CHAPTER9

9.0 OXIDATION AND REDUCTION REACTION

9.1 FUNDAMENTAL CONCEPT OF OXIDATION AND REDUCTION REACTION

Oxidation and reduction reactions are two processes which usually occur simultaneously. The term ***redox*** is used by chemist as an abbreviation for the reactions and it involves not only the addition and removal of hydrogen and oxygen, but has been extended to include all electron- transfer processes. There definitions can be done under four headings.

9.1.1. IN TERM OF ADDITION AND REMOVAL OF OXYGEN

Oxidation is the addition of oxygen while reduction is the removal of oxygen.

i. $ZnO + C \longrightarrow Zn + CO$

Zinc is reduced while carbon is oxidized

ii. $CuO + CO \longrightarrow Cu + CO_2$

CuO reduced while carbon II oxide is oxidized.

9.1.2. In terms of addition and removal of hydrogen

Oxidation is the removal of hydrogen while reduction is the addition of hydrogen

i. $4HCI + O_2 \longrightarrow 2H_2O + 2CI_2$

Chlorine is oxidized while oxygen is reduced

ii. $H_2S + CI_2 \longrightarrow 2HCI + S$

Sulphur is oxidized while chlorine is reduced

9.1.3. In terms of electron transfer

Oxidation is the loss of electrons while reduction is the gain of electrons.

$2FeCI_2 + CI_2 \longrightarrow 2FeCl_3$

Iron (II) is oxidized while chlorine is reduced. The two half reaction can be written thus:

$2Fe^{2+} - 2e^- \longrightarrow 2Fe^{3+}$ (oxidized)

$CI_2 + 2e^- \longrightarrow 2Cl^-$ (reduced)

9.1.4. In terms of change in oxidation number

Oxidation is the increase in oxidation number while reduction is the decrease in oxidation number. A substance is oxidized if its oxidation number increases from left to right while decrease in the oxidation number of a substance from left to right is reduction.

$2C + 2HNO_3 \longrightarrow 2CO + H_2O + 2NO_2$

Here, the oxidation number of C = O on the left and on the right it became C = 2+. Therefore carbon has being oxidized.

In summary, oxidation is:

1. Addition of Oxygen
2. Removal of hydrogen
3. loss of electron
4. increase in oxidation number

While reduction is:

1. Removal of Oxygen
2. Addition of hydrogen
3. gain of electrons
4. decrease in oxidation number

9.2 OXIDISING AND REDUCING AGENTS

An ***oxidizing agent*** is a substance which brings about oxidation and its reduced in the cause of a redox reaction.

Also a ***reducing agent*** is a substance which brings about reduction and it‟s oxidized in the cause of a redox reaction. Illustration;

(i) $CuO + CO \longrightarrow Cu + CO_2$

Here copper has been reduced; therefore copper is the oxidizing agent while carbon that has been oxidized is the reducing agent.

(ii) $CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$

Here copper which is reduced is the oxidizing agent while zinc is oxidized hence the reducing agent.

$$CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$$

$$Cu^{2+} + \overset{0}{Zn} \rightarrow \underset{\substack{reduced \\ (Oxidising\ Agent)}}{\overset{o}{Cu}} + \underset{\substack{Oxidised \\ (Reducing\ Agent)}}{Zn^{2+}}$$

9.3 TESTS FOR OXIDING AGENTS

1. Most oxidizing agent give off iodine from acidified potassium iodide solution, forming a red-brown solution which turns dark-blue upon the addition of starch
2. Bubbling sulphur (IV) oxide through an aqueous solution of the substance will give tetraoxosulphate (VI) ion.

9.4 TESTS FOR REDUCING AGENTS

1. Reducing agents decolorize the deep purple colour of acidified potassium tetraoxomanganate (VII) ($KMnO_4$)
2. Reducing agents produce a green solution upon warming with an orange solution of acidified dipotassiumhepta-oxochromate (VI) ($K_2Cr_2O_7$)

9.5 OXIDATION NUMBER

Oxidation numbers arecharge assigned to element in the free or combined states according to some set rules. Oxidation number can also be known as oxidation state.

