Competitive electron transfer reactions

Dip a zinc rod in copper nitrate solution taken in beaker A and a copper rod in silver nitrate solution in another beaker B. After a few minutes we can see that in beaker A, zinc rod partially dissolves and its surface is coated with metallic copper. The blue colour of the copper nitrate solution fades and finally it becomes colourless. This is due to the following reaction taking place in beaker A.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

It may be represented more clearly as

release of $2\bar{e}$ (oxidation)

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \quad ..... \text{(i)}$$

gain of $2\bar{e}$ (Reduction)

In this reaction zinc acts as the reducing agent and copper ion acts as oxidising agent.

In beaker B, copper rod dissolves partially and its surface is coated with metallic silver from silver nitrate solution. The solution develops blue colour due to the formation of Cu^{2+} ions.

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

It may be represented as

release of $2\bar{e}$ (oxidation)

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s) .... \text{(ii)}$$

gain of $2\bar{e}$ (reduction)

It is interesting to note that in reaction (i), Cu^{2+} is reduced to Cu while in reaction (ii), Cu is oxidised to Cu^{2+}. Thus zinc releases electrons to copper and copper releases electrons to silver and hence the electron releasing tendency of them is in the order $Zn > Cu > Ag$. Like this one can develope a '*metal reactivity series*' (or electrochemical series).

Oxidation state (oxidation number)

Oxidation number of an element denotes the oxidation state of the element in a compound assigned according to a set of rules formulated on the basis that an electron in a covalent bond belongs completely to the more electronegative atom.

Atoms can assume positive, zero or negative values of oxidation numbers depending on their state of combination. Oxidation number can be a fraction in some cases.

General rules for assigning oxidation number to an atom

Oxidation number is actually the charge assigned to the atom in a species according to some arbitrary rules

1. *The oxidation number of an element in the free or elementary state is always zero.*

   For example, Oxidation number of oxygen in O_2 is zero and that of iron in Fe is zero.

2. *The oxidation number of an element in monoatomic ion is equal to the charge on the ion.*

   For example, in KCl, the oxidation number of K^+ is +1 and that of Cl^- is –1. The oxidation number of Ca^{2+} ion is +2 and that of Al^{3+} is +3.

3. *The oxidation number of fluorine is always –1 in all its compounds.*
4. *Hydrogen is assigned oxidation number +1 in all its compounds except in metal hydrides.* In metal hydrides like NaH, MgH_2 CaH_2, LiH etc, the oxidation number of hydrogen is –1.
5. *In compounds containing oxygen, the oxidation number of oxygen is –2 except in peroxides such as Na_2O_2 and in OF_2.* The oxidation number of oxygen in peroxides (Na_2O_2) is –1 and in OF_2, the oxidation number is +2.
6. *The oxidation number of alkali metals is +1 in all their compounds and the oxidation number of alkaline earth metals is +2 in all their compounds.*
7. *The algebraic sum of the oxidation numbers of all the atoms in a neutral molecules is zero. In case of polyatomic ion, the sum of the oxidation numbers of all the atoms is equal to the charge on the ion.*

   For example, in SO_4^{2-} (sulphate ion), the sum of the oxidation numbers of sulphur atom and four oxygen atoms will be equal to –2.

8. *In binary compounds of metal and non–metal, the oxidation number of metal is always positive while that of the non–metal is negative.* For example, in KI, the oxidation number of potassium is +1 and that of iodine is –1.
9. *In binary compounds of non–metals, the more electronegative atom has negative oxidation number and the less electronegative atom has positive oxidation number.* For example, the oxidation number of chlorine in ClF_3 is +3 while that in ICl it is –1.

Stock Notation

Oxidation state of a metal in a compound is sometimes represented by ***Stock notation.*** According to this, the oxidation number is written as Roman Numeral in brackets after the symbol of the metal in the molecular formula. e.g., Fe (II) O, Sn (IV) Cl_4, Mn (IV) O_2

Example 8.1: Calculate the oxidation number of nitrogen in HNO_3

Solution:

Let the oxidation number of N be x

Sum of oxidation numbers of all atoms in $HNO_3 = 1 + x + 3(-2) = 0$

i.e., $= x - 5 = 0 \qquad \therefore x = +5$

Example 8.2: Calculate the oxidation number of Cr in (i) $K_2Cr_2O_7$ (ii) CrO_4^{2-}

Solution:

(i) Cr in $K_2Cr_2O_7$; Let the O.N. of Cr be x

Sum of the oxidation numbers of all atoms in $K_2Cr_2O_7 = 2 \times (+1) + 2x + (7\times-2)$

