

## NITTY-GRITTY

For centuries, burning animal fat, in torches, lamps, and eventually in candles – provided light for humans. Wood fires supplied warmth, as well as a means to cook meals. These were the main uses of combustion, aside from the occasional use of fire in warfare or for other purposes (including that ghastly medieval form of execution, burning at the stake). One notable military application, incidentally, was "Greek fire," created by the Byzantines in the seventh century A.D. A mixture of petroleum, potassium nitrate, and possibly quicklime, Greek fire could burn on water, and was used in naval battles to destroy enemy ships.

Nuclear bombs release far more energy than any ordinary explosive, but the resulting blast also causes plenty of ordinary combustion. When the United States dropped atomic bombs on the Japanese cities of Hiroshima and Nagasaki in August 1945, those cities suffered not only the effects of the immediate blast, but also massive fires resulting from the explosion itself.

Combustion, though it can do much good, can also do much harm.

As with any type of chemical reaction, combustion takes place when chemical bonds are broken and new bonds are formed. It so happens that combustion is a particularly dramatic type of oxidation-reduction reaction: whereas we cannot watch iron rust, combustion is a noticeable event. Even more dramatic is combustion that takes place at a rate so rapid that it results in an explosion. Coal is almost pure carbon, and its combustion in air is a textbook example of oxidation-reduction. Although there is far more nitrogen than oxygen in air (which is a mixture rather than a compound), nitrogen is very unreactive at low temperatures. For this reason, it can be used to clean empty fuel tanks, a situation in which the presence of pure oxygen is extremely dangerous. In any case, when a substance burns, it is reacting with the oxygen in air. As one might expect from what has already been said about oxidation-reduction, the oxygen is reduced while the carbon is oxidized. In terms of oxidation numbers, the oxidation number of carbon jumps from 0 to 4, while that of oxygen is reduced to  $-2$ . As

they burn, these two form carbon dioxide or  $\text{CO}_2$ , in which the two  $-2$  charges of the oxygen atoms cancel out the  $+4$  charge of the carbon atom to yield a compound that is electrically neutral. The steam engine applied the combustion of coal to the production of heat for boiling water, which in turn provided the power to run machinery. By the beginning of the twentieth century, combustion had found a new application in the internal combustion engine, used to power automobiles.

Oxidation-reduction reactions also fuel the most advanced form of transportation known today, the space shuttle. The actual orbiter vehicle is relatively small compared to its external power apparatus, which consists of two solid rocket boosters on either side, along with an external fuel tank. Inside the solid rocket boosters are ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) and powdered aluminum, which undergo an oxidation-reduction reaction that gives the shuttle enormous amounts of extra thrust. As for the larger single external fuel tank, this contains the gases that power the rocket: hydrogen and oxygen. Because these two are extremely explosive, they must be kept in separate compartments. When they react, they form water, of course, but in doing so, they also release vast quantities of energy.

The importance of oxidation-reduction reactions was recognized from the beginning of chemistry. In oxidation-reduction, some entity is given or taken between two reacting chemicals. The situation is similar to that in acid-base reactions. In brief, oxidation-reduction and acid-base reactions form a pair of systems in chemistry. Oxidation-reduction and acid-base reactions share a common feature in that both had been put into practice before the nature of the reactions was clarified.

In reference to organic molecules, Oxidation is a process by which a carbon atom gains bonds to more electronegative elements, most commonly oxygen. Reduction is a process by which a carbon atom gains bonds to less electronegative elements, most commonly hydrogen.