9.5.1 RULES FOR DETERMING OXIDATION NUMBER

1. The oxidation number of atoms of elements in an uncombined state is zero.

2. The oxidation number of a monoatomic ion is equal to the charge on the ion.

3. The sum of all the oxidation numbers of atoms in a molecule (or a polyatomic ion) is the charge on the particle.

4. In many compounds of oxygen, the oxidation number of oxygen is -2. But in peroxides it is -1 and when oxygen is combined with fluorine (e.g. OF_2), the oxidation number of oxygen is +2

5. In many compound of Hydrogen, the oxidation number of hydrogen is + 1 except in metal hydride where hydrogen has an oxidation number of -1

6. Halogens have a negative oxidation number but when they combine with oxygen e.g. in oxide, oxoacids and oxoanions, they have a positive oxidation number

Example 9.1

Calculate the oxidation states of chlorine in

(a) HOCI (b) $HClO_3$*(c)* $KClO_3$

Solutions

(a)

Because the molecule is not carrying any charge, then the sum of all its oxidation numbers will be equal to zero:-

$+ 1 - 2 + x = 0$

Making x subject we get

$x = +2 -1$

$x = + 1$: - The oxidation number of chlorine is + 1.

(b) H = 1

Cl = x

0=-6

Because it is triatomic we multiply the oxidation number of one oxygen atom (-2) by 3 to get -6

$+1 + X -6 = 0$

$x = +6 -1$

$x = +5$

(c) K = 1

CI= x, 0=-6

1 + x -6 =

0 x = +6-1

$x = +5$

Example 9.2

Find the oxidation number of chromium atom in potassium heptaoxodicromate (VI) $K_2Cr_2O_7$

K=1 x 2 = 2
Cr = xX 2 = 2x
0 = -2 x7 = -14

2 + 2x - 14 = 0
2x =+ 14-2
2x = +12
x = + $\frac{12}{2}$
x = +6
Cr = +6

9.6 BALANCING OF REDOX EQUATION

9.6.1 By ion-electron or half reaction method

This method is a limited method as it is appliedonly in balancing redox reactions taking place in aqueous solution, involving complete transfer of electrons. This method involves the following steps;

i. Identify the oxidizing agent and the reducing agents
ii. Write half equation for the reaction
iii. In acid and neutral solutions, balance first for oxygen and next for hydrogen as follows
   (a) Balance for every excess oxygen on one side, by adding water on the other side and $2H^+$ on the same side.
   (b) In alkaline medium, balance for every excess oxygen on one side by adding $2OH^-$ on the other side. And one H_2O on the same side and vice versa. If bothH and O are in excess on the same side, add OH^- to the other side for each pair of excess H and O
iv. Balance each half reaction for charge.
vi. Cross multiply with the number of charges and cancel out as necessary (equalize the electrons).
vii. Add the two half equations, so that the electrons cancel out as well as other terms.
viii. Finally, insert necessary coefficients for the oxidizing and reducing agent according to the law of conservation of mass

Example 9.3
Balance the redox equation
$MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$

$$\underset{(Oxidizing\ Agent)}{\overset{7+}{MnO4^-}} \rightarrow Mn^{2+}\ (reduced)$$

$$\underset{(\mathrm{Re}ducing\ agent)}{Fe^{2+}} \rightarrow Fe^{3+}\ (oxidized)$$

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

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

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

Cross multiply with the number of charges and cancel out as necessary (equalize the electrons)

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

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

Sum up

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

Example 9.4

Balance the following equation using the half reaction method.

Reaction in acid medium

$BiO_3^- + Mn^{2+} \longrightarrow Bi^{3+} + MnO_4^-$

$\underset{(OA)}{BiO_3^-} \longrightarrow Bi^{3+}$ (reduced)

$\underset{(RA)}{Mn^{2+}} \longrightarrow \overset{+7}{Mno_4^-}$ (*oxidized*)

$\underset{(OA)}{BiO_3^-} + 6H^+ \longrightarrow Bi^{3+} + 3H_2O$

$\underset{(OA)}{BiO_3^-} + 6H^+ + 2e^- \longrightarrow Bi^{3+} + 3H_2O$

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

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

$5BiO_3^- + 3\overset{16}{OH}{}^{+} + 10e^- \rightarrow 5Bi^{3+} + \overset{7}{15}H_2O$

