less electronegative element is assigned positive oxidation state.

7. The algebric sum of the oxidation numbers of all the atoms combined in a molecule or complex ion must equal the net charge on the molecule or ion.

Illustration 4

Question: **Calculate the oxidation state of the underlined atoms in the given species.**

        (a) $\underline{N}O_2^+$ **(b)** $\underline{N}O_3^-$

        (c) $K\underline{Mn}O_4$ **(d)** $\underline{Cr}_2O_7^{2-}$

        (e) $\underline{Fe}_2O_3$ **(f)** $\underline{Fe}_3O_4$
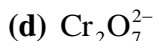
Solution:

    (a)   Let the oxidation state of N in NO_2^+ be x.

        $x + [2(-2)] = +1$ $x = +5$ Thus, oxidation state of N in NO_2^+ is **+5**.

(b)   Let x be the oxidation state of N in NO_3^-.

$x + [3(-2)] = -1$

$x = +5$

Thus, oxidation state of N in NO_3^- is + **5**.

(c)   Let the oxidation state of $KMnO_4$ be x.

$[1(+1)] + x + [4(-2)] = 0$

$x = +7$

Thus, oxidation state of Mn in $KMnO_4$ is + **7**.

(d)   Let the oxidation state of Cr in $Cr_2O_7^{2-}$ be x.

$2x + [7(-2)] = -2$

$x = +6$

Thus, oxidation state of Cr in $Cr_2O_7^{2-}$ is +**6**.

(e)   Let x be the oxidation state of Fe in Fe_2O_3.

$2x + [3(-2)] = 0$

$x = +3$

Thus, oxidation state of Fe in Fe_2O_3 is +**3**.

(f)   Let the oxidation state of Fe in Fe_3O_4 be x.

$3x + [4(-2)] = 0$

$x = +8/3$

Thus, oxidation state of Fe in Fe_3O_4 is +**8/3**. This is the average oxidation state of Fe in Fe_3O_4. Actually, Fe_3O_4 is made up of equimolar quantity of FeO and Fe_2O_3.

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

There are 2 common and useful methods to balance redox reactions. These are

(a) Oxidation number method and

(b) Ion–electron method.

4.2 Balancing Redox Reactions by Oxidation state Method

For balancing a redox reaction by oxidation number method, follow the order of steps as listed below (of course, all steps may not be required for balancing some reactions).

(i) For each redox reaction, deduce the oxidation state of the elements that are undergoing oxidation and reduction.

(ii) Separate the reactants and products into two half–reactions involving the elements that change their oxidation state. Write the skeletal equations for each half–reaction.

(iii) For each half–reaction, first balance the number of atoms of the element undergoing change in oxidation state.

(iv) Now find the total change in oxidation number by determining the change per atom and multiplying it by the total number of atoms that undergoes change. Also, decide whether electrons are lost or gained. An increase in oxidation state is loss of electrons and a decrease in oxidation state is gain of electrons.

(v) Add the electrons lost or gained to the half equation. Lost electrons are placed on the product side and gained electrons are kept on the reactant side.

(vi) Now add both the half reactions after multiplying by suitable integers to make the number of electrons lost and gained same.

(vii) Transfer the coefficients of each reactant and product to the main skeleton equation.

(viii) If the coefficients developed are not correct, then change them by inspection Such coefficient changes are required when an element from a compound goes in 2 different compounds, one with the same oxidation state & the other with different oxidation state.

(ix) Count the charges on both sides of the equation and balance the charges in the equation by adding requisite H^+ or OH^- to the required side. If the reaction occurs in acidic solution, use H^+ and if it occurs in basic solution, use OH^-. If the reaction occurs in neutral solution, use H^+ or OH^- on any of the side as needed i.e. in a neutral solution, if negative charges are needed for balancing, use OH^- and if positive charges are needed, use H^+.

(x) Balance the hydrogens and oxygens by adding the appropriate number of H_2O molecules on the required side.

Illustration 5

Question: **Balance the following oxidation−reduction equation,**
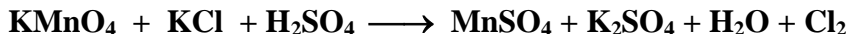
$$KMnO_4 + KCl + H_2SO_4 \longrightarrow MnSO_4 + K_2SO_4 + H_2O + Cl_2$$

by oxidation number method.

Solution:

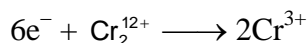(i) Identify the oxidation & reduction half equations in ionic form.

Reduction half: $Mn^{7+} \longrightarrow Mn^{2+}$

Oxidation half: $Cl^- \longrightarrow Cl_2$

(ii) Balance the atoms that undergo change in oxidation state.

Reduction half: $Mn^{7+} \longrightarrow Mn^{2+}$

Oxidation half: $2Cl^- \longrightarrow Cl_2$

(iii) Add the electrons lost or gained to each half equation.

Reduction half: $5e^- + Mn^{7+} \longrightarrow Mn^{2+}$ ………………..(A)

Oxidation half: $2Cl^- \longrightarrow Cl_2 + 2e^-$ ………………..(B)
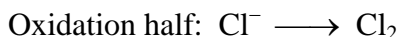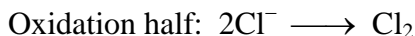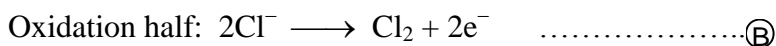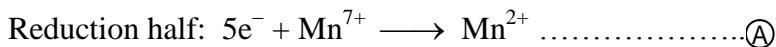
(iv) Multiply equation (A) with 2 and equation (B) with 5 and then add the two half reactions.

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

$$\underline{2\,Cl^- \longrightarrow Cl_2 + 2e^- \ ] \times 5}$$

$$2Mn^{7+} + 10\,Cl^- \longrightarrow 5Cl_2 + 2Mn^{2+}$$

(v) Transfer the coefficients to the main equation.

$$2KMnO_4 + 10KCl + H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + H_2O + 5Cl_2$$

(vi) Balance H & O atoms

$$2KMnO_4 + 10KCl + 8H_2SO_4 \longrightarrow 5Cl_2 + 2MnSO_4 + 8H_2O + K_2SO_4$$
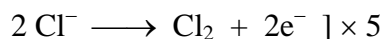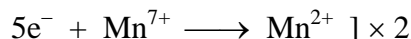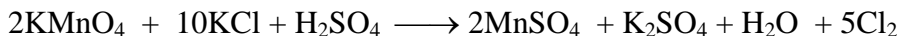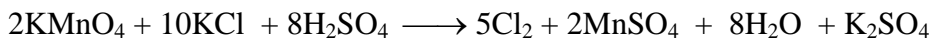
(vii) Finally balance by inspection method.

$$2KMnO_4 + 10KCl + 8H_2SO_4 \longrightarrow 2MnSO_4 + 6K_2SO_4 + 8H_2O + 5Cl_2$$
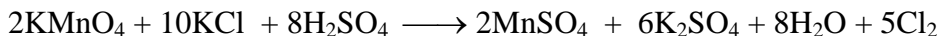
Illustration 6

Question: **Balance the following redox equation,**

$K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + Cl_2 + H_2O$

using oxidation number method.

Solution:

(i) Identify the oxidation & reduction half equations in ionic form.

Reduction half: $Cr_2^{12+} \longrightarrow Cr^{3+}$

Oxidation half: $Cl^- \longrightarrow Cl_2$

(ii) Balance the atoms that undergo change in oxidation state.

Reduction half: $Cr_2^{12+} \longrightarrow 2Cr^{3+}$

Oxidation half: $2Cl^- \longrightarrow Cl_2$

(iii) Add the electrons lost or gained to each half equation.

Reduction half: $6e^- + Cr_2^{12+} \longrightarrow 2Cr^{3+}$ ………………..Ⓐ

Oxidation half: $2Cl^- \longrightarrow Cl_2 + 2e^-$ ………………..Ⓑ
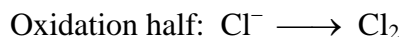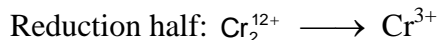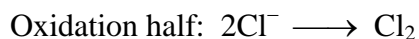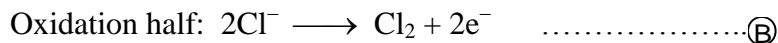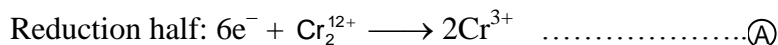
(iv) Multiply equation Ⓑ by 2 and add it to equation Ⓑ.

$6e^- + Cr_2^{12+} \longrightarrow 2Cr^{3+}$

$2Cl^- \longrightarrow Cl_2 + 2e^-] \times 3$

$\overline{Cr_2^{12+} + 6Cl^- \longrightarrow 2Cr^{3+} + 3Cl_2}$

(v) Transfer the coefficients to the main equation.

$K_2Cr_2O_7 + 6HCl \longrightarrow KCl + 2CrCl_3 + 3Cl_2 + H_2O$
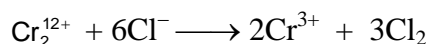
(vi) By inspection, it is seen that the coefficient of HCl developed is not correct, as the number of moles of Cl atoms on the product side are 13 while on the reactant side are only 6. So, the coefficient is changed appropriately, seeing that the net reaction is completely balanced.

$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$

4.3 Balancing Redox Reactions by Ion–Electron Method

This method of balancing redox reaction involves following steps.

(i) For each redox reaction, deduce the oxidation state of the elements that are undergoing oxidation and reduction.

(ii) Separate the reactants and products into two half–reactions involving the elements that changes its oxidation state. Write the skeleton equations for each half–reaction.

(iii) Balance each half–reaction separately involving given steps.

   1. First balance the atoms of the element undergoing oxidation or reduction.

   2. Then balance atoms of the elements other than hydrogen and oxygen.

   3. For balancing oxygen atoms in acidic or neutral medium, add suitable number of H_2O molecules to the side deficient in O while in alkaline medium, add equal number of H_2O molecules as the excess of O on the side having excess of O atoms and add double the number of OH^- ions on the opposite side of the equation.

   4. In order to balance the hydrogen atoms in acidic or neutral medium, add required number of H^+ to the side deficient in H while in alkaline medium, add equal number of OH^- ions as the excess number of H atoms on the side having excess H and add equal number of H_2O molecules on the opposite side of the equation.

(iv) Multiply each half–reaction by suitable integer to make the number of electrons lost and gained same and add both the half–equations to get a completely balanced reaction.

Illustration 7

Question: **Balance the redox equation,**

$HNO_3 + H_2S \longrightarrow NO + S$

by ion–electron method (acidic medium).

Solution:

(i) Identify the oxidation & reduction halves.

Reduction half: $HNO_3 \longrightarrow NO$

Oxidation half: $H_2S \longrightarrow S$

(ii) Atoms of the element undergoing oxidation and reduction are already balanced.