Table 5.1

Oxidation		Reduction	
Addition of oxygen	$2\text{Mg} + \text{O}_2 \longrightarrow 2\text{MgO}$	Removal of oxygen	$\text{CuO} + \text{C} \longrightarrow \text{Cu} + \text{CO}$
Removal of hydrogen	$\text{H}_2\text{S} + \text{Cl}_2 \longrightarrow 2\text{HCl} + \text{S}$	Addition of hydrogen	$\text{Cl}_2 + \text{H}_2 \longrightarrow 2\text{HCl}$
Addition of non-metal	$\text{Fe} + \text{S} \longrightarrow \text{FeS}$	Removal of non-metal	$2\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$
Removal of metal	$2\text{KI} + \text{H}_2\text{O}_2 \longrightarrow 2\text{KOH} + \text{I}_2$	Addition of metal	$\text{HgCl}_2 + \text{Hg} \longrightarrow \text{Hg}_2\text{Cl}_2$
Increase in +ve valency	$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-$	Decrease of +ve valency	$\text{Fe}^{3+} \longrightarrow \text{Fe}^{2+}$ (+ve valency decreases)
			$[\text{Fe}(\text{CN})_6]^{3-} \longrightarrow [\text{Fe}(\text{CN})_6]^{4-}$ (-ve valency increases)
De-electronation (loss of $\text{e}^-$ )	$\text{H}^0 \longrightarrow \text{H}^+ + \text{e}^-$	Electronation (gain of $\text{e}^-$ )	$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \longrightarrow \text{Zn}_{(\text{s})}$
	$\text{MnO}_4^{2-} \longrightarrow \text{MnO}_4^- + \text{e}^-$		$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}^0$
Increase in oxidation number	$\text{Mg}^0 \longrightarrow \text{Mg}^{2+} + 2\text{e}^-$	Decrease on oxidation number	$\text{Mg}^{2+} \longrightarrow \text{Mg}^0 - 2\text{e}^-$
	From 0 to +2		From +2 to 0

**Oxidizing and Reducing agents:** Oxidizing agents (oxidants) are substances containing the element(s) that accept electrons, allowing another element(s) to be oxidized, by accepting electrons, the element(s) in the oxidizing agent are reduced. Reducing agents (reductants) are substances containing the element(s) that donate electrons, allowing another element(s) to be reduced, by donating electrons, the element(s) in the reducing agent are oxidized.

#### Example:

Oxidants	Reductants
$\text{I}_{2(\text{aq})} + 2\text{e}^- \longrightarrow 2\text{I}^-_{(\text{aq})}$	$\text{Zn}_{(\text{s})} \longrightarrow \text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^-$
$\text{Br}_{2(\text{aq})} + 2\text{e}^- \longrightarrow 2\text{Br}^-_{(\text{aq})}$	$\text{H}_{2(\text{g})} \longrightarrow 2\text{H}^+_{(\text{aq})} + 2\text{e}^-$
$\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})} + 14\text{H}^+_{(\text{aq})} + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}_{(\text{aq})} + 7\text{H}_2\text{O}_{(\text{l})}$	$\text{H}_2\text{S}_{(\text{aq})} \longrightarrow 2\text{H}^+_{(\text{aq})} + \text{S}_{(\text{s})} + 2\text{e}^-$
$\text{Cl}_{2(\text{aq})} + 2\text{e}^- \longrightarrow 2\text{Cl}^-_{(\text{aq})}$	$\text{Sn}^{2+}_{(\text{aq})} \longrightarrow \text{Sn}^{4+}_{(\text{aq})} + 2\text{e}^-$
$\text{MnO}_4^-_{(\text{aq})} + 8\text{H}^+_{(\text{aq})} + 5\text{e}^- \longrightarrow \text{Mn}^{2+}_{(\text{aq})} + 4\text{H}_2\text{O}_{(\text{l})}$	$\text{Fe}^{2+}_{(\text{aq})} \longrightarrow \text{Fe}^{3+}_{(\text{aq})} + \text{e}^-$
$\text{S}_2\text{O}_8^{2-}_{(\text{aq})} + 2\text{e}^- \longrightarrow 2\text{SO}_4^{2-}_{(\text{aq})}$	

#### Important oxidising agents

- Molecules made up of electronegative elements.  
e.g.  $\text{O}_2$ ,  $\text{O}_3$  and  $\text{X}_2$  (halogens).
- Compounds containing an element which is in the highest oxidation state.  
e.g.  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{CrO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{FeCl}_3$ ,  $\text{HgCl}_2$ ,  $\text{KClO}_4$ ,  $\text{SO}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}_2$ , etc.
- Oxides of elements,  $\text{MgO}$ ,  $\text{CuO}$ ,  $\text{CrO}_3$ ,  $\text{CO}_2$ ,  $\text{P}_4\text{O}_{10}$ , etc.
- Fluorine is the strongest oxidising agent.

