



11083CH08

## UNIT 7

# REDOX REACTIONS

### Objectives

After studying this unit you will be able to

- identify redox reactions as a class of reactions in which oxidation and reduction reactions occur simultaneously;
- define the terms oxidation, reduction, oxidant (oxidising agent) and reductant (reducing agent);
- explain mechanism of redox reactions by electron transfer process;
- use the concept of oxidation number to identify oxidant and reductant in a reaction;
- classify redox reaction into combination (synthesis), decomposition, displacement and disproportionation reactions;
- suggest a comparative order among various reductants and oxidants;
- balance chemical equations using (i) oxidation number (ii) half reaction method;
- learn the concept of redox reactions in terms of electrode processes.

*Where there is oxidation, there is always reduction – Chemistry is essentially a study of redox systems.*

Chemistry deals with varieties of matter and change of one kind of matter into the other. Transformation of matter from one kind into another occurs through the various types of reactions. One important category of such reactions is **Redox Reactions**. A number of phenomena, both physical as well as biological, are concerned with redox reactions. These reactions find extensive use in pharmaceutical, biological, industrial, metallurgical and agricultural areas. The importance of these reactions is apparent from the fact that burning of different types of fuels for obtaining energy for domestic, transport and other commercial purposes, electrochemical processes for extraction of highly reactive metals and non-metals, manufacturing of chemical compounds like caustic soda, operation of dry and wet batteries and corrosion of metals fall within the purview of redox processes. Of late, environmental issues like **Hydrogen Economy** (use of liquid hydrogen as fuel) and development of '**Ozone Hole**' have started figuring under redox phenomenon.

### 7.1 CLASSICAL IDEA OF REDOX REACTIONS – OXIDATION AND REDUCTION REACTIONS

Originally, the term **oxidation** was used to describe the addition of oxygen to an element or a compound. Because of the presence of dioxygen in the atmosphere (~20%), many elements combine with it and this is the principal reason why they commonly occur on the earth in the form of their oxides. The following reactions represent oxidation processes according to the limited definition of oxidation:



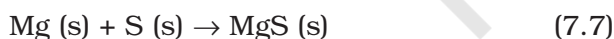
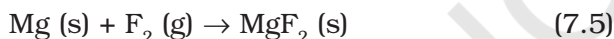
In reactions (7.1) and (7.2), the elements magnesium and sulphur are oxidised on account of addition of oxygen to them. Similarly, methane is oxidised owing to the addition of oxygen to it.



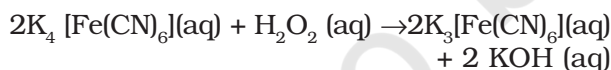
A careful examination of reaction (7.3) in which hydrogen has been replaced by oxygen prompted chemists to reinterpret oxidation in terms of removal of hydrogen from it and, therefore, the scope of term oxidation was broadened to include the removal of hydrogen from a substance. The following illustration is another reaction where removal of hydrogen can also be cited as an oxidation reaction.



As knowledge of chemists grew, it was natural to extend the term oxidation for reactions similar to (7.1 to 7.4), which do not involve oxygen but other electronegative elements. The oxidation of magnesium with fluorine, chlorine and sulphur etc. occurs according to the following reactions :



Incorporating the reactions (7.5 to 7.7) within the fold of oxidation reactions encouraged chemists to consider not only the removal of hydrogen as oxidation, but also the removal of electropositive elements as oxidation. Thus the reaction :

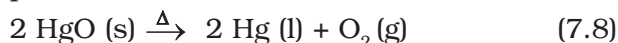


is interpreted as oxidation due to the removal of electropositive element potassium from potassium ferrocyanide before it changes to potassium ferricyanide. To summarise, the term “**oxidation**” is defined as the **addition of oxygen/electronegative element to a substance or removal of hydrogen/electropositive element from a substance.**

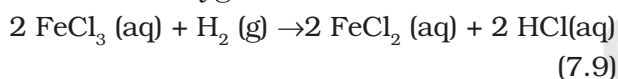
In the beginning, reduction was considered as removal of oxygen from a compound. However, the term **reduction** has been

broadened these days to include **removal of oxygen/electronegative element from a substance or addition of hydrogen/electropositive element to a substance.**

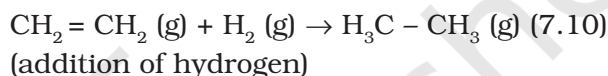
According to the definition given above, the following are the examples of reduction processes:



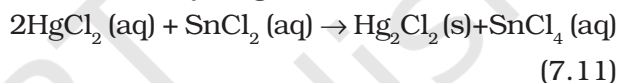
(removal of oxygen from mercuric oxide )



(removal of electronegative element, chlorine from ferric chloride)



(addition of hydrogen)

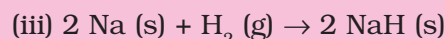
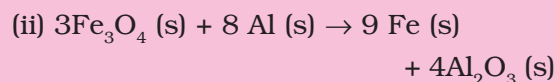
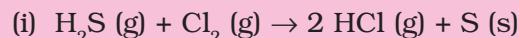


(addition of mercury to mercuric chloride)

In reaction (7.11) simultaneous oxidation of stannous chloride to stannic chloride is also occurring because of the addition of electronegative element chlorine to it. It was soon realised that oxidation and reduction always occur simultaneously (as will be apparent by re-examining all the equations given above), hence, the word “**redox**” was coined for this class of chemical reactions.

### Problem 7.1

In the reactions given below, identify the species undergoing oxidation and reduction:



### Solution

(i)  $\text{H}_2\text{S}$  is oxidised because a more electronegative element, chlorine is added to hydrogen (or a more electropositive element, hydrogen has been removed from S). Chlorine is reduced due to addition of hydrogen to it.

(ii) Aluminium is oxidised because oxygen is added to it. Ferrous ferric oxide

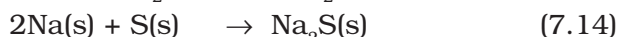
(Fe<sub>3</sub>O<sub>4</sub>) is reduced because oxygen has been removed from it.

(iii) With the careful application of the concept of electronegativity only we may infer that sodium is oxidised and hydrogen is reduced.

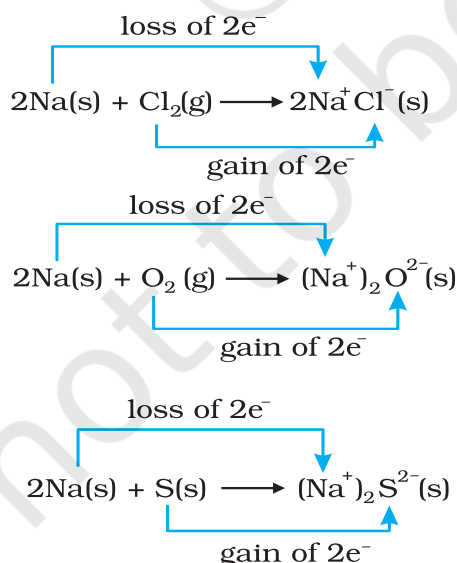
Reaction (iii) chosen here prompts us to think in terms of another way to define redox reactions.

## 7.2 REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER REACTIONS

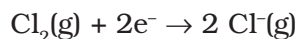
We have already learnt that the reactions



are redox reactions because in each of these reactions sodium is oxidised due to the addition of either oxygen or more electronegative element to sodium. Simultaneously, chlorine, oxygen and sulphur are reduced because to each of these, the electropositive element sodium has been added. From our knowledge of chemical bonding we also know that sodium chloride, sodium oxide and sodium sulphide are ionic compounds and perhaps better written as Na<sup>+</sup>Cl<sup>-</sup>(s), (Na<sup>+</sup>)<sub>2</sub>O<sup>2-</sup>(s), and (Na<sup>+</sup>)<sub>2</sub>S<sup>2-</sup>(s). Development of charges on the species produced suggests us to rewrite the reactions (7.12 to 7.14) in the following manner :



For convenience, each of the above processes can be considered as two separate steps, one involving the loss of electrons and the other the gain of electrons. As an illustration, we may further elaborate one of these, say, the formation of sodium chloride.



Each of the above steps is called a half reaction, which explicitly shows involvement of electrons. Sum of the half reactions gives the overall reaction :



Reactions 7.12 to 7.14 **suggest that half reactions that involve loss of electrons are called oxidation reactions. Similarly, the half reactions that involve gain of electrons are called reduction reactions.** It may not be out of context to mention here that the new way of defining oxidation and reduction has been achieved only by establishing a correlation between the behaviour of species as per the classical idea and their interplay in electron-transfer change. In reactions (7.12 to 7.14) sodium, which is oxidised, acts as **a reducing agent** because it donates electron to each of the elements interacting with it and thus helps in reducing them. Chlorine, oxygen and sulphur are reduced and act as oxidising agents because these accept electrons from sodium. To summarise, we may mention that

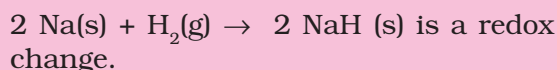
**Oxidation** : Loss of electron(s) by any species.