$2Mn^{2+} \quad 8H_2O \rightarrow 2MnO_4^- + 16H^+ + 10e^-$

$5BiO_3^- + 2Mn^{2+} + 14H^+ \rightarrow 5Bi^{3+} + 2MnO_4^- + 7H_2O$

Example 9.5

Balance the redox equation using half –reaction method

$MnO_4^- + Fe^{2+} \rightarrow MnO_2 + Fe^{3+}$

Reaction in alkaline Medium

Solution

$$\underset{(OA)}{\overset{+7}{Mn}O_4^-} \rightarrow \overset{+4}{Mn}O_2 \quad (reduced)$$

$$\underset{(RA)}{Fe^{2+}} \rightarrow Fe^{3+} \qquad (oxidized)$$

$$MnO_4^- + 2H_2O \rightarrow MnO_2 + 4OH^-$$

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

$$Fe^{2+} \rightarrow Fe^{3+} + 3e^-$$

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

$$3Fe^{2+} \rightarrow 3Fe^{3+} + 3e^-$$

$$MnO_4^- + 3Fe^{3+} + 2H_2O \rightarrow MnO_2 + 3Fe^{3+} + 4OH^-$$

Example 11.11

Balance the redox equation in alkaline medium using the half-reaction method.

$$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$$

$$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + 2CO_2$$

$$\underset{(OA)}{\overset{+7}{Mn}O_4^-} \rightarrow Mn^{2+} \quad (reduced)$$

$$\overset{+6}{C_2}O_4^{2-} \rightarrow 2\overset{+8}{C}O_2 \quad (Oxidation)$$

$$MnO_4^- + 4H_2O \rightarrow Mn^{2+} + 8OH \qquad (BFO)$$

$$MnO_4^- + 4H_2O + 5e^- \rightarrow Mn^{2+} + 8OH^- \qquad (BFC)$$

$$C_2O_4^{2-} - \rightarrow 5CO_2 + 2e^-$$

$$2MnO_4^- + 8H_2O + 10e^- \rightarrow 2Mn^{2+} + 16OH^-$$

$$5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$$

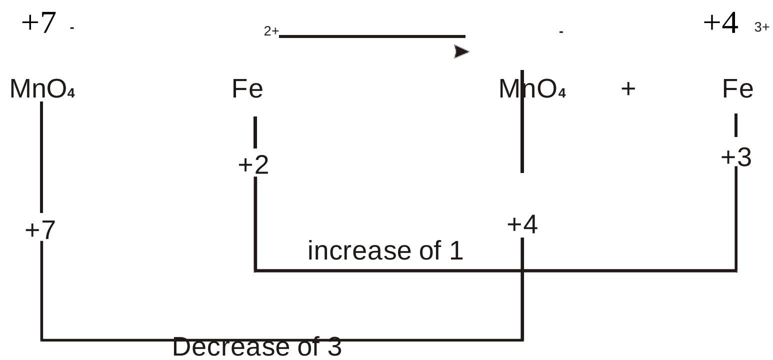
$$2MnO_4^- + 5C_2O_4^{2-} + 8H_2O \rightarrow 2Mn^{2+} + 10CO_2 + 16OH^-$$

9.6.2 OXIDATION NUMBER METHOD

Not all redox reaction occurs in aqueous solution and a complete transfer of electrons is always the casethus, to accommodate for this a wider balancing method is required.

The method is based on the fact that the partial or complete gain of electrons by the oxidizing agent must be equal to the partial or complete loss of electrons by the reducing agent. This method entails the following steps

I. Determine the oxidation number for every element in the equation. Record new oxidation number below affected element. Indicate all increases and decreases in oxidation number. Disregard signs



Ii Cross multiply each half equation by their respective change in oxidation state. To do this, multiply the Mn⁻ half equations by 1 while the Fe half equation by 3.