(iii) Balancing O atoms,

Reduction half: $HNO_3 \longrightarrow NO + 2H_2O$
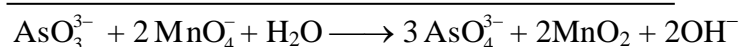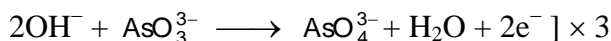
Oxidation half: $H_2S \longrightarrow S$

(iv)   Balancing H atoms,

Reduction half: $3H^+ + HNO_3 \longrightarrow NO + 2H_2O$

Oxidation half: $H_2S \longrightarrow S + 2H^+$

(v)   Balancing charge,

Reduction half: $3e^- + 3H^+ + HNO_3 \longrightarrow NO + 2H_2O$……………….Ⓐ

Oxidation half: $H_2S \longrightarrow S + 2H^+ + 2e^-$……………..Ⓑ

(vi)   Multiplying equation Ⓐ by 2 and equation Ⓑ by 3 and then adding them.

$3e^- + 3H^+ + HNO_3 \longrightarrow NO + 2H_2O \ ] \times 2$ ……………….Ⓐ

$H_2S \longrightarrow S + 2H^+ + 2e^- \ ] \times 3$ ……………….Ⓑ

$2HNO_3 + 3H_2S \longrightarrow 3S + 2NO + 4H_2O$

Illustration 8

Question: **Balance the following redox equation,**

$FeC_2O_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + CO_2 + MnSO_4 + K_2SO_4$

using ion−electron method (acidic medium).

Solution:

(i)   Identify the oxidation & reduction halves.

Oxidation half: $KMnO_4 \longrightarrow MnSO_4$

Reduction half: $FeC_2O_4 \longrightarrow Fe_2(SO_4)_3 + CO_2$

(ii)   In both the half−reactions, all the atoms (other then O and H) are not appearing on both sides of the reaction. So, in the oxidation half, H_2SO_4 is to be added on the reactant side while in reduction half, H_2SO_4 and K_2SO_4 are to be added on reactant and product side respectively.

(iii)   Balancing of the atoms of the element undergoing oxidation & reduction.

Reduction half: $H_2SO_4 + 2KMnO_4 \longrightarrow 2MnSO_4 + K_2SO_4$

Oxidation half: $H_2SO_4 + 2FeC_2O_4 \longrightarrow Fe_2(SO_4)_3 + 4CO_2$

(iv)   Balancing of the atoms of elements other than O and H.

Reduction half: $3H_2SO_4 + 2KMnO_4 \longrightarrow 2MnSO_4 + K_2SO_4$

Oxidation half: $3H_2SO_4 + 2FeC_2O_4 \longrightarrow Fe_2(SO_4)_3 + 4CO_2$

(v)   Balancing O atoms,

Reduction half: $3H_2SO_4 + 2KMnO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O$

Oxidation half: $3H_2SO_4 + 2FeC_2O_4 \longrightarrow Fe_2(SO_4)_3 + 4CO_2$

(vi)   Balancing H atoms,

Reduction half: $10H^+ + 3H_2SO_4 + 2KMnO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O$

Oxidation half: $3H_2SO_4 + 2FeC_2O_4 \longrightarrow Fe_2(SO_4)_3 + 4CO_2 + 6H^+$

(vii)   Balancing charge,

Reduction half: $10e^- + 10H^+ + 3H_2SO_4 + 2KMnO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O$ ……..Ⓑ

Oxidation half: $3H_2SO_4 + 2FeC_2O_4 \longrightarrow Fe_2(SO_4)_3 + 4CO_2 + 6H^+ + 6e^-$ …………..Ⓐ

(viii)   Multiply equation Ⓐ by 5 and equation Ⓑ by 3 and then adding them.

$10e^- + 10H^+ + 3H_2SO_4 + 2KMnO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O] \times 3$

$\underline{3H_2SO_4 + 2FeC_2O_4 \longrightarrow Fe_2(SO_4)_3 + 4CO_2 + 6H^+ + 6e^-\ ] \times 5}$

$10FeC_2O_4 + 6KMnO_4 + 24H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4 + 20CO_2 + 24H_2O$
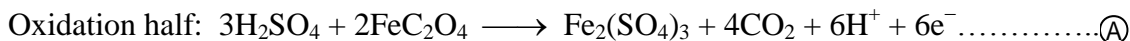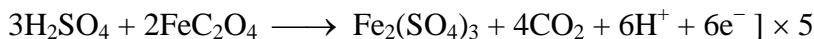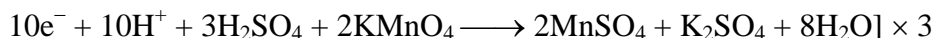
Illustration 9

Question: **Balance the following redox equation,**

$$AsO_3^{3-} + MnO_4^- \longrightarrow AsO_4^{3-} + MnO_2$$
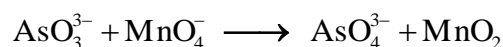
using ion–electron method (alkaline medium).

Solution:

(i)   Identify the oxidation & reduction halves.

Reduction half: $MnO_4^- \longrightarrow MnO_2$

Oxidation half: $AsO_3^{3-} \longrightarrow AsO_4^{3-}$

(ii)   Atoms of the element undergoing oxidation and reduction are already balanced.

(iii)   Balancing O atoms,

Reduction half: $2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$

Oxidation half: $2OH^- + AsO_3^{3-} \longrightarrow AsO_4^{3-} + H_2O$

(iv)   Balancing H atoms,

H atoms are already balanced in both the half–reactions.

(v)   Balancing charge,

Reduction half: $3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$…………..Ⓑ

Oxidation half: $2OH^- + AsO_3^{3-} \longrightarrow AsO_4^{3-} + H_2O + 2e^-$…………..Ⓐ

(vi)   Multiply equation Ⓐ by 3 and equation Ⓑ by 2 and then add Ⓐ and Ⓑ.

$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-] \times 2$

$\underline{2OH^- + AsO_3^{3-} \longrightarrow AsO_4^{3-} + H_2O + 2e^-] \times 3}$

$AsO_3^{3-} + 2\,MnO_4^- + H_2O \longrightarrow 3\,AsO_4^{3-} + 2MnO_2 + 2OH^-$
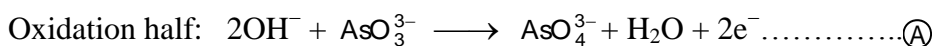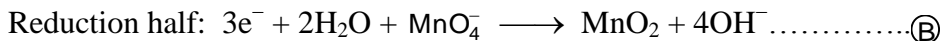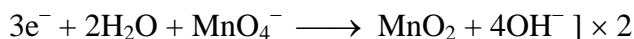
Mostly, the medium in which a redox reaction is to be balanced is given in the problem but if the problem does not state the medium explicitly, then the medium is decided by looking at the reactants or products. If an acid or base is one of the reactants or products, then the medium is the same. If ammonia is

present, the solution would be basic, for example ammonium ion is present, it would be acidic. If metals which form insoluble hydroxides are shown in their ionic form, the solution is acidic.

Although, the oxidation number method and ion−electron method both lead to the correct form of the balanced redox reaction but ion−electron method is considered superior to oxidation number method due to following advantages:

(i) In ion−electron method, all reactants and products are completely balanced (i.e. coefficient is developed for each one of them) whether they participate in the redox change or not, while in oxidation number method, the balancing coefficient is developed only for the species involved in redox change.

(ii) The balancing coefficients developed in ion−electron method are always correct and needs no amendment while such coefficients are to be changed sometimes in oxidation number method.

5. EXPRESSING CONCENTRATION OF SOLUTIONS

5.1 MOLARITY (M)

It is defined as the number of moles of solute present in one litre of solution.

$$\text{Molarity (M)} = \frac{\text{number of moles of solute}}{\text{Volume of solution (in litres)}}$$

Let the weight of solute be w g, molar mass of solute be M_1 g/mol and the volume of solution be V litre.

$$\text{Number of moles of solute} = \frac{\text{weight of solute}}{\text{Atomic or molar mass of solute}} = \frac{w}{M_1}$$

$$\therefore M = \frac{w}{M_1} \times \frac{1}{V \text{(in litres)}}$$

$$\therefore \textbf{Number of moles of solute} = \frac{w}{M_1} = \textbf{M} \times \textbf{V (in litres)}$$

5.2 NORMALITY (N)

It is defined as the number of equivalents of a solute present in one litre of solution. Equivalent is also the term used for amount of substance like mole with the difference that one equivalent of a substance in different reactions may be different as well as the one equivalent of each substance is also different. One equivalent of a substance can be defined as n^{th} part of one mole of that substance.

$$\text{Normality (N)} = \frac{\text{number of equivalents of solute}}{\text{Volume of solution (in litres)}}$$

Let the weight of solute be w g, equivalent mass of solute be E g/eqv. and the volume of solution be V litre.

$$\text{Number of equivalents of solute} = \frac{\text{weight of solute}}{\text{Equivalent mass of solute}} = \frac{w}{E}$$

$$\therefore N = \frac{w}{E} \times \frac{1}{V \text{(in litres)}} \qquad \therefore \textbf{Number of equivalents of solute} = \frac{w}{E} = N \times V \text{ (in litre)}$$

5.3 EQUIVALENT MASS

$$\text{Equivalents mass} = \frac{\text{Atomic or molecular mass}}{\text{'n' factor}} = \frac{M_1}{n}$$

$$\therefore \text{Number of equivalents of solute} = \frac{w}{E} = \frac{w}{M_1/n} = \frac{w \times n}{M_1}$$

$$\therefore \textbf{Number of equivalents of solute = n} \times \textbf{number of moles of solute}$$

Also, $N = \dfrac{w}{M_1/n} \times \dfrac{1}{v \text{ (in litre)}} = \dfrac{w}{M_1} \times \dfrac{1}{V \text{ (in litre)}} \times n$

$N = M \times n$

$\therefore$ **Normality of solution = n × molarity of solution**

5.4 DILUTION EFFECT

When a solution is diluted, the moles and equivalents of solute do not change but molarity and normality changes while on taking out a small volume of solution from a larger volume, the molarity and normality of solution do not change but moles and equivalents change proportionately.

In stoichiometry, the biggest problem is that for solving a problem we need to know a balanced chemical reaction. Since the number of chemical reactions are too many, it is not possible to remember all those chemical reactions. So, there is need to develop an approach which does not require the use of balanced chemical reaction. This approach makes use of a law called law of equivalence. The law of equivalence provides us the molar ratio of reactants and products without knowing the complete balanced reaction, which is as good as having a balanced chemical reaction. The molar ratio of reactants and products can be known by knowing the n–factor of relevant species.

According to the law of equivalence, whenever two substances react, the equivalents of one will be equal to the equivalents of other and the equivalents of any product will also be equal to that of the reactant.

Let us suppose we have a reaction, $A + B \longrightarrow C + D$. In this reaction, the number of moles of electrons lost by 1 mole of A are x and the number of mole of electrons gained by 1 mole of B are y. Since, the number of mole of electrons lost and gained are not same, the molar ratio in which A & B react cannot be 1 : 1. Thus, if we take y moles of A, then the total moles of electrons lost by y moles of A would be $(x \times y)$. Similarly, if x moles of B are taken, then the total mole of electrons gained by x moles of B would be $(y \times x)$. Thus, the number of electrons lost by A and number of electrons gained by B becomes equal. For reactant A, its n–factor is x and the number of moles used are y. So,

The equivalents of A reacting = moles of A reacting × n–factor of A = $y \times x$.