**Reduction** : Gain of electron(s) by any species.

**Oxidising agent** : Acceptor of electron(s).

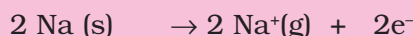
**Reducing agent** : Donor of electron(s).

**Problem 7.2** Justify that the reaction:

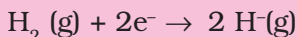


**Solution**

Since in the above reaction the compound formed is an ionic compound, which may also be represented as Na<sup>+</sup>H<sup>-</sup>(s), this suggests that one half reaction in this process is :



and the other half reaction is:

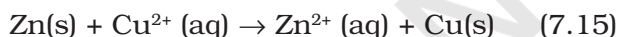


This splitting of the reaction under examination into two half reactions automatically reveals that here sodium is oxidised and hydrogen is reduced, therefore, the complete reaction is a redox change.

### 7.2.1 Competitive Electron Transfer Reactions

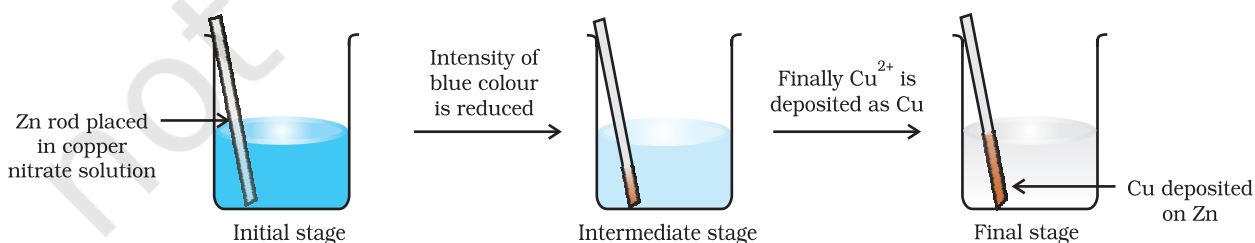
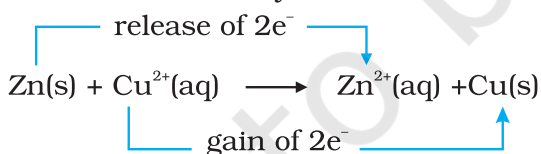
Place a strip of metallic zinc in an aqueous solution of copper nitrate as shown in Fig. 7.1, for about one hour. You may notice that the strip becomes coated with reddish metallic copper and the blue colour of the solution disappears. Formation of  $\text{Zn}^{2+}$  ions among the products can easily be judged when the blue colour of the solution due to  $\text{Cu}^{2+}$  has disappeared. If hydrogen sulphide gas is passed through the colourless solution containing  $\text{Zn}^{2+}$  ions, appearance of white zinc sulphide,  $\text{ZnS}$  can be seen on making the solution alkaline with ammonia.

The reaction between metallic zinc and the aqueous solution of copper nitrate is :



In reaction (7.15), zinc has lost electrons to form  $\text{Zn}^{2+}$  and, therefore, zinc is oxidised. Evidently, now if zinc is oxidised, releasing electrons, something must be reduced, accepting the electrons lost by zinc. Copper ion is reduced by gaining electrons from the zinc.

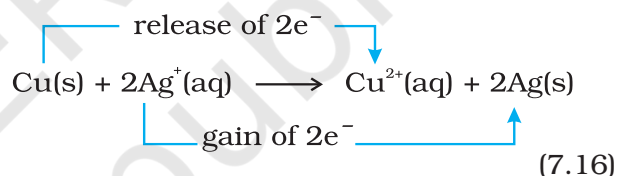
Reaction (7.15) may be rewritten as :