#### Important reducing agents

- All metals e.g. Na, Zn, Fe, Al, etc.
- A few non-metals e.g. C,  $\text{H}_2$ , S etc.
- Hydrides :  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{H}_2\text{S}$ , etc.
- A few compounds containing an element in the lower oxidation state (ous).  
e.g.  $\text{FeCl}_2$ ,  $\text{FeSO}_4$ ,  $\text{SnCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{Cu}_2\text{O}$ , etc.
- Metallic hydrides e.g.  $\text{NaH}$ ,  $\text{LiH}$ , etc.
- Organic compounds like  $\text{HCOOH}$  and  $(\text{COOH})_2$  and their salts, aldehydes, alkanes etc.
- Lithium is the strongest reducing agent in solution.
- Cesium is the strongest reducing agent in absence of water. Other reducing agents are  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{KI}$ .
- Hypo prefix indicates that central atom of compound has the minimum oxidation state so it will act as a reducing agent.  
e.g.  $\text{H}_3\text{PO}_2$  (hypophosphorous acid).
- Substances which act as oxidising as well as reducing agents**

e.g.  $\text{H}_2\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{NaNO}_2$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{O}_3$

**Redox Reaction:** an overall reaction in which oxidation and reduction takes place simultaneously is called redox (oxidation-reduction) reaction. These reactions involve transfer of  $\text{e}^-$  from one atom to another. Thus every redox reaction is made up of two half reaction, one half reaction represents the oxidation and other half reaction represent the reduction.

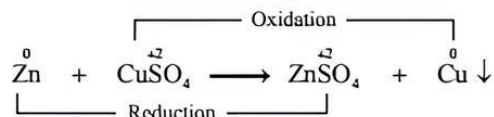
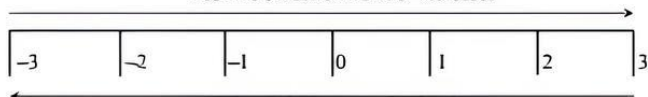




Table 5.2

<b>Direct redox reaction</b>	Reactions in which oxidation and reduction takes place in the same vessels.
<b>Indirect redox reaction</b>	Reactions in which oxidation and reduction takes place in different vessels, it is basis on electro-chemical cells.
<b>Intermolecular redox reaction</b>	In which one substance is oxidized while other is reduced. E.g.; $2\text{Al} + \text{Fe}_2\text{O}_3 \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$ Al is oxidized to $\text{Al}_2\text{O}_3$ , while $\text{Fe}_2\text{O}_3$ is reduced to Fe.
<b>Intramolecular redox reaction</b>	In which one element of a compound is oxidized while the other is reduced. $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$ $\text{Cl}^{+5}$ in $\text{KClO}_3$ is reduced to $\text{Cl}^{-1}$ in $\text{KCl}$ while $\text{O}^{2-}$ in $\text{KClO}_3$ is oxidized to $\text{O}_2^0$

Loss of electrons = oxidation  
Positive oxidation number increases

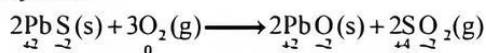


**Oxidation Numbers** of an element in a particular compound represents the number of electrons lost or gained by an element during its change from free state into that compound.