Similarly, for reactant B, its n–factor is y and the number of moles used are x. So,

The equivalents of B reacting = moles of B reacting × n–factor of B

$$= x \times y$$

Thus, the equivalents of A reacting would be equal to the equivalents of B reacting. Thus, the balancing coefficients of the reactant would be as

yA   + xB $\longrightarrow$ C   +   D
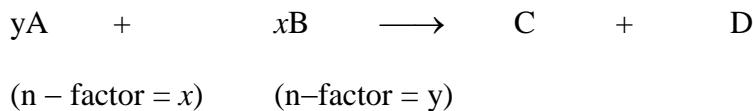
(n – factor = x)   (n–factor = y)

The n–factor of A & B are in the ratio of $x : y$, and their molar ratio is $y : x$. Thus, molar ratio is inverse of the n–factor ratio.

In general, whenever two substances react with their n–factors in the ratio of a : b, then their molar ratio in a balanced chemical reaction would be b : a.

To get the equivalents of a substance, its n–factor is to be known. Let the weight of the substance used in the reaction be w g.

Then, equivalents of substance reacted would be $\dfrac{w}{E}$ or $\dfrac{w}{M_1/n} = \dfrac{w}{M_1} \times n$ (where E and M_1 are the equivalent mass and molar mass of the substance) Thus, in order to calculate the equivalents of a substance, knowledge of n–factor is a must.

6.   N-FACTOR CALCULATION

6.1   ACIDS

Acids are the species which furnish H^+ ions when dissolved in a solvent. For acids, n–factor is defined as the number of H^+ ions replaced by 1 mole of acid in a reaction. Note that the n–factor for acid is not equal to its basicity; i.e. the number of moles of replaceable H^+ atoms present in one mole of acid.

For example,   n–factor of HCl = 1,

n–factor of HNO_3 = 1,

n–factor of H_2SO_4 = 1 or 2, depending upon extent of reaction it undergoes.

$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$.
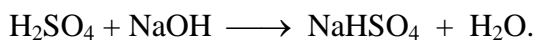
Although one mole of H_2SO_4 has 2 replaceable H atoms but in this reaction H_2SO_4 has given only one H^+ ion, so its n–factor would be 1.

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$
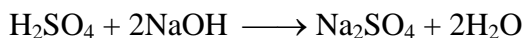
The n–factor of H_2SO_4 in this reaction would be 2.

Similarly, n–factor of H_2SO_3 = 1 or 2

n–factor of H_2CO_3 = 1 or 2

n–factor of H_3PO_4 = 1 or 2 or 3

n–factor of H_3PO_3 = 1 or 2 because one of the H is not replaceable in H_3PO_3. This can be

seen using its structure $\underset{\displaystyle H}{\overset{\displaystyle O}{\underset{|}{\overset{\|}{H-O-P-O-H}}}}$. The H atoms which are linked to oxygen are replaceable while the H atom linked directly to central atom (P) is non-replaceable.

n–factor of $H_3BO_3 = 1$

In H_3BO_3, although all three H are linked to oxygen, yet all 3 H are not replaceable. Here, boron atom is electron deficient, so it acts as a Lewis acid. When H_3BO_3 is added to water, then oxygen atom of H_2O through its lone pair attack the boron atom, as follows
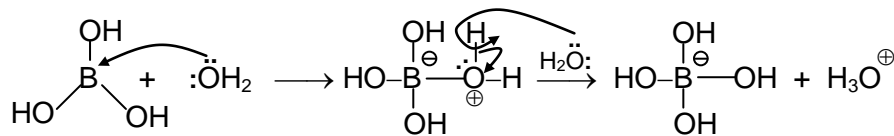
The net reaction is $H_3BO_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$.

Thus, one mole of H_3BO_3 in solution gives only one mole of H^+, so its n–factor is 1.

6.2   BASES

Bases are the species, which furnish OH^- ions when dissolved in a solvent. For bases, n–factor is defined as the number of OH^- ions replaced by 1 mole of base in a reaction. Note that n–factor is not equal to its acidity i.e. the number of moles of replaceable OH^- ions present in 1 mole of base.

For example, n–factor of NaOH = 1

n–factor of $Zn(OH)_2 = 1$ or 2

n factor of $Ca(OH)_2 = 1$ or 2

n factor of $Al(OH)_3 = 1$ or 2 or 3

n factor of $NH_4(OH) = 1$.

6.3   SALTS WHICH REACT SUCH THAT NO ATOM UNDERGOES CHANGE IN OXIDATION STATE

The n–factor for such salts is defined as the total moles of cationic /anionic charge replaced in 1 mole of the salt. For the reaction,

$Na_3PO_4 + BaCl_2 \longrightarrow NaCl + Ba_3(PO_4)_2$
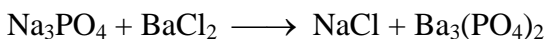
To get one mole of $Ba_3(PO_4)_2$, two moles of Na_3PO_4 are required, which means six moles of Na^+ are completely replaced by 3 moles of Ba^{2+} ions. So, six moles of cationic charge is replaced by 2 moles of Na_3PO_4, thus each mole of Na_3PO_4 replaces 3 moles of cationic charge. Hence, n–factor of Na_3PO_4 in this reaction is 3.

6.4   SALTS WHICH REACT IN A MANNER THAT ONLY ONE ATOM UNDERGOES CHANGE IN OXIDATION STATE AND GOES IN ONLY ONE PRODUCT

The n–factor of such salts is defined as the number of moles of electrons exchanged (lost or gained) by one mole of the salt.

Let us have a salt A_aB_b in which oxidation state of A is $+x$. It changes to a compound, which has atom D in it. The oxidation state of A in A_cD be $+y$.

$$A_a^{+x}B_b \longrightarrow A_c^{+y}D$$
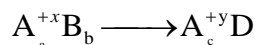
The n–factor of A_aB_b is calculated as

$$n = |ax - ay|$$

To calculate n–factor of a salt of such type, we take one mole of the reactant and find the number of mole of the element whose oxidation state is changing. This is multiplied with the oxidation state of the element in the reactant, which gives us the total oxidation state of the element in the reactant. Now, we calculate the total oxidation state of the same element in the product for the same number of mole of atoms of that element in the reactant. Remember that the total oxidation state of the same element in the product is not calculated for the number of mole of atoms of that element in the product.

For example, let us calculate the n–factor $KMnO_4$ for the given chemical change.

$$KMnO_4 \xrightarrow{\ H^+\ } Mn^{+2}.$$
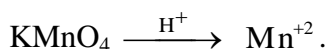
In this reaction, oxidation state of Mn changes from +7 to +2. Thus, $KMnO_4$ is acting as oxidizing agent, since it is reduced.

$\therefore$ n–factor of $KMnO_4 = |1 \times (+7) - 1 \times (+2)| = 5$

Similarly,

(a) $KMnO_4 \xrightarrow{\ H_2O\ } Mn^{+4}$
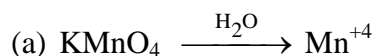
n–factor of $KMnO_4 = |1 \times (+7) - 1 \times (+4)| = 3$

(b) $KMnO_4 \xrightarrow{\ OH^-\ } Mn^{+6}$
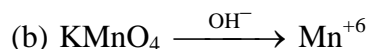
n–factor of $KMnO_4 = |1 \times (+7) - 1 \times (+6)| = 1$

It can be seen that in all the above chemical changes, $KMnO_4$ is acting as oxidizing agent, yet its n–factor is not same in all reactions. Thus, the n–factor of a compound is not fixed, it depends on the type and the extent of reaction it undergoes.

Illustration 10

Question: **Calculate the n–factor of reactants in the given chemical changes?**

(a) $K_2Cr_2O_7 \xrightarrow{\ H^+\ } Cr^{3+}$

(b) $C_2O_4^{2-} \longrightarrow CO_2$

(c) $S_2O_3^{2-} \xrightarrow{\ alkaline\ } SO_4^{2-}$

(d) $I^- \longrightarrow ICl$

Solution: (a) $K_2 \overset{+6}{Cr_2} O_7 \xrightarrow{\;H^+\;} Cr^{3+}$
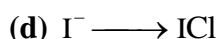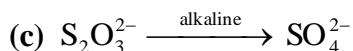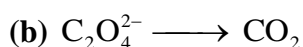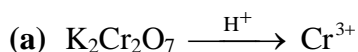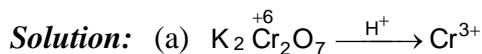
The oxidation state of Cr changes from +6 to +3.

$\therefore n = |\, 2 \times (+6) - 2 \times (+3) \,| = 6$

(b) $\overset{+3}{C_2} O_4^{2-} \longrightarrow \overset{+4}{C}O_2$
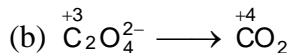
Carbon get oxidized from +3 to +4.

$\therefore n = |\, 2 \times (+3) - 2 \times (+4) \,| = 2$

(c) $\overset{+2}{S_2} O_3^{2-} \xrightarrow{\;alkaline\;} \overset{+6}{S}O_4^{2-}$
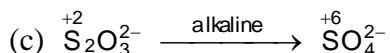
The oxidation state of sulphur changes from +2 to +6.

$\therefore n = |\, 2 \times (+2) - 2 \times (+6) \,| = 8$

(d) $I^- \longrightarrow \overset{+1}{I}Cl$
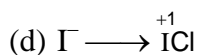
I^- get oxidized to I^+.

$\therefore n = |\, 1 \times (-1) - 1 \times (+1) \,| = 2$

6.5 SALTS THAT REACT IN A MANNER THAT ONLY ONE ATOM UNDERGO CHANGE IN OXIDATION STATE BUT GOES IN TWO PRODUCTS WITH THE SAME OXIDATION STATE.

Let us have a salt A_aB_b in which oxidation state of A is $-x$. It undergoes a reaction such that element A changes it oxidation state and goes in more than one (two) products with the same oxidation state (but different oxidation state than in the reactant). In such case, the n−factor is calculated in the same manner as in case 4.

Let the chemical change be

$$A_a^{+x} B_b \longrightarrow A_c^{+y} D + A_e^{+y} F$$
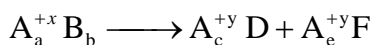
In such cases, the number of products in which element A is present is of no significance since the oxidation state of A in both the products is same. The point of importance is not the number of products containing that element which undergoes change in oxidation state but the oxidation state of the element is of importance. The n−factor of A_aB_b is calculated in the same way as in case 4.

$\therefore$ n−factor of $A_aB_b = |ax - ay|$

For example, let us calculate the n−factor of $K_2Cr_2O_7$ for the given chemical change.

$$Cr_2O_7{}^{2-} \longrightarrow Cr^{3+} + Cr^{3+}$$
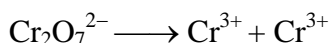
In this reaction, oxidation state of Cr changes from +6 to +3 in both products.