**Fig. 7.1** Redox reaction between zinc and aqueous solution of copper nitrate occurring in a beaker.

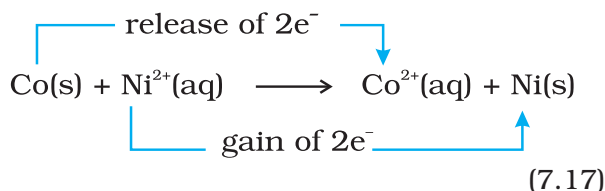
At this stage we may investigate the state of equilibrium for the reaction represented by equation (7.15). For this purpose, let us place a strip of metallic copper in a zinc sulphate solution. No visible reaction is noticed and attempt to detect the presence of  $\text{Cu}^{2+}$  ions by passing  $\text{H}_2\text{S}$  gas through the solution to produce the black colour of cupric sulphide,  $\text{CuS}$ , does not succeed. Cupric sulphide has such a low solubility that this is an extremely sensitive test; yet the amount of  $\text{Cu}^{2+}$  formed cannot be detected. We thus conclude that the state of equilibrium for the reaction (7.15) greatly favours the products over the reactants.

Let us extend electron transfer reaction now to copper metal and silver nitrate solution in water and arrange a set-up as shown in Fig. 7.2. The solution develops blue colour due to the formation of  $\text{Cu}^{2+}$  ions on account of the reaction:

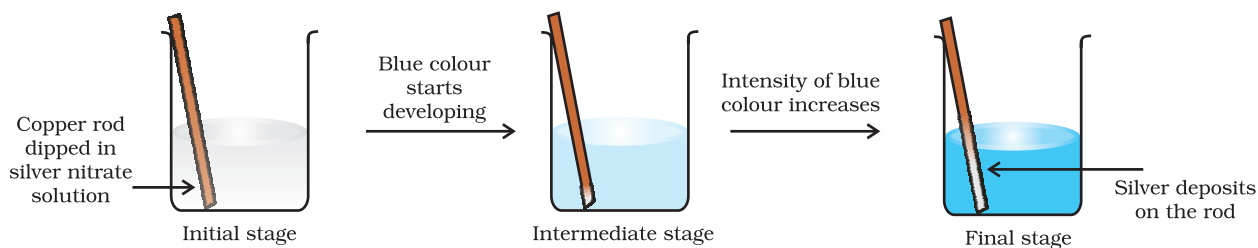


Here,  $\text{Cu}(\text{s})$  is oxidised to  $\text{Cu}^{2+}(\text{aq})$  and  $\text{Ag}^+(\text{aq})$  is reduced to  $\text{Ag}(\text{s})$ . Equilibrium greatly favours the products  $\text{Cu}^{2+}(\text{aq})$  and  $\text{Ag}(\text{s})$ .

By way of contrast, let us also compare the reaction of metallic cobalt placed in nickel sulphate solution. The reaction that occurs here is :







**Fig. 7.2** Redox reaction between copper and aqueous solution of silver nitrate occurring in a beaker.

At equilibrium, chemical tests reveal that both  $\text{Ni}^{2+}(\text{aq})$  and  $\text{Co}^{2+}(\text{aq})$  are present at moderate concentrations. In this case, neither the reactants [ $\text{Co}(\text{s})$  and  $\text{Ni}^{2+}(\text{aq})$ ] nor the products [ $\text{Co}^{2+}(\text{aq})$  and  $\text{Ni}(\text{s})$ ] are greatly favoured.

This competition for release of electrons incidentally reminds us of the competition for release of protons among acids. The similarity suggests that we might develop a table in which metals and their ions are listed on the basis of their tendency to release electrons just as we do in the case of acids to indicate the strength of the acids. As a matter of fact we have already made certain comparisons. By comparison we have come to know that zinc releases electrons to copper and copper releases electrons to silver and, therefore, the electron releasing tendency of the metals is in the order:  $\text{Zn} > \text{Cu} > \text{Ag}$ . We would love to make our list more vast and design a **metal activity series or electrochemical series**. The competition for electrons between various metals helps us to design a class of cells, named as Galvanic cells in which the chemical reactions become the source of electrical energy. We would study more about these cells in Class XII.

### 7.3 OXIDATION NUMBER

A less obvious example of electron transfer is realised when hydrogen combines with oxygen to form water by the reaction:



Though not simple in its approach, yet we can visualise the H atom as going from a neutral (zero) state in  $\text{H}_2$  to a positive state in  $\text{H}_2\text{O}$ , the O atom goes from a zero state in  $\text{O}_2$  to a dinegative state in  $\text{H}_2\text{O}$ . It is assumed that there is an electron transfer from H to O and consequently  $\text{H}_2$  is oxidised and  $\text{O}_2$  is reduced.