- Oxidation numbers of elements (including allotropes) are always 0.
- For any monoatomic ion, the oxidation number equals the charge on the ion.  $\text{K}^+$ ,  $\text{O}^{2-}$ ,  $\text{Al}^{+3}$  etc.
- Non-metals usually have negative oxidation numbers.
- The oxidation number of O is usually  $-2$ .
- The oxidation number of H is  $+1$  when it is bonded to a non metal ( $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_3\text{PO}_4$  etc) and  $-1$  when it is bonded to a metal ( $\text{CaH}_2$ ,  $\text{NaH}$ , etc.)
- Oxidation numbers of alkali metals (Li, Na, K etc.) are  $+1$  and those of alkaline earth metals (Be, Mg, Ca, Ba etc.) are  $+2$ .
- The oxidation number of F is always  $-1$ . The other halogens are usually  $-1$  but when combined with oxygen in oxyanions it is  $+1$  ( $\text{OCl}^{-1}$ ,  $\text{O}_2\text{Cl}^{-2}$  etc.)

**For Example determine the oxidation number:** In the smelting of lead from its ore (lead sulfide) the following two-step oxidation-reduction reactions occur. Indicate the oxidants and reductants in these reactions and find the oxidation numbers of each atom.

The oxidation number of each atom is indicated under its atomic symbol.



In the 1st stage of the reaction, the oxidation number of S changed from  $-2$  to  $+4$ , and hence was oxidized. Thus  $\text{PbS}$  is a reductant. The oxidation number of O decreased from  $0$  to  $-2$ . Thus oxygen is an oxidant.

In the 2nd stage of the reaction, the oxidation number of C changed from  $+2$  to  $+4$ , and hence was oxidized. Thus  $\text{CO}$  is a reductant. The oxidation number of Pb decreased from  $+2$  to  $0$ . Thus  $\text{PbO}$  is an oxidant. In the smelting of metals such as iron, carbon monoxide often is a reductant.

**Balancing Oxidation Reduction Reactions:** Redox reactions can be balanced by (i) oxidation number method and (ii) Ion electron method (half reaction method)

Balancing in a acidic solution

1. Divide the reaction into half-reactions
2. Balance each half-reaction
  - First balance elements other than O & H
  - Balance O atoms using  $\text{H}_2\text{O}$
  - Balance H atoms with  $\text{H}^+$
  - Balance charge with  $\text{e}^-$
3. Multiply each half reaction by an integer so each has the same number of electrons
4. Add half reactions and simplify

Balancing in a basic solution

Use  $\text{OH}^-$  &  $\text{H}_2\text{O}$

**Oxidation number method by Johnson**

- Skeleton equation  
 $\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO}_2 + \text{H}_2\text{O}$
- Writing the oxidation number of all the atoms  
 $\overset{0}{\text{Cu}} + \overset{+1}{\text{H}}\overset{+5}{\text{N}}\overset{-2}{\text{O}_3} \longrightarrow \overset{+2}{\text{Cu}}(\overset{+5}{\text{N}}\overset{-2}{\text{O}_3})_2 + \overset{+4}{\text{N}}\overset{-2}{\text{O}_2} + \overset{+1}{\text{H}}\overset{-2}{\text{O}}$
- Change in oxidation number has occurred in copper and nitrogen  
 $\overset{0}{\text{Cu}} \longrightarrow \overset{+2}{\text{Cu}}(\text{NO}_3)_2 \quad \dots \text{(i)}$   
 $\overset{+5}{\text{HNO}_3} \longrightarrow \overset{+4}{\text{NO}_2} \quad \dots \text{(ii)}$

Increase in oxidation number of copper = 2 units per molecules of Cu

Decrease in oxidation number of nitrogen = 1 unit per molecule of  $\text{HNO}_3$

- To make increase and decrease equal equation (ii) is multiplied by 2.  
 $\text{Cu} + 2\text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + \text{H}_2\text{O}$
- Balancing nitrate ions, hydrogen and oxygen  
 $\text{Cu} + 4\text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$

## Balancing of Half Reaction by Jette & LaMev



- Write element whose oxidation number changes with their symbol and oxidation number.



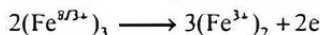
- Write the state of element in which it exists in reaction as shown ahead



- Balance number of atoms on two sides.