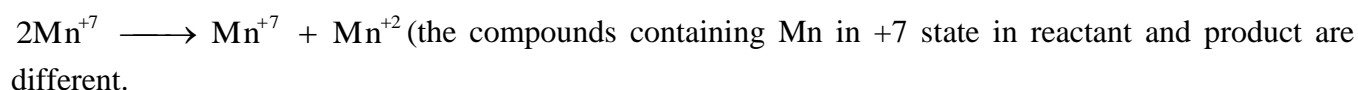$\therefore$ n–factor of $K_2Cr_2O_7 = |\,2 \times (+6) - 2 \times (+3)\,| = 6$

6.6 SALTS WHICH REACT IN A MANNER THAT ONLY ONE ATOM UNDERGOES CHANGE IN OXIDATION STATE BUT GOES IN TWO PRODUCTS WITH DIFFERENT OXIDATION STATE (DIFFERENT THAN IN THE REACTANT) AS A RESULT OF EITHER OXIDATION OR REDUCTION.

Let the chemical change be

$$A_a^{+x} B_b \longrightarrow A_c^{+y} D + A_e^{+z}F$$
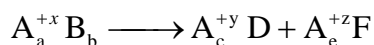
In such cases, n–factor calculation is not possible until we know that how much of A has changed its oxidation state to +y and how much of A has changed its oxidation state. to +z. This is because the number of moles of electrons lost or gained by one mole of A_aB_b would depend on the fact that how much of A underwent change to oxidation state +y and how much of A underwent change to oxidation state +z. This is possible only by knowing the balanced chemical reaction. If we know the balanced chemical reaction, then the n–factor calculation is of no use because problem can be solved using mole concept. But nevertheless, n–factor calculation in such cases can be done as follows.

Let us take a chemical change, $2Mn^{+7} \longrightarrow Mn^{+4} + Mn^{+2}$ out of the two moles of Mn^{+7}, one mole Mn^{+7} changes to Mn^{+4} by gaining 3 mole of electrons and the other mole of Mn^{+7} changes to Mn^{+2} by gaining 5 mole of electrons, so in all 8 mole of electrons are gained by 2 mole of Mn^{+7}. So each mole of Mn^{+7} has gained 8/2 = 4 mole of electrons. Thus, 4 would be the n–factor of Mn^{+7} in this reaction.

If the reaction would have been

$$3Mn^{+7} \longrightarrow 2Mn^{+2} + Mn^{+4}.$$
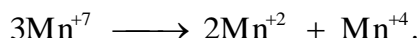
Out of 3 moles of Mn^{+7}, two moles of Mn^{+7} changes to Mn^{+2} by gaining 10 mole of electrons and one mole of Mn^{+7} changes to Mn^{+4} by gained 3 mole of electrons. Thus each mole of Mn^{+7} have gained 13/3 mole of electrons. Therefore, the n–factor of Mn^{+7} in this reaction would be 13/3.

Note that n–factor can be a fraction because it is not the number of electrons exchanged but it is the number of moles of electrons exchanged which can be a fraction.

Now, if the reaction would have been $3Mn^{+7} \longrightarrow Mn^{+2} + 2Mn^{+4}$. Thus, each mole of Mn^{+2}. Thus, each mole of Mn^{+7} have gained 11/3 mole of electron. Therefore, n–factor of Mn^{+7} in this reaction would be 11/3.

6.7   Salts which react in a fashion that only one atom undergoes change in oxidation state but goes in two products with different oxidation state (in one product with same oxidation state and in other with different oxidation state than in the reactant)

Let the reaction be

$$A_a^{+x}B_b \longrightarrow A_e^{+x}F + A_c^{+y}D$$
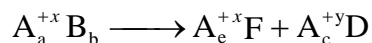
For such reactions also, the n−factor calculation is not possible without the knowledge of balanced chemical reaction because n−factor of A_aB_b would depend on the fact that how much of A underwent change to oxidation state +y and how much of A remained in the same oxidation state +x.

For example, if we have a chemical change as

$2Mn^{+7} \longrightarrow Mn^{+7} + Mn^{+2}$ (the compounds containing Mn in +7 state in reactant and product are different.

In this reaction, 5 moles of electrons are gained by 2 moles of Mn^{+7}, so each mole of Mn^{+7} takes up 5/2 mole of electrons. Therefore, n−factor of Mn^{+7} in this reaction would be 5/2.

6.8 SALTS THAT REACT IN A MANNER THAT TWO TYPE OF ATOMS IN THE SALT UNDERGO CHANGE IN OXIDATION STATE (BOTH THE ATOMS ARE EITHER GETTING OXIDISED OR REDUCED).

Let the change be represented as

$$A_a^{+x}B_b \longrightarrow A_c^{+y}D + E_f B^{+z}$$
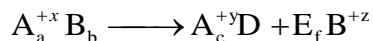
In this reaction, both A and B are changing their oxidation states and both of them are either getting oxidized or reduced. In such cases, the n−factor of the compound would be the sum of individual n−factors of A and B.

n−factor of A = $|ax - ay|$

n−factor of B = $|-ax - bz|$ because the total oxidation state of 'b' B's in the reactant is $-ax$ (as the total oxidation state of 'a' A's in the reactant is $+ax$) and the total oxidation state of y B's in the product is bz.

$\therefore$ n−factor of $A_aB_b = |ax - ay| + |-ax - bz|$

In general, the n−factor of the salt will be the total number of mole of electrons lost or gained by one mole of the salt.

For example, we have a reaction, $Cu_2^{+1}S^{-2} \longrightarrow Cu^{2+} + \overset{+4}{S}O_2$

in which Cu^+ and S^{2-} both are getting oxidized to Cu^{2+} and S^{+4} respectively.

$\therefore$ n−factor of $Cu_2S = |2 \times (+1) - 2 \times (+2)| + |1 \times (-2) - 1 \times (+4)| = 8$

6.9 SALTS THAT REACT IN A MANNER THAT TWO ATOMS IN THE SALT UNDERGOES CHANGE IN OXIDATION STATE (ONE ATOM IS GETTING OXIDISED AND THE OTHER IS GETTING REDUCED).

If we have a salt which react in a fashion that atoms of one of the element are getting oxidized and the atoms of another element are getting reduced and no other element on the reactant side is getting oxidized or reduced, than the n−factor of such a salt can be calculated either by taking the total number of moles of electrons lost or total number of mole of electrons gained by one mole of the salt.

For example, decomposition reaction of $KClO_3$ is represented as

$$K\overset{+5}{Cl}\overset{-2}{O_3} \longrightarrow K\overset{-1}{Cl} + \overset{0}{O_2}$$
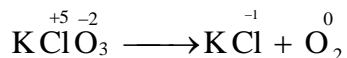
In this reaction, O^{2-} is getting oxidized to O_2 and Cl^{+5} is getting reduced to Cl^{-1}. In each case, 6 moles of electrons are exchanged whether we consider oxidation or reduction.

n−factor of $KClO_3$ considering oxidation = $|3(-2) - 3(0)| = 6$

or n−factor of $KClO_3$ considering reduction = $|1 \times (+5) - 1 \times (-1)| = 6$

6.10 SALTS OR COMPOUNDS WHICH UNDERGOES DISPROPORTIONATION REACTION.

Disproportionation reactions are the reactions in which oxidizing and reducing agents are same or the same element from the same compound is getting oxidized as well as reduced. n−factor of a disproportionation reaction can only be calculated using a balanced chemical reaction. We will categorize disproportionation reactions into two types.

(a) Disproportionation reactions in which moles of compound getting oxidized and reduced are same i.e. moles of oxidizing agent and reducing agent are same. The n−factor for such compounds is calculated by either the number of mole of electrons lost or gained by one mole of the compound because in such a case, n−factor of the compound acting as oxidizing agent or as reducing agent would be same.

For example, $2H_2O_2 \longrightarrow 2H_2O + O_2$

Out of the 2 mole of H_2O_2 used in reaction, one mole of H_2O_2 gets oxidized to O_2 (oxidation state of O changes from −1 to 0) while the other mole of H_2O_2 gets reduced to H_2O (oxidation state of O changes from −1 to −2). When 1 mole of H_2O_2 gets oxidized to O_2, the half−reaction would be

$$O_2^{2-} \longrightarrow O_2^0 + 2e^-$$

and when 1 mole of H_2O_2 gets reduced to H_2O, the half−reaction would be $O_2^{2-} + 2e^- \longrightarrow 2O^{2-}$

Thus, it is evident that one mole of H_2O_2 (which is either getting oxidized or reduced) will lose or gain 2 mole of electrons. Therefore, n−factor of H_2O_2 as oxidizing as well as reducing agent in this reaction is 2. Thus,

$$H_2O_2 + H_2O_2 \longrightarrow 2H_2O + O_2$$

Reducing agent   Oxidizing agent

  (n = 2)   (n = 2)   (n = 1) (n = 2)

Or when the reaction is written as

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
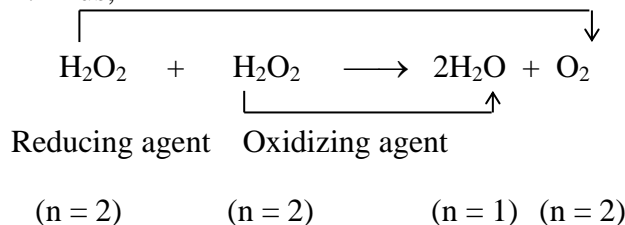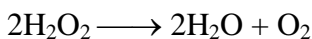
where, H_2O_2 is not distinguished as how much of it functions as oxidizing agent and how much as reducing agent, then n−factor calculation can be done in the following manner. Find the number of electrons exchanged (lost or gained) using the balanced equation and divide it by the number of moles of H_2O_2 involved in the reaction. Thus, the n−factor of H_2O_2 when the reaction is written without segregating oxidizing and reducing agent is $\frac{2}{2} = 1$.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

  (n = 1)   (n = 1) (n = 2)
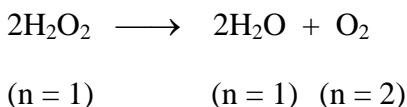
(b) Disproportionation reactions in which moles of compound getting oxidized and reduced are not same i.e. moles of oxidizing agent and reducing agent are not same.

For example,

$$6Br_2 + 12\,OH^- \longrightarrow 10Br^- + 2BrO_3^- + 6H_2O$$
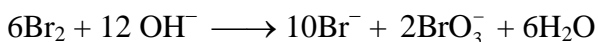
In this reaction, the mole of electrons lost by the oxidation of some of the moles of Br_2 are same as the number of mole of electrons gained by the reduction of rest of the moles of Br_2. Of the 6 moles of Br_2 used, one mole is getting oxidized, losing 10 electrons (as reducing agent) and 5 moles of Br_2 are getting reduced and accepts 10 moles of electron (as oxidizing agent).

$$Br_2 \longrightarrow 2Br^{+5} + 10e^-$$

$$5Br_2 + 10e^- \longrightarrow 10Br^-$$

$$\overline{Br_2 \quad + \quad 5Br_2 \longrightarrow 10Br^- + \quad 2Br^{+5}}$$

Reducing agent Oxidizing agent

   (n = 10)   (n = 2)   (n = 1)   (n = 5)
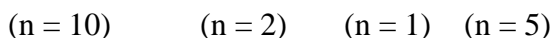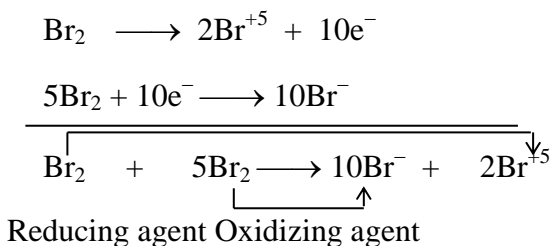
Thus, n–factor of Br_2 acting as oxidizing agent is 2 and that Br_2 acting as reducing agent has n–factor 10.