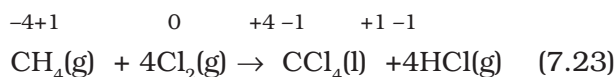
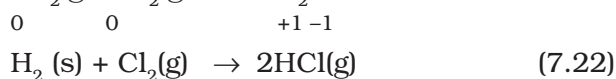
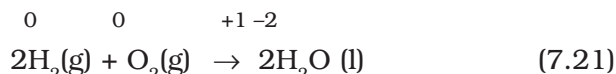
However, as we shall see later, the charge transfer is only partial and is perhaps better described as an electron shift rather than a complete loss of electron by H and gain by O. What has been said here with respect to equation (7.18) may be true for a good number of other reactions involving covalent compounds. Two such examples of this class of the reactions are:



and,



In order to keep track of electron shifts in chemical reactions involving formation of covalent compounds, a more practical method of using **oxidation number** has been developed. In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electronegative atom. For example, we rewrite equations (7.18 to 7.20) to show charge on each of the atoms forming part of the reaction :



It may be emphasised that the assumption of electron transfer is made for book-keeping purpose only and it will become obvious at a later stage in this unit that it leads to the simple description of redox reactions.

**Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that electron pair**

**in a covalent bond belongs entirely to more electronegative element.**

It is not always possible to remember or make out easily in a compound/ion, which element is more electronegative than the other. Therefore, a set of rules has been formulated to determine the oxidation number of an element in a compound/ion. If two or more than two atoms of an element are present in the molecule/ion such as  $\text{Na}_2\text{S}_2\text{O}_3/\text{Cr}_2\text{O}_7^{2-}$ , the oxidation number of the atom of that element will then be the average of the oxidation number of all the atoms of that element. We may at this stage, state the rules for the calculation of oxidation number. These rules are:

1. In elements, in the free or the uncombined state, each atom bears an oxidation number of zero. Evidently each atom in  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{P}_4$ ,  $\text{S}_8$ , Na, Mg, Al has the oxidation number zero.
2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion. Thus  $\text{Na}^+$  ion has an oxidation number of +1,  $\text{Mg}^{2+}$  ion, +2,  $\text{Fe}^{3+}$  ion, +3,  $\text{Cl}^-$  ion, -1,  $\text{O}^{2-}$  ion, -2; and so on. In their compounds all alkali metals have oxidation number of +1, and all alkaline earth metals have an oxidation number of +2. Aluminium is regarded to have an oxidation number of +3 in all its compounds.
3. The oxidation number of oxygen in most compounds is -2. However, we come across two kinds of exceptions here. One arises in the case of peroxides and superoxides, the compounds of oxygen in which oxygen atoms are directly linked to each other. While in peroxides (e.g.,  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_2$ ), each oxygen atom is assigned an oxidation number of -1, in superoxides (e.g.,  $\text{KO}_2$ ,  $\text{RbO}_2$ ) each oxygen atom is assigned an oxidation number of  $-(1/2)$ . The second exception appears rarely, i.e. when oxygen is bonded to fluorine. In such compounds e.g., oxygen difluoride ( $\text{OF}_2$ ) and dioxygen difluoride ( $\text{O}_2\text{F}_2$ ), the oxygen is assigned an oxidation number of +2 and +1, respectively. The number assigned to oxygen will depend upon the

bonding state of oxygen but this number would now be a positive figure only.

4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds (that is compounds containing two elements). For example, in LiH, NaH, and  $\text{CaH}_2$ , its oxidation number is -1.
5. In all its compounds, fluorine has an oxidation number of -1. Other halogens (Cl, Br, and I) also have an oxidation number of -1, when they occur as halide ions in their compounds. Chlorine, bromine and iodine when combined with oxygen, for example in oxoacids and oxoanions, have positive oxidation numbers.
6. The algebraic sum of the oxidation number of all the atoms in a compound must be zero. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion. Thus, the sum of oxidation number of three oxygen atoms and one carbon atom in the carbonate ion,  $(\text{CO}_3)^{2-}$  must equal -2.

By the application of above rules, we can find out the oxidation number of the desired element in a molecule or in an ion. It is clear that the metallic elements have positive oxidation number and nonmetallic elements have positive or negative oxidation number. The atoms of transition elements usually display several positive oxidation states. The highest oxidation number of