- Balance charge on two sides using electrons



## Electrochemistry

- Voltaic Cell:** A device in which a spontaneous oxidation reduction reaction occurs with the passage of electrons through an external circuit.
- Electrodes:** Two solid metals connected by the external circuit.
- Anode:** Electrode at which oxidation occurs;  
**Cathode:** Electrode at which reduction occurs.
- Salt Bridge:** Electrical contact between the two solutions that prevents them from mixing but permits ion flow.

## Standardization of the electromotive force

- The concentration and temperature of the electrolytic solution are to be maintained under a constant condition, i.e., 25°C and 1 mol dm<sup>-3</sup> (S.T.P). In facts the experimental values are extrapolated to those standard values.
- A cell is constructed with a common electrode that acts as a standard electrode.
- The electromotive force of this cell is determined including the sign (i.e., which electrode will act as the positive electrode is determined).
- By definition, the contribution of the standard electrode to the electromotive force of the cell is zero. Then the measured potential difference is a value characteristic of the electrode in question. This is called the **normal electrode potential** of this electrode.
- The electromotive force of any two cells is equal to the sum of the standard electrode potentials of the electrodes.

## Corrosion

- Corrosion occurs when a metal undergoes a spontaneous redox reaction and is converted to an unwanted substance.
- Oxidation is usually the thermodynamically favoured process for a metal.
- Corrosion of iron is called rusting.
- Preventing iron from Corroding.

## Illustrations

**Illustration 1:** Determine the oxidation no. of following elements given compounds:

- (a)  $\text{KMnO}_4$ , (b)  $\text{H}_2\text{SO}_5$ , (c)  $\text{H}_2\text{S}_2\text{O}_8$ , (d)  $\text{NH}_4\text{NO}_3$ , (e)  $\text{K}_4\text{Fe}(\text{CN})_6$ , (f)  $\text{HCN}$ , (g)  $\text{HNO}_3$ , (h)  $\text{KO}_2$ , (i)  $\text{Fe}_3\text{O}_4$ , (j)  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , (k)  $\text{NOCl}$ , (l)  $\text{Na}_2\text{S}_4\text{O}_6$ , (m)  $\text{Na}_2\text{S}_2\text{O}_3$

**Solution:** (a)  $\text{KMnO}_4$  :

Oxidation Number of K = +1 by rules

Oxidation Number of Mn = a

Oxidation Number of O = -2 by rules

$$\therefore 1 + a + 4 \times (-2) = 0 \quad \therefore a = +7$$

(b)  $\text{H}_2\text{SO}_5$  :

Oxidation Number of H = +1

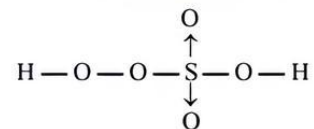
Oxidation Number of O = -2

Oxidation Number of S = a

$$\therefore 2 \times 1 + a + 5 \times (-2) = 0 \quad a = +8 \text{ (wrong)}$$

But this cannot be true as maximum ox. no. of S (VI gp) stands +6.

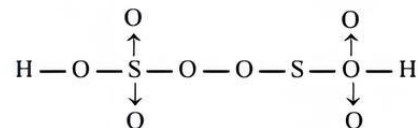
The exceptional value is due to the fact that two O atoms in  $\text{H}_2\text{SO}_5$  show peroxide linkage, i.e.,



Thus, evaluation of ox. no. of S should be made as  $2 \times 1 + a + 3 \times (-2) + 2 \times (-1) = 0$

$$a = +6$$

(c)  $\text{H}_2\text{S}_2\text{O}_8$  : Here too, O atoms form peroxide linkage. i.e.,



$$\therefore 2 \times 1 + 2a + 6 \times (-2) + 2 \times (-1) = 0 \text{ by rules}$$

$$a = +1 \quad \text{(wrong)}$$

(d)  $\text{NH}_4\text{NO}_3$  :

No doubt there are two N atoms in  $\text{NH}_4\text{NO}_3$ , but one N atom has negative ox. no. (attached to H) and the other has positive ox. no. (attached to O). Therefore, evaluation should be made separately as