Or when the reaction is written as

$$6Br_2 \longrightarrow 10Br^- + 2Br^{+5}$$

where, Br_2 is not distinguished as how much of it functions as oxidizing agent and how much as reducing agent, then for calculating n–factor of compound in such reactions, first

find the total number of mole of electrons exchanged (lost or gained) using the balanced equation and divide it with the number of mole of Br_2 involved in the reaction to get the number of mole of electrons exchanged by one mole of Br_2.

In the overall reaction, the number of mole of electrons exchanged (lost or gained) is 10 and the moles of Br_2 used in the reaction are 6. Thus, each mole of Br_2 has exchanged 10/6 or 5/3 mole of electrons. Therefore, the n–factor of Br_2 when the reaction is written without segregating oxidizing and reducing agent is 5/3.

$$6Br_2 \longrightarrow 10Br^- + 2Br^{+5}$$

   (n = 5/3)   (n = 1)   (n = 5)
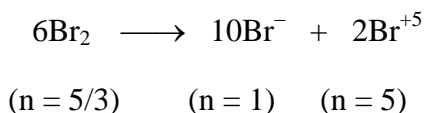
7. VOLUMETRIC ANALYSIS

Now, we have developed enough platforms to understand the law of equivalents and volumetric analysis.

The volumetric analysis is an analytical method of estimating the concentration of a substance in a solution by adding exactly same number of equivalents of another substance present in a solution of known concentration.

This is the basic principle of titration. Volumetric analysis is also known as *titrimetric analysis*.

The substance whose solution is employed to estimate the concentration of unknown solution is called *titrant* and the substance whose concentration is to be estimated is called *titrate*.

The volumetric analysis is divided into following types:

(a) Simple titrations

(b) Back titrations

(c) Double titrations

7.1   SIMPLE TITRATIONS

The aim of simple titration is to find the concentration of an unknown solution with the help of the known concentration of another solution.

Let us take a solution of a substance 'A' of unknown concentration. We are provided with solution of another substance 'B' whose concentration is known (N_1). We take a certain known volume (V_2 litre) of 'A' in a flask and start adding 'B' from burette to 'A' slowly till all the 'A' is consumed by 'B'. This can be known with the aid of suitable indicator, which shows colour change after the complete consumption of 'A'. Let the volume of B consumed is V_1 litre. According to the law of equivalents, the number of equivalents of 'A' would be equal to the number of equivalents of 'B'.

$\therefore$ $N_1V_1 = N_2V_2$, where N_2 is the concentration of 'A'.

Thus using this equation, the value of N_2 can be calculated.

There are four types of simple titrations, namely

(a) Acid–base titrations

(b) Redox titrations

(c) Precipitation titrations and

(d) Complexometric titrations

STOICHIOMETRY & REDOX REACTIONS

7.1.1 ACID–BASE TITRATIONS

In this type of titration, the concentration of an acid in a solution is estimated by adding a solution of standard base and vice versa. The equivalence point is detected by adding a few drops of a suitable indicator to the solution whose concentration is to be estimated. An acid–base indicator gives different colours with acids and bases. The choice of indicator in a particular titration depends on the pH–range of the indicator and the pH change near the equivalence point. For example,

(i) STRONG ACID–STRONG BASE TITRATION

In the titration of HCl Vs NaOH, the equivalence point lies in the pH–range of 4–10. Thus, methyl red (pH–range 4.2 to 6.3), methyl orange (pH–range 3.1 to 4.4) and phenolphthalein (pH–range 8.3 −10) are suitable indicators of such titrations.

(ii) WEAK ACID–STRONG BASE TITRATION

In the titration of CH_3COOH and NaOH, the equivalence point lies between 7.5 and 10. Thus, phenolphthalein is the suitable indicator.

(iii) WEAK BASE–STRONG ACID TITRATION

In the titration of NH_4OH and HCl, the equivalence point lies in the pH range of 4 to 6.5. Thus, methyl orange and methyl red are suitable indicators.

(iv) WEAK ACID–WEAK BASE TITRATION

In the titration of CH_3COOH and NH_4OH, the equivalence point lies between 6.5 and 7.5 and the pH change is not sharp at the equivalence point. Thus, no simple indicator can be employed to detect the equivalence point.

7.1.2 REDOX TITRATIONS

In a redox titration, an oxidant is estimated by adding reductant or vice–versa. For example, Fe^{2+} ions can be estimated by titration against acidified $KMnO_4$ solution when Fe^{2+} ions are oxidized to Fe^{3+} ions and $KMnO_4$ is reduced to Mn^{2+} in the presence of acidic medium. $KMnO_4$ functions as self–indicator as its purple colour is discharged at the equivalence point.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$$

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$
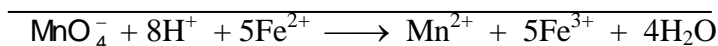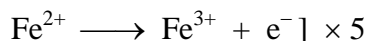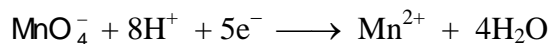
$$(n = 5) \qquad (n = 1)$$

In addition to acidified $KMnO_4$, acidified KCr_2O_7 can also be employed. Other redox titrations are iodimetry, iodometry etc.

(i) IODIMETRY

This titration involves free iodine. Such direct estimation of iodine is called *iodimetry*. This involves the titration of iodine solution with known sodium thiosulphate solution, whose normality is N. Let the volume of sodium thiosulphate used be V litre.

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

$(n=2) \qquad (n=1)$
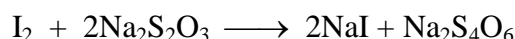
Equivalents of I_2 = Equivalents of $Na_2S_2O_3$ used = $N \times V$

Moles of $I_2 = \dfrac{N \times V}{2}$

Mass of free I_2 in the solution $= \left[\dfrac{N \times V}{2} \times 254 \right] g$

(ii) IODOMETRY

This is an indirect method of estimation of iodine. An oxidising agent is made to react with excess of solid KI. The oxidising agent oxidises I^- to I_2. This liberated iodine is then made to react with $Na_2S_2O_3$ solution of normality N. Let the volume of thiosulphate solution required be V litre.

$$\text{Oxidising Agent (A)} + KI \longrightarrow I_2 \xrightarrow{2Na_2S_2O_3} 2NaI + Na_2S_4O_6$$

$$+$$
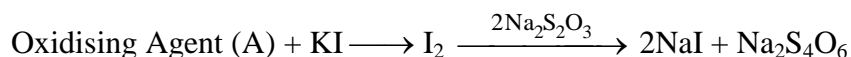
$$\text{reduced form of}$$
$$\text{oxidizing agent}$$

Equivalents of 'A' = Equivalents of I_2 = Equivalents of $Na_2S_2O_3$ used = $N \times V$

Equivalents of I_2 liberated from KI = $N \times V$

Equivalents of 'A' = $N \times V$

Let the n−factor of 'A' in its reaction with KI be x, then

Mass of 'A' consumed $= \dfrac{N \times V}{x} \times M_A$ \qquad (where M_A is the molar mass of A)

7.1.3 PRECIPITATION TITRATIONS

In a titration of this kind, cations and anions combine to form a compound of very low solubility. Thus, a solid residue separates out. For example,

$$AgNO_3 \ + \ NaCl \ \longrightarrow \ AgCl\downarrow \ + \ NaNO_3$$

<div align="center">white</div>

$$BaCl_2 \ + \ H_2SO_4 \ \longrightarrow \ BaSO_4\downarrow \ + \ 2HCl$$
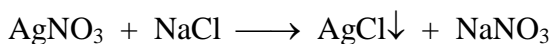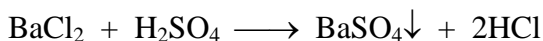
<div align="center">white</div>

7.1.4 COMPLEXOMETRIC TITRATIONS

In this type of titration, the titrate combines with the titrant to form complex salts. The complex salts may or may not be soluble. For example,

$$CuSO_4 + 4NH_4OH \ \longrightarrow \ [Cu(NH_3)_4]SO_4 \ + \ 4H_2O$$

$$AgNO_3 + 2KCN \ \longrightarrow \ K[Ag(CN)_2] + KNO_3$$
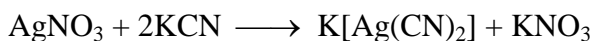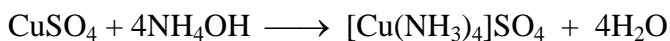
7.2 BACK TITRATIONS

Let us assume that we have an impure solid substance 'C', weighing 'w' g and we are required to calculate the percentage purity of 'C' in the sample. We are also provided with two solutions 'A' and 'B', where the concentration of 'B' is known (N_1) and that of 'A' is unknown. For the back titration to work, following conditions are to be satisfied (a) Compounds 'A', 'B' and 'C' should be such that 'A' and 'B' react with each other. (b) 'A' and pure 'C' also react with each other but the impurity present in 'C' does not react with 'A'. (c) Also the product of 'A' and 'C' should not react with 'B'.

Now we take out certain volume of 'A' in a flask (the equivalents of 'A' taken should be $\geq$ equivalents of pure 'C' in the sample) and perform a simple titration using 'B'. Let us assume that the volume of 'B' used be V_1 litre.

Equivalents of 'B' reacted with 'A' = N_1V_1

$\therefore$ Equivalents of 'A' initially = N_1V_1

In another flask, we again take same volume of 'A' but now 'C' is added to this flask. Pure part of 'C' reacts with 'A' and excess of 'A' is back titrated with 'B'. Let the volume of 'B' consumed is V_2 litre.

Equivalents of 'B' reacted with excess of 'A' = N_1V_2

$\therefore$ Equivalents of 'A' in excess = N_1V_2

Equivalents of 'A' reacted with pure 'C' = $(N_1V_1 - N_1V_2)$

Equivalents of pure 'C' = $(N_1V_1 - N_1V_2)$

Let the n–factor of 'C' in its reaction with 'A' be x, then the moles of pure 'C' $= \dfrac{(N_1V_1 - N_1V_2)}{x}$

$\therefore$ Mass of pure 'C' $= \dfrac{(N_1V_1 - N_1V_2)}{x} \times$ Molar mass of 'C'.

$\therefore$ Percentage purity of 'C' $= \dfrac{(N_1V_1 - N_1V_2)}{x} \times \dfrac{\text{Molar mass of 'C'}}{w} \times 100$

7.3 DOUBLE TITRATIONS

The purpose of double titration is to determine the percentage composition of an alkali mixture or an acid mixture. In the present case, we will find the percentage composition of an alkali mixture. Let us consider a solid mixture of NaOH, Na_2CO_3 and some inert impurities, weighing 'w' g. We are required to find the % composition of this alkali mixture. We are also given an acid reagent (HCl) of known concentration M_1 that can react with the alkali sample.