$$MnO_4^- + 3Fe^{2+} \rightarrow MnO_2 + 3Fe^{3+}$$

iii. Balance for oxygen by adding water to every side short of oxygen

$$MnO_4^- + 3Fe^{2+} \rightarrow MnO_2 + 3Fe^{3+} + 2H_2O$$

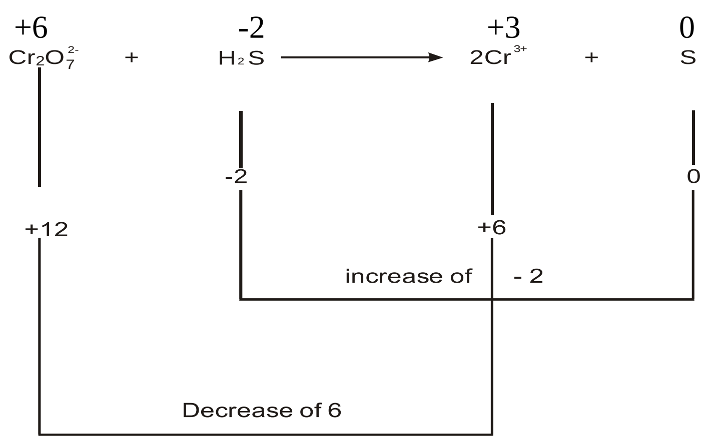
iv. Balance for hydrogen by adding hydrogen ion to any side short of hydrogen.

$$MnO_4^- + 3Fe^{2+} + 4H^+ \rightarrow MnO_2 + 3Fe^{3+} + 2H_2O$$

Example 9.6

Using the change in oxidation number method, balance the redox equation.

$Cr_2O_7^{2-} + H_2S \rightarrow Cr^{3+} + S$



$$2Cr_2O7^{2-} + 6H_2S \rightarrow 4Cr^{3+} + 6S$$
$$2Cr_2O7^{2-} + 6H_2S \rightarrow 4Cr^{3+} + 6S + 14H_2O$$

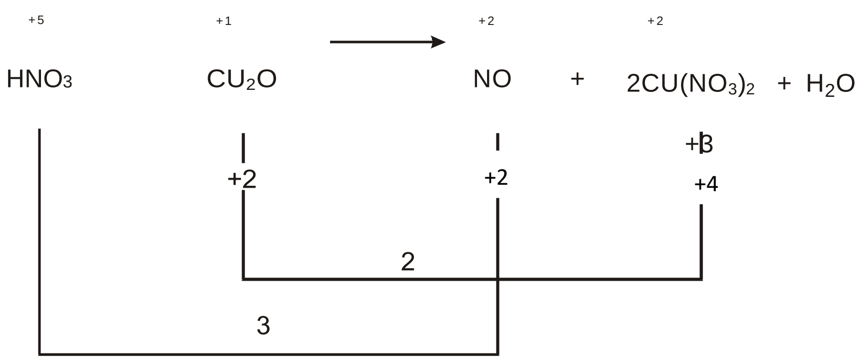
$$2Cr_2O7^{2-} + 16H^+ + 6H_2S \rightarrow 4Cr^3 + 6S + 14H_2O$$

Example 9.7

Balance the redox equation using the oxidation number method

Solution:

$$\overset{+1\,+5\,-2}{HNO_3} + \overset{+1}{CU_2O} \rightarrow \overset{+2\quad +5}{CU(NO_3)_2} + \overset{+2}{NO} + H_2O$$



$$2HNO_3 + 3CU_2O \rightarrow 6CU(NO_3)_2 + 2NO + H_2O$$
$$14HNO_3 + 3CU_2O \rightarrow 6CU(NO_3)_2 + 2NO + H_2O$$
$$14HNO_3 + 3CU_2O \rightarrow 6CU(NO_3)_2 + 2NO + 7H_2O$$

PRACTICE QUESTIONS

1. What is the oxidation number of (a) Aluminium in AI_2O_3 (b) Bromine in NaBr (c) Sulphur in $Na_2S_2O_3$ (d) Hydrogen in NH_3 (e) Magnesium in $KMnO_4$ (f) Chromium in K_2CrO_4
2. Balance the redox equation, using the half-reaction method and assume that the reaction takes places in an acidic medium.

   $Ag + NO_3^- \rightarrow Ag^+ + NO$

3. Iron (iii) chloride reacted with zinc to yield Zinc (ii) chloride and pure iron metal. Balance the redox equation assuming that the reaction occurred in an alkaline medium: $FeCl_3 + Zn \rightarrow ZnCl_2 + Fe$

4. Use the oxidation number method to balance the following redox equation

(a) $Cu + HNO_3 \rightarrow Cu\ (NO_3)_2 + H_2O + NO$

(b) $Ag + NO_3^- \rightarrow Ag^+ + NO$

(c) $MnO_4^- + H_2C_2O_4 \rightarrow Mn^{2+} + CO_2$

8. Balance the redox equation

$Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NO_2 + H_2O$

9. Balance the redox equation using the oxidation number method

(a) $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NH_4NO_3$

(b) $KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$