Oxidation number of N in  $\text{NH}_4^+$  and

Oxidation number of N in  $\text{NO}_3^-$

$$a + 4 \times (+1) = +1$$

$$\therefore a = -3$$

$$a + 3 \times (-2) = -1$$

$$\therefore a = +5$$



(e)  $K_4Fe(CN)_6$  : By rules, Oxidation number of  $K = +1$

Oxidation number of  $CN^{-1} = -1$

Oxidation number of  $Fe = a$

$$\therefore 4 \times 1 + a + 6 \times (-1) = 0 \quad \therefore a = +2$$

(f)  $OsO_4$  :  $a + 4 \times (-2) = 0 \quad \therefore a = +8$

Note: 1. The element Os and Ru show highest oxidation state i.e., +8.

2. Recently  $Ba_2XeO_6$  has been reported in which ox. no. of Xe is +8.

(f) HCN: The evaluation cannot be made directly in some cases, e.g., HCN by using rules proposed earlier since we have no rule for ox. no. of both N and C.

In all such case evaluation of ox. no. should be made using indirect concept or using fundamentals by which rules have been framed.

1. Each covalent bond contributes one unit for ox. no.
2. Covalently bonded atoms with less electronegativity acquires positive ox. no. whereas other with more electronegativity acquires negative ox. no.
3. In case of co-ordinate bond, give +2 value for ox. no. to atom from which co-ordinate bond is directed to a more electronegative atom and -2 value to more electronegative atom.

If co-ordinate bond is directed from more electronegative to less electronegative atom, then neglect contribution of co-ordinate bond for both atoms in which co-ordinate bond exist.

Thus,  $H-C \equiv N$

$\therefore$  Three bonds on N atom and N is more

$1 + a + 3 \times (-1) = 0$  electronegative

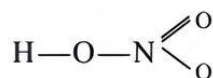
$$a = +2$$

$\therefore$  Oxidation number of  $N = 3 \times (-1) = -3$

(g)  $HNO_3$  : By rules

$$1 + a + 3 \times (-2) = 0$$

$\therefore a = +5$  by fundamental approach



Oxidation number of  $H = +1$

Oxidation number of  $N = +1$

$$+ (+2) \quad + (+2) \quad = -3$$

Covalent bond      two covalent      Co-ordinate  
with O              bond with O      bond

$\therefore$  N being less electronegative than O.

(h)  $KO_2$  : A super oxide of K; Oxidation number of  $K = +1$

Oxidation number of  $O = a$

$$1 + 2 \times a = 0$$

$$\therefore a = -\frac{1}{2}$$

(i)  $Fe_3O_4$  :  $3 \times a + 4 \times (-2) = 0$

$$\therefore a = +\frac{8}{3}$$

or  $Fe_3O_4$  is a mixed oxide of  $FeO \cdot Fe_2O_3$

$\therefore$  Fe has two oxidation no. +2 and +3 separately. However, factually speaking oxidation number of Fe in  $Fe_3O_4$  is an average of two values (i.e., +2 and +3).

$$\text{Average oxidation number} = \frac{+2 + 2 \times (+3)}{3} = +\frac{8}{3}$$

(j)  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$  : Oxidation number  $Fe = a$

Sum of oxidation number for  $(NH_4)_2SO_4 = 0$

Sum of oxidation number for  $H_2O = 0$

Sum of oxidation number for  $SO_4^{2-} = -2$

$$\therefore a + (-2) + 0 + 6 \times (0) = 0$$

$$\therefore a = +2$$

(k)  $NOCl$  :  $Cl-N \equiv O$  or use  $NO^+Cl^-$

Oxidation number of  $N = +1$  (for covalent bond with Cl)

Oxidation number of  $N = +2$  (for two covalent bonds with O)

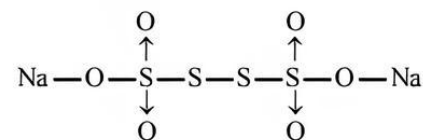
$\therefore$  Total Oxidation number of N in  $NOCl = +3$

(l)  $Na_2S_4O_6$  :

$$2 \times (+1) + 4a + 6 \times (-2) = 0$$

$$\therefore a = +\frac{5}{2}$$

Here also this value is the average oxidation no. of S. The structure of  $Na_2S_4O_6$  is



Thus oxidation number of each S atom forming co-ordinate bond is +5 whereas, ox. no. of each S atom involved in pure covalent bonding is zero.