We first dissolve this mixture in water to make an alkaline solution and then we add two indicators, (Indicators are substances that indicate colour change of solution when a reaction gets completed), namely phenolphthalein and methyl orange to the solution. Now, we titrate this alkaline solution with standard HCl.

NaOH is a strong base while Na_2CO_3 is a weak base. So it is obvious that NaOH reacts first with HCl completely and Na_2CO_3 reacts only after complete NaOH is neutralized.

$$NaOH + HCl \longrightarrow NaCl + H_2O \qquad \text{.....(i)}$$
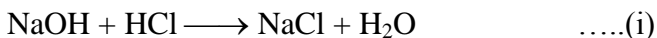
Once NaOH has reacted completely, then Na_2CO_3 starts reacting with HCl in two steps, shown as

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl \qquad \text{.....(ii)}$$

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O \qquad \text{.....(iii)}$$

It is clear that when we add HCl to the alkaline solution, alkali is neutralized and the pH of the solution decreases. Initially the pH decrease would be rapid as strong base (NaOH) is neutralized completely. When Na_2CO_3 is converted to $NaHCO_3$ completely, the solution is still weakly basic due to the presence of $NaHCO_3$ (which is weaker as compared to Na_2CO_3). At this point, phenolphthalein changes colour since it requires this weakly basic solution to show its colour change. When HCl is further added, the pH again decreases and when all the $NaHCO_3$ reacts to form NaCl, CO_2 and H_2O the solution becomes weakly acidic due to the presence of the weak acid (H_2CO_3). At this point, methyl orange changes colour as it requires this weakly acidic solution to show its colour change.

Thus in general, phenolphthalein shows colour change when the solution contains weakly basic NaHCO₃ along with other neutral substances while methyl orange shows colour change when solution contains weakly acidic H₂CO₃ along with other neutral substances.

STOICHIOMETRY & REDOX REACTIONS

Let the volume of HCl used up for the first and the second reaction be V_1 litre (this is the volume of HCl used from the beginning of the titration up to the point when phenolphthalein shows colour change) and the volume of HCl required for the third reaction be V_2 litre (this is the volume of HCl used from the point where phenolphthalein had changed colour upto the point when methyl orange shows colour change). Then,

Moles of HCl consumed by $NaHCO_3$ = Moles of $NaHCO_3$ reacted = M_1V_2

Moles of $NaHCO_3$ formed from Na_2CO_3 = M_1V_2

Moles of Na_2CO_3 in the mixture = M_1V_2

Mass of Na_2CO_3 in the mixture = $M_1V_2 \times 106$

% of Na_2CO_3 in the mixture = $\dfrac{M_1V_2 \times 106}{w} \times 100$

Moles of HCl used in the reaction (i) and (ii) = M_1V_1

Moles of HCl used in reaction (ii) = M_1V_2

Moles of HCl used in reaction (i) = $(M_1V_1 - M_1V_2)$

$\therefore$ Moles of NaOH = $(M_1V_1 - M_1V_2)$

Mass of NaOH = $(M_1V_1 - M_1V_2) \times 40$

% of NaOH in the mixture = $\dfrac{(M_1V_1 - M_1V_2) \times 40}{w} \times 100$

Here, we have determined the percentage composition of the mixture using mole concept, as the balanced reactions were available. If we were to solve this by equivalent concept, then the procedure adopted would be

$$NaOH + HCl \longrightarrow NaCl + H_2O \qquad\qquad .....(i)$$
$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl \qquad .....(ii)$$
$$(n = 1) \quad (n = 1) \qquad\qquad\qquad (n = 1)$$
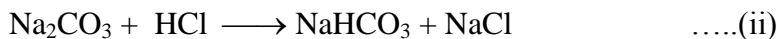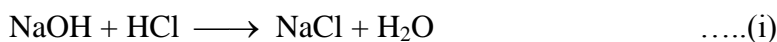
Phenolphthalein shows end point after reaction (ii)

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O \qquad .....(iii)$$
$$(n = 1) \quad (n = 1)$$
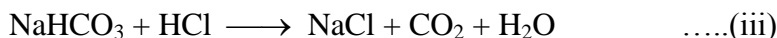
and methyl orange shows end point after reaction (iii).

At Phenolphthalein end point,

(Equivalents of HCl)$_1$ = Equivalents of NaOH + Equivalents of Na_2CO_3 (n = 1) .....(iv)

$$= M_1V_1$$

or (Equivalents of HCl)$_1$ = Equivalents of NaOH +½ Equivalents of Na$_2$CO$_3$ (n = 2) …..(iv)

At methyl orange end point,

(Equivalents of HCl)$_2$ = Equivalents of NaHCO$_3$ reacted (n = 1)

= Equivalents of NaHCO$_3$ produced (n = 1) = Equivalents of Na$_2$CO$_3$ (n = 1)

∴ M$_1$V$_2$ = Equivalents of Na$_2$CO$_3$ (n = 1) = ½ Equivalents of Na$_2$CO$_3$ (n = 2) …...(v)

Substracting equation (v) from equation (iv),

Equivalents of NaOH = (M$_1$V$_1$ − M$_1$V$_2$)

∴ Moles of NaOH = (M$_1$V$_1$ − M$_1$V$_2$)　　　　　(Since n−factor of NaOH is 1)

∴ % of NaOH in the mixture $= \dfrac{(M_1V_1 - M_1V_2) \times 40}{w} \times 100$

Equivalents of Na$_2$CO$_3$ (n = 1) = M$_1$V$_2$

and moles of Na$_2$CO$_3$ = M$_1$V$_2$　　　　　(Since n−factor of Na$_2$CO$_3$ is 1)

∴ % of Na$_2$CO$_3$ in the mixture = $\dfrac{M_1V_2 \times 106}{w} \times 100$

In the above case, we have taken alkali mixture of NaOH & Na$_2$CO$_3$. But other alkali mixtures can also be taken. For example,

(i) If a mixture of NaOH and NaHCO$_3$ has been taken

(a) Equivalents of NaOH = Equivalents of HCl required upto phenolphthalein end point

(b) Equivalents of NaHCO$_3$ = Equivalents of HCl required from phenolphthalein end point to methyl orange end point.

(ii) If a mixture of Na$_2$CO$_3$ and NaHCO$_3$ has been taken

(a) ½ Equivalents of Na$_2$CO$_3$ (n = 2) = Equivalents of HCl required upto phenolphthalein end point

(b) ½ Equivalents of Na$_2$CO$_3$ (n = 2) + Equivalents of NaHCO$_3$ initially (n = 1)

= Equivalents of HCl required from phenolphthalein end point to methyl orange end point.

(iii) If a mixture of NaOH, Na$_2$CO$_3$ and NaHCO$_3$ has been taken

(a) Equivalents of NaOH + ½ Equivalents of Na$_2$CO$_3$ (n = 2)

= Equivalents of HCl required upto phenolphthalein end point

(b) ½ Equivalents of Na$_2$CO$_3$ (n = 2) + Equivalents of NaHCO$_3$ initially (n = 1)

= Equivalents of HCl required from phenolphthalein end point to methyl orange end point.

Illustration 11

Question: **A solution contains a mixture of Na_2CO_3 and NaOH. Using phenolphthalein as indicator, 25 ml of mixture required 21 ml of 1.1 N HCl for the end point. With methyl orange as indicator, 25 ml of solution required 25 ml of the same HCl for the end point. Calculate grams per litre of each substance in the mixture.**

Solution: Since, the volume of HCl required in titration using methyl orange is greater than the volume of HCl required using phenolphthalein, this means that the titration is carried out separately two times using phenolphthalein and methyl orange indicators, respectively.

$$NaOH \ + \ HCl \ \longrightarrow \ NaCl \ + \ H_2O \qquad ……(i)$$

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl \qquad ……(ii)$$

$$NaHCO_3 + HCl \longrightarrow NaCl \ + \ CO_2 \ + \ H_2O ……(iii)$$

Thus, the volume of HCl used in third reaction = (25 − 21) = 4.0 ml

∴ Moles of HCl used in third reaction = $4.0 \times 10^{-3} \times 1.1$

Moles of $NaHCO_3$ reacted = 4.4×10^{-3}

Moles of $NaHCO_3$ produced = 4.4×10^{-3}

∴ Moles of Na_2CO_3 present in 25 ml = 4.4×10^{-3}

∴ Mass of Na_2CO_3 present in 1 litre = $4.4 \times 10^{-3} \times 106 \times 40 = 18.656$ g

Moles of HCl reacted in second reaction = 4.4×10^{-3}

Moles of HCl used in first two reactions = $21 \times 10^{-3} \times 1.1 = 23.1 \times 10^{-3}$

∴ Moles of HCl used in first reaction = $(23.1 - 4.4) \times 10^{-3} = 18.7 \times 10^{-3}$

Moles of NaOH present in 25 ml = 18.7×10^{-3}

∴ Mass of NaOH present in 1 litre = $18.7 \times 10^{-3} \times 40 \times 40 = 29.92$ g

8. VOLUME STRENGTH OF H_2O_2 SOLUTION

When a solution of H_2O_2 is labeled as '*x* volumes', it means that *1 volume (1 ml or 1 litre) of H_2O_2 solution would liberate x volumes (1 ml or 1 litre) of O_2 at STP on complete decomposition.*

$$H_2O_2 \xrightarrow{\Delta} H_2O + \tfrac{1}{2} O_2 \qquad \dots(i)$$
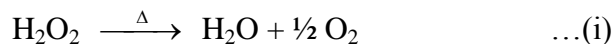
If a H_2O_2 solution (acting as reducing agent) has normality N and it is to be reacted with $KMnO_4$ solution (acting as oxidising agent). Our task is to determine its volume strength. We can say that there are N equivalents of H_2O_2 present in 1 litre of this H_2O_2 solution.

$\therefore$ 1 ml of H_2O_2 of this solution would contain $\dfrac{N}{1000}$ equivalents.

$$H_2O_2 + KMnO_4 \xrightarrow{H^+} O_2 + Mn^{+2} \quad \dots(ii)$$

$$(n = 2) \quad (n = 5)$$
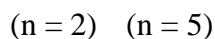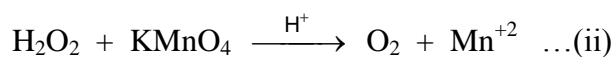
$\therefore$ Moles of H_2O_2 in 1 ml of this solution $= \dfrac{1}{2} \times \dfrac{N}{1000}$ [from equation (ii)]

When these many moles of H_2O_2 in 1 ml of solution are allowed to decompose according to the reaction, $H_2O_2 \xrightarrow{\Delta} H_2O + \tfrac{1}{2}O_2$, the volume of O_2 released (in ml) by them at STP will give the volume strength of H_2O_2 solution.