$\therefore 2 + 2x - 14 = 0; \qquad 2x = 12; \qquad x = +6$

Ans: O.N. of Cr in $K_2Cr_2O_7$ is +6

(ii) Cr in CrO_4^{2-} ion; Let the O.N. of Cr be x

Sum of O.N. of all atoms in $CrO_4^{2-} = x + (4 \times (-2))$

$\therefore x - 8 = -2; \qquad x = +6$

Ans: Oxidation number of Cr in CrO_4^{2-} ion is +6

Example 8.3: Calculate the oxidation number of sulphur in

(i) S_8 (ii) H_2S (iii) H_2SO_4 (iv) $Na_2S_2O_3$ (v) SO_3^{2-}

Solution:

(i) Oxidation number of S in S_8 is zero.

(ii) Let x be the oxidation number of S in H_2S.

Sum of oxidation number of all elements in $H_2S = 2(+1) + x = 0$

i.e., Oxidation number of S in $H_2S = -2$

(iii) Sum of oxidation numbers of all elements in

$H_2SO_4 = 2(+1) + x + 4(-2) = 0$

i.e., $x - 6 = 0 \qquad \therefore x = +6$

(iv) Sum of oxidation numbers of all elements in $Na_2S_2O_3 = 2(+1) + 2x + 3(-2) = 0$

i.e., $2x - 4 = 0 \qquad \therefore x = +2$

(v) Sum of oxidation numbers of all elements in

$SO_3^{2-} = x + 3(-2) = -2$

i.e., $x - 6 = -2$ or $x = -2 + 6 = +4$

Example 8.4: Represent the following compounds using Stock notation:

$FeO, Fe_2O_3, CuO, MnO, MnO_2, HAuCl_4$

Solution: $Fe(II)O, Fe_2(III)O_3, Cu(II)O, Mn(II)O, HAu(III)Cl_4$

Problems for Practice

1. Identify the species undergoing oxidation and reduction in the following reactions

   (a) $H_2 + Cl_2 \rightarrow 2HCl + S$

   (b) $Mg + S \rightarrow MgS$

2. Justify that the following reaction is a redox reaction.

   $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

   identify the oxidant and reductant in the above reaction (*Ans*: Cu(I) of Cu_2O is the oxidant sulphur of Cu_2S is the reductant)

Oxidation and Reduction in terms of oxidation number

In terms of oxidation number, oxidation may be defined as a chemical change in which there occurs an increase in the oxidation number of an element in the given substance. Reduction may be defined as a chemical change in which there occurs a decrease in the oxidation number of an element in the given substance. Thus, a redox reaction may be defined as a reaction which involve change in oxidation number of the reacting species. For example,

increase of O.N.

$$\overset{+1}{H_2}\overset{-2}{S} + \overset{0}{Cl_2} \rightarrow 2\overset{+1}{H}\overset{-1}{Cl} + \overset{0}{S}$$

decrease of O.N.

Here, Cl_2 is reduced to HCl because the oxidation number of Cl decreases from zero to –1. The oxidation number of sulphur increases from –2 to zero and hence H_2S is oxidised.

Thus the above reaction is a redox reaction. In this reaction, Cl_2 oxidises H_2S to sulphur. So Cl_2 is the oxidising agent and H_2S is the reducing agent.

An oxidising agent (or oxidant) is a reagent which can increase the oxidation number of an element in a reacting substance. A reducing agent (or reductant) is a reagent which lowers the oxidation number of an element in a reacting substance.

It may be noted that an oxidising agent suffers a decrease in oxidation number of one of its elements and a reducing agent suffers an increase in oxidation number of one of its elements during redox reactions.

Example 8.5: $2Na + H_2 \longrightarrow 2NaH$

Is this reaction a redox reaction? Justify your answer.

Solution:

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

In this reaction, oxidation number of sodium increases from 0 to +1 and hence it is oxidised. The oxidation state of hydrogen decreases from 0 to –1 and hence it is reduced. So the reaction is a redox reaction.

Example 8.6: Identify the oxidant and reductant and the atoms undergoing oxidation and reduction in the following redox reactions.