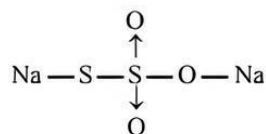
$$\therefore \text{Average ox. no.} = \frac{+5 + 5 + 0 + 0}{4} = +\frac{5}{2}$$

(m)  $Na_2S_2O_3$  :

$$2 \times 1 + 2 \times a + 3 \times (-2) = 0$$

$$\therefore a = +2$$

Here too it is the average ox. no. The structure of  $\text{Na}_2\text{S}_2\text{O}_3$  is



The ox. no. of S involved in co-ordinate bond i.e., donor S atom is +5.

The ox. no. of other S atom is -1.

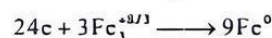
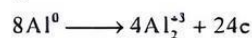
**Illustration 2:** In the reaction  $\text{Al} + \text{Fe}_3\text{O}_4 \longrightarrow \text{Al}_2\text{O}_3 + \text{Fe}$

(a) Which element is oxidized and which is reduced? (b) Total no. of electrons transferred during the change.

**Solution:**  $2\text{Al}^0 \longrightarrow \text{Al}_2^{+3} + 6\text{e}^- \quad \dots \text{(i)}$

$8\text{e}^- + \text{Fe}_3^{+8/3} \longrightarrow 3\text{Fe}^0 \quad \dots \text{(ii)}$

Multiplying equation (i) by 4 and equation (ii) by 3, then adding



or  $8\text{Al} + 3\text{Fe}_3\text{O}_4 \longrightarrow 4\text{Al}_2\text{O}_3 + 9\text{Fe}$

Therefore, it is clear that

(a) Al is oxidized and  $\text{Fe}^{+8/3}$  is reduced.

(b) Total no. of electrons transferred during change = 24

**Illustration 3:** Identify the substance acting as oxidant or reductant reduced if any in the following:

(a)  $\text{AlCl}_3, 3\text{K} \longrightarrow \text{Al} + 3\text{KCl}$

(b)  $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 3\text{S} + \text{H}_2\text{O}$

(c)  $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + 2\text{NaCl}$

(d)  $3\text{I}_2 + 6\text{NaOH} \longrightarrow \text{NaIO}_3 + 5\text{NaI} + 3\text{H}_2\text{O}$

**Solution:** In a conjugate pair, oxidant has higher ox. no.

(a) For  $\text{AlCl}_3$ :  $\text{Al}^{+3} + 3\text{e}^- \longrightarrow \text{Al}^0$  ;

For K:  $\text{K}^0 \longrightarrow \text{K}^{+1} + \text{e}^-$

Oxidant is  $\text{AlCl}_3$  and reductant is K.

(b) For  $\text{SO}_2$ :  $\text{S}^{+4} + 4\text{e}^- \longrightarrow \text{S}^0$  ; For  $\text{H}_2\text{S}$ :  $\text{S}^{-2} \longrightarrow \text{S}^0 + 2\text{e}^-$

$\text{SO}_2$  is oxidant.

$\therefore \text{H}_2\text{S}$  is reductant.

(c) No change in ox. no. of either of the conjugate pair.

None is oxidant or reductant.

(d) For  $\text{I}_2$ :  $\text{I}_2^0 \longrightarrow 2\text{I}^{+5} + 10\text{e}^-$  and  $\text{I}_2^0 + 2\text{e}^- \longrightarrow 2\text{I}^{-1}$

$\text{I}_2$  acts as oxidant and reductant both.