Moles of O_2 given by 1 ml of this solution $= \dfrac{1}{2} \times \dfrac{1}{2} \times \dfrac{N}{1000}$ [from equation (i)]

$\therefore$ Volume of O_2 at STP given by 1 ml of this solution $= \dfrac{1}{2} \times \dfrac{1}{2} \times \dfrac{N}{1000} \times 22400 = 5.6 \times N$

$\therefore$ **Volume strength of H_2O_2 = 5.6 × Normality of H_2O_2**

9. PERCENTAGE LABELING OF OLEUM

Oleum contains H_2SO_4 and SO_3 only. When oleum is diluted (by adding water), SO_3 reacts with H_2O to form H_2SO_4, thus increasing the mass of the solution.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
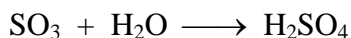
The total mass of H_2SO_4 obtained by diluting 100 g of oleum sample with required amount of water, is equal to the percentage labeling of oleum.

$\therefore$ Percentage labeling of oleum = Total mass of H_2SO_4 present in oleum after dilution.

= mass of H_2SO_4 initially present + mass of H_2SO_4 produced on dilution.

If we have a sample of oleum labeled as 109%, this means that 100 g of oleum on dilution gives 109 g of H_2SO_4.

Let us calculate the composition of oleum, which is labeled as 109%.

Let the mass of SO_3 in the sample be x g, then the mass of H_2SO_4 would be $(100 - x)$ g. On dilution,

$$SO_3 \ + \ H_2O \ \longrightarrow \ H_2SO_4$$
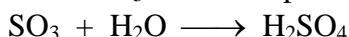
Moles of SO_3 in oleum $= \dfrac{x}{80} =$ Moles of H_2SO_4 formed on dilution

$\therefore$ Mass of H_2SO_4 formed on dilution $= \dfrac{x \times 98}{80}$

Total mass of H_2SO_4 present in oleum after dilution $= \left(\dfrac{x \times 98}{80} \right) + (100 - x) = 109$

$\therefore x = 40$

Thus, oleum contained 40% SO_3 & 60% H_2SO_4.

Alternatively,

Let the mass of oleum sample be 100 g, which on dilution becomes 109 g. This implies that 9 g of H_2O was added.

$$SO_3 \ + \ H_2O \ \longrightarrow H_2SO_4$$
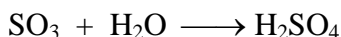
Moles of H_2O added $= \dfrac{9}{18} =$ Moles of SO_3 present in oleum sample.

Mass of SO_3 in oleum $= \dfrac{9}{18} \times 80 = 40$ g

Thus, oleum sample contained 40% SO_3 and 60% H_2SO_4.

10. MODIFICATIONS IN LAW OF EQUIVALENCE

There are certain modifications required in order to use law of equivalence. These modifications are

(i) The equivalents of a substance produced and reacted may not necessarily be same. If the n−factor of the substance, in the reaction in which it is produced were different than the n−factor of the same substance, when it is reacting, then the equivalent of the substance produced and reacted would be different.

(ii) The equivalents of the same substances can be added or subtracted only when they are of the similar n−factor.

(iii) In a reaction, the equivalents of oxidising agents would always be equal to the equivalents of reducing agents, irrespective of the number of agents used in the reaction.

11. SOME IMPORTANT CHEMICAL REACTIONS

There are some chemical reactions, which a student should remember in order to solve problems on stoichiometry. These are categorised as

11.1 COMBINATION OF ELEMENTS WITH OXYGEN

(i) Heating mercury at its boiling point in air.

$Hg + O_2 \longrightarrow 2HgO$ (red mercuric oxide)

(ii) Heating magnesium in air. It forms mostly magnesium oxide and some magnesium nitride.

$2Mg + O_2 \longrightarrow 2MgO$

$3Mg + N_2 \longrightarrow Mg_3N_2$
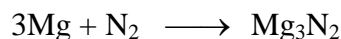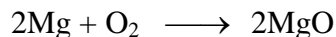
(iii) Calcium behaves similarly.

$2Ca + O_2 \longrightarrow 2CaO$

$3Ca + N_2 \longrightarrow Ca_3N_2$
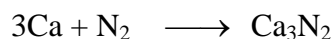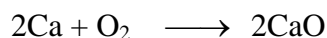
(iv) Silver does not combine with oxygen, as Ag_2O is unstable to heat.

(v) Many non-metals burn in O_2 forming their respective oxides.

$2H_2 + O_2 \longrightarrow 2H_2O$; $S + O_2 \longrightarrow SO_2$

$C + O_2 \longrightarrow CO_2$; $P_4 + 5O_2 \longrightarrow P_4O_{10}$

$N_2 + O_2 \underset{}{\overset{3000°C}{\rightleftharpoons}} 2NO$
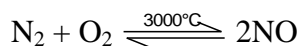
Cl_2, Br_2 and I_2 do not directly combine with oxygen.

11.2 ACTION OF HEAT ON CERTAIN OXIDES:

(i) Mercuric oxide and silver oxide are unstable to heat and decompose readily.

$2HgO \xrightarrow{\Delta} 2Hg + O_2$; $2Ag_2O \xrightarrow{\Delta} 4Ag + O_2$

(ii) Various higher oxides, dioxides, mixed oxides and peroxides are decomposed to oxygen and a lower oxide.

$2Pb_3O_4 \longrightarrow 6PbO + O_2$; $2PbO_2 \longrightarrow 2PbO + O_2$

$3MnO_2 \longrightarrow Mn_3O_4 + O_2$; $2BaO_2 \longrightarrow 2BaO + O_2$
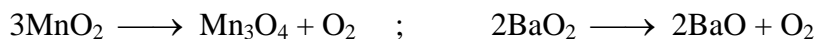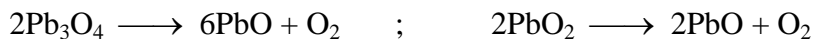
11.3 COMPOUNDS RICH IN OXYGEN DECOMPOSE TO GIVE OXYGEN

(i) $2KNO_3 \longrightarrow 2KNO_2 + O_2 \uparrow$

(ii) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2 \uparrow$

       (purple)   (green)   (black)

(iii) $4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2 \uparrow$

     (orange-red)   (yellow)   (green)
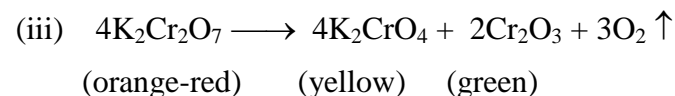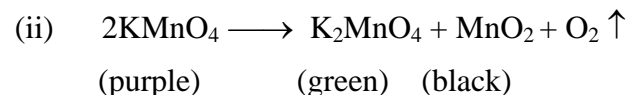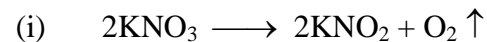
Potassium chlorate when heated just above its melting point decomposes into potassium perchlorate and potassium chloride. This reaction is called **disproportionation** or auto-oxidation and auto-reduction. On heating further, $KClO_4$ decomposes to KCl and oxygen.

(iv) $4KClO_3 \longrightarrow 3KClO_4 + KCl$

$\qquad KClO_4 \longrightarrow KCl + 2O_2$
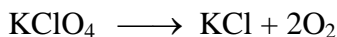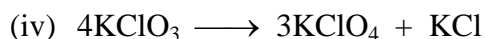
11.4 ACTION OF HEAT ON NITRATES

Generally heavy metal nitrates decompose to metal oxide, reddish brown nitrogen dioxide gas and oxygen.

(i) Lead nitrate decomposes to PbO, NO_2 & O_2.

$\qquad 2Pb(NO_3)_2 \longrightarrow 2PbO \quad + \quad 4NO_2 \uparrow \; + \; O_2$

$\qquad\qquad\qquad\qquad$ litharge or lead (II) oxide

$\qquad\qquad\qquad\qquad$ (red when hot and yellow when cold)

(ii) Cupric nitrate decomposes to CuO, NO_2 & O_2.

$\qquad 2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$
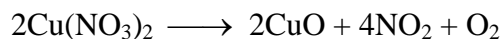
$\qquad$ (green)(black)

(iii) Zinc nitrate decomposes to ZnO, NO_2 & O_2.

$\qquad 2Zn(NO_3)_2 \longrightarrow 2ZnO + 4NO_2 + O_2$
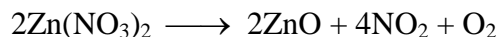
$\qquad$ (zinc oxide, yellow when hot and white when cold)

$\qquad$ Knowing the colours of some oxides will be useful in qualitative analysis.

(iv) Nitrates of mercury and silver, whose oxides are unstable, decompose into the metal, NO_2 and O_2.

$\qquad Hg(NO_3)_2 \longrightarrow Hg + 2NO_2 + O_2$

$\qquad 2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$
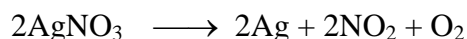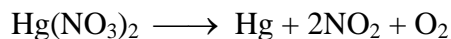
(v) Alkali metal nitrates decompose to give the metal nitrite and O_2 (No reddish brown NO_2 gas).

$\qquad 2KNO_3 \longrightarrow 2KNO_2 + O_2$

$\qquad 2NaNO_3 \longrightarrow 2NaNO_2 + O_2$
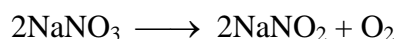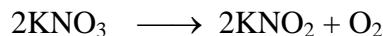
(vi) Ammonium nitrate on heating leaves no residue and forms nitrous oxide and steam.

$\qquad NH_4NO_3 \longrightarrow N_2O + 2H_2O$
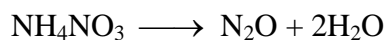
11.5 ACTION OF HEAT ON AMMONIUM COMPOUNDS

Generally an ammonium compound decomposes into ammonia and an acid or acidic oxide if the acid is unstable to heat.

(i) $NH_4Cl \longrightarrow NH_3 + HCl$

(ii) $(NH_4)_2SO_4 \longrightarrow 2NH_3 + H_2SO_4$

(iii) $(NH_4)_3PO_4 \longrightarrow 3NH_3 + H_3PO_4$

(iv) $(NH_4)_2CO_3 \longrightarrow 2NH_3 + CO_2 + H_2O$
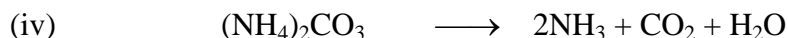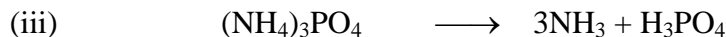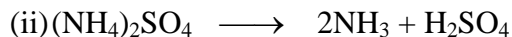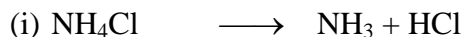
(v) Ammonium compounds which do not give ammonia on heating are ammonium nitrate, ammonium nitrite and ammonium dichromate.

$NH_4NO_3 \longrightarrow N_2O + 2H_2O$

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$

$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + 4H_2O + Cr_2O_3$
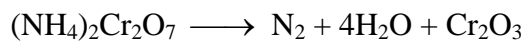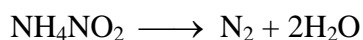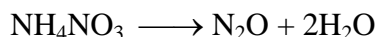
(Green fluffy chromic oxide)

11.6 ACTION OF HEAT ON METALLIC CARBONATES

(i) Generally metallic carbonates decompose to give metal oxide and CO_2.