(i) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

(ii) $H_2S + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + S$

Solution:

(i)

increase of O.N.

$$\overset{+4}{Mn}\overset{-2}{O_2} + 4\overset{+1}{H}\overset{-1}{Cl} \rightarrow \overset{+2}{Mn}\overset{-1}{Cl_2} + \overset{0}{Cl_2} + 2\overset{+1}{H_2}\overset{-2}{O}$$

decrease of ON

Oxidation number of Mn decreases from +4 (in MnO_2) to +2 (in $MnCl_2$). This means that MnO_2 is reduced and hence it is the oxidant. HCl is oxidised to Cl_2 and it is the reductant (O.N. of Cl increases from –1 to 0 and hence it gets oxidised)

(ii)

increase of O.N.

$$\overset{+1}{H_2}\overset{-2}{S} + 2\overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \rightarrow 2\overset{+4}{N}\overset{-2}{O_2} + 2\overset{+1}{H_2}\overset{-2}{O} + \overset{0}{S}$$

decrease of O.N.

H_2S is oxidised to sulphur because oxidation number of S increases from –2 to zero. H_2S is thus the reductant. HNO_3 is reduced to NO_2 because the oxidation number of N decreases from +5 to +4. Hence HNO_3 is the oxidant.

Types of redox reactions

1. Combination reactions

A reaction in which one element combines with another element or compound to form product is known as combination reaction. Such reactions are generally redox reactions.

$$C + O_2 \longrightarrow CO_2$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

All combustion reactions are combination reactions and are examples of redox reactions.

2. Decomposition reactions

A reaction in which a compound breaks down to form two or more components is known as decomposition reaction. If at least one of the products of decomposition is in the elemental state, the reaction becomes a redox reaction.

$$2H_2O \xrightarrow{heat} 2H_2 + O_2$$

$$2KClO_3 \xrightarrow{heat} 2KCl + 3O_2$$

It may be noted that all decomposition reactions are not redox reactions. For example, the decomposition of calcium carbonate on heating to form calcium oxide and CO_2 is not a redox reaction.

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

In this reaction, there is no change in oxidation number of any of the atoms during the change. That is why it is not a redox reaction.

3. Displacement reactions

A reaction in which an atom or ion in a compound is replaced by another atom or ion is called a displacement reaction. Displacement reactions are of two types.

(a) *Metal displacement reactions:* In this type of redox reactions, a metal in a compound is displaced by another metal.

$$CuSO_4\,(aq) + Zn\,(s) \longrightarrow Cu\,(s) + ZnSO_4\,(aq)$$

$$Cr_2O_3\,(s) + 2Al\,(s) \xrightarrow{heat} Al_2O_3 + 2Cr\,(s)$$

(b) Non-metal displacement reactions: In this type of redox reactions, a non-metal in a compound is displaced by another metal or non-metal.

$$2Na\,(s) + 2H_2O\,(l) \longrightarrow 2NaOH\,(aq) + H_2\,(g)$$

$$Cl_2\,(g) + 2KBr\,(aq) \longrightarrow 2KCl\,(aq) + Br_2\,(l)$$

4. Disproportionation reaction

A reaction in which the same species gets simultaneously oxidised and reduced is called a disproportionation reaction. For example, consider the following reaction

$$Cl_2 + 2OH^- \longrightarrow ClO^- + Cl^- + H_2O$$

(or $Cl_2 + 2NaOH \longrightarrow NaClO + NaCl^- + H_2O$)

The oxidation numbers of chlorine in Cl_2, ClO^- and Cl^- are 0, +1 and –1 respectively. In this reaction, chlorine present in zero oxidation state is converted to +1 state in ClO^- and decreases to –1 in Cl^-. In other words, chlorine undergoes simultaneous oxidation and reduction.

Some other examples are

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

$$P_4 + 3OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^-$$

(or $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$)

Example 8.7: ClO_3^- undergoes disproportionation, but ClO_4^- does not. Explain why?

Solution:

In ClO_4^-, the oxidation state of Cl is +7. This is the highest oxidation state possible for Cl. It can only decrease its oxidation number but cannot increase it. So ClO_4^- does not undergo disproportionation.

In ClO_3^-, the oxidation state of Cl is +5. It can increase and decrease its oxidation number. So it undergoes disproportionation

$$4ClO_3^- \rightarrow Cl^- + 3ClO_4^-$$

Problem for Practice

1. Classify the following redox reactions into various types

(a) $N_2 + O_2 \rightarrow 2NO$

(b) $2Pb(NO_3)_2 \rightarrow 2PbO + 2NO_2 + \frac{1}{2} O_2$

(c) $NaH + H_2O \rightarrow NaOH + H_2$

(d) $2NO_2 + 2OH^- \rightarrow NO_2^- + NO_3^- + H_2O$

(*Ans:* (d) Disproportionation reaction)