$CaCO_3 \xrightarrow{900^\circ C} CaO + CO_2 \uparrow$

$MgCO_3 \longrightarrow MgO + CO_2 \uparrow$

$CuCO_3 \longrightarrow CuO + CO_2 \uparrow$

(pale green)   (black)

$PbCO_3 \longrightarrow PbO + CO_2 \uparrow$

(yellow)

$ZnCO_3 \longrightarrow ZnO + CO_2 \uparrow$
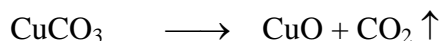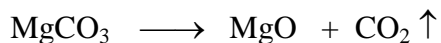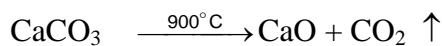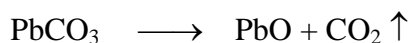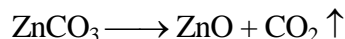
(ii) Carbonates of strongly electropositive metals (alkali metals except lithium) do not decompose on heating.

(iii) Silver carbonate decomposes to give the metal, CO_2 & O_2.

$2Ag_2CO_3 \longrightarrow 4Ag + 2CO_2 + O_2$
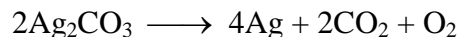
(iv) Ammonium carbonate (smelling salt) decomposes to give NH_3, H_2O & CO_2. All the products are in gaseous phase and there is no residue left.

$(NH_4)_2CO_3 \longrightarrow 2NH_3 + H_2O + CO_2$
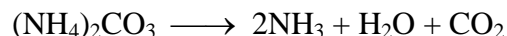
11.7   ACTION OF HEAT ON METALLIC BICARBONATES

Only $NaHCO_3$ and $KHCO_3$ are solids; others are known in solution. All bicarbonates decompose to give the metal carbonate, H_2O & CO_2.

$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \uparrow$

$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2 \uparrow$

$Mg(HCO_3)_2 \longrightarrow MgCO_3 + H_2O + CO_2 \uparrow$

11.8   ACTION OF HEAT ON CERTAIN HYDRATED CHLORIDES

Hydrated halides on heating are converted to oxides, H_2O and halo acids.

(i) $MgCl_2 \cdot 6H_2O$ does not get completely dehydrated because $MgCl_2$ is hydrolysed by water to give basic $MgCl_2$.

$MgCl_2 \cdot 6H_2O \longrightarrow Mg(OH)Cl + 5H_2O + HCl$
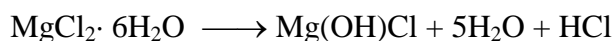
(ii) $Al_2Cl_6 \cdot 12H_2O \longrightarrow Al_2O_3 + 6HCl + 9H_2O$

(iii) $SnCl_2 \cdot 2H_2O$ undergoes hydrolysis to form basic chloride.

$SnCl_2 \cdot 2H_2O \longrightarrow Sn(OH)Cl + H_2O + HCl$
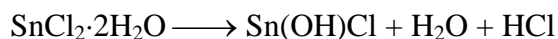
(iv) On heating, certain halides of metal ions in higher oxidation state changes to halides of lower oxidation state.

$2FeCl_3 \longrightarrow 2FeCl_2 + Cl_2$

$2CuCl_2 \longrightarrow Cu_2Cl_2 + Cl_2$
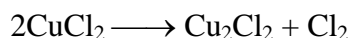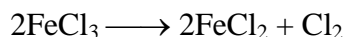
11.9   ACTION OF HEAT ON SOME OTHER COMPOUNDS

(i)   When sodium sulphite is heated, it undergoes disproportionation reaction.

$4Na_2SO_3 \longrightarrow 3Na_2SO_4 + Na_2S$
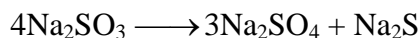
(ii) Sodium thiosulphate $Na_2S_2O_3 \cdot 5H_2O$ loses water of hydration and becomes anhydrous salt, which on further heating gives a mixture of sodium sulphate, sodium sulphide and sulphur.

$Na_2S_2O_3 \cdot 5H_2O \longrightarrow Na_2S_2O_3 + 5H_2O$

$4Na_2S_2O_3 \longrightarrow 3Na_2SO_4 + Na_2S + 4S$
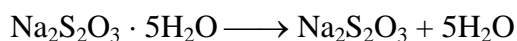
(iii) When hydrated copper sulphate (blue vitriol) is heated, CuO & SO_2 formed.

$$CuSO_4 \cdot 5H_2O \xrightarrow{100^\circ C} CuSO_4 \cdot H_2O + 4H_2O$$

$$CuSO_4 \cdot H_2O \xrightarrow{230^\circ C} CuSO_4 + H_2O$$

$$CuSO_4 \xrightarrow{750^\circ C} CuO + SO_3$$

$$2SO_3 \longrightarrow 2SO_2 + O_2$$
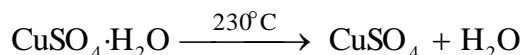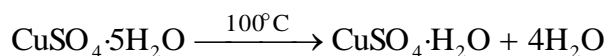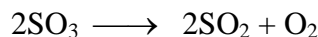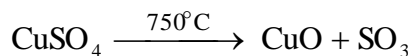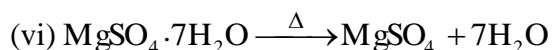
(iv) Gypsum $CaSO_4 \cdot 2H_2O$, when heated to $120-130^\circ C$ forms a hemihydrate called Plaster of Paris.

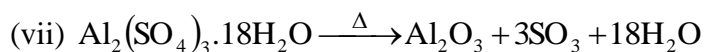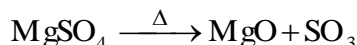$$CaSO_4.2H_2O \longrightarrow CaSO_4. \frac{1}{2} H_2O + 3/2 \; H_2O$$

If heated above $200^\circ C$, it forms anhydrous calcium sulphate which does not set with water.

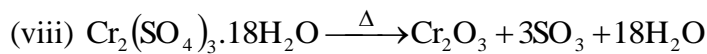(v) Green vitriol, $FeSO_4 \cdot 7H_2O$, when heated forms Fe_2O_3, SO_2, SO_3 & H_2O.

$$2FeSO_4 \cdot 7H_2O \longrightarrow Fe_2O_3 + SO_2 + SO_3 + 14H_2O$$

(vi) $MgSO_4 \cdot 7H_2O \xrightarrow{\Delta} MgSO_4 + 7H_2O$

　　(Epsom salt)

$$MgSO_4 \xrightarrow{\Delta} MgO + SO_3$$

(vii) $Al_2(SO_4)_3.18H_2O \xrightarrow{\Delta} Al_2O_3 + 3SO_3 + 18H_2O$

　　　(purple)　　　　　(white)

(viii) $Cr_2(SO_4)_3.18H_2O \xrightarrow{\Delta} Cr_2O_3 + 3SO_3 + 18H_2O$

　　　　　　　　　　(green)

(ix) $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 \quad + \quad 3SO_3$
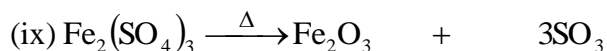
　　(yellow)　　　(blackish brown)

(x) $2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_3 + SO_2$
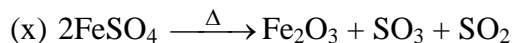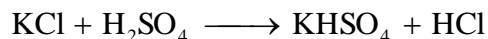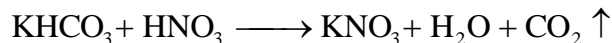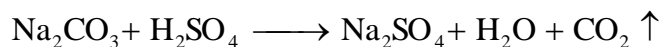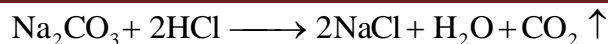
　　(light green)

11.10 ACID–BASE REACTIONS

(i) A strong acid liberates a relatively weaker acid from its salt. The common strong acids are perchloric acid, sulphuric acid, hydrochloric acid and nitric acid. The weaker acids are carbonic acid, sulphurous acid, hydrocyanic acid and most of organic acids. Thus concentrated sulphuric acid displaces most other acids from their salts.

$$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$$
$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$
$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$
$$CH_3CO_2Na + HCl \longrightarrow CH_3CO_2H + NaCl$$
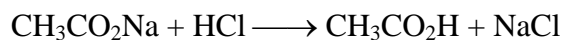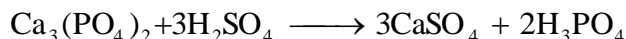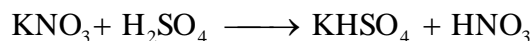
(ii) Almost all acids displace carbonic acid from carbonates and bicarbonates. Since carbonic acid is unstable, it decomposes liberating CO_2 with effervescence (Test for acids).
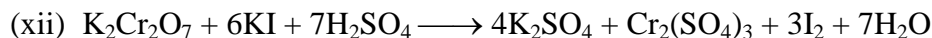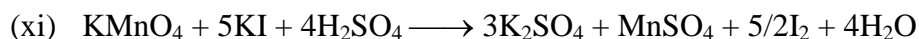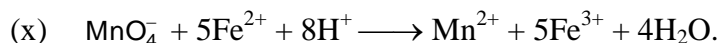
$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2 \uparrow$$

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2 \uparrow$$

$$KHCO_3 + HNO_3 \longrightarrow KNO_3 + H_2O + CO_2 \uparrow$$

(iii) A strong base can displace a weak base from a salt of strong acid and weak base.

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH.$$
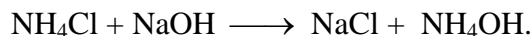
(iv) A salt of strong acid and strong base donot react with any acid or base.

11.11 SOME OTHER USEFUL REACTIONS

(i) $O_3 + 2KI + H_2O \longrightarrow 2KOH + I_2 + O_2$

(ii) $BaCO_3 + HCl \longrightarrow BaCl_2 + CO_2 + H_2O$
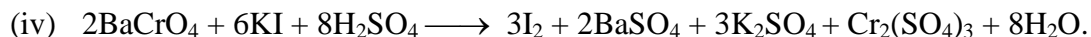
(iii) $BaCl_2 + H_2CrO_4 \longrightarrow BaCrO_4 + 2HCl$

(iv) $2BaCrO_4 + 6KI + 8H_2SO_4 \longrightarrow 3I_2 + 2BaSO_4 + 3K_2SO_4 + Cr_2(SO_4)_3 + 8H_2O.$

(v) $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + I_2 + 2K_2SO_4$

(vi) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$

(vii) $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$

(viii) $Mn_3O_4 + 2FeSO_4 + 4H_2SO_4 \longrightarrow 3MnSO_4 + Fe_2(SO_4)_3 + 4H_2O$

(ix) $2NH_2OH + 4Fe^{3+} \longrightarrow N_2O + H_2O + 4Fe^{2+} + 4H^+$

(x) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O.$

(xi) $KMnO_4 + 5KI + 4H_2SO_4 \longrightarrow 3K_2SO_4 + MnSO_4 + 5/2I_2 + 4H_2O$

(xii) $K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$

11.12 HARDNESS OF WATER

The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of Ca and Mg. The temporary hardness is due to the bicarbonates and permanent hardness is due to chlorides and sulphates of Ca and Mg. The extent of hardness is known as degree of hardness defined as the number of parts by weight of $CaCO_3$ present in one million parts by weight of water.

$$\text{Hardness of water} = \frac{\text{g of } CaCO_3}{10^6 \text{ g of water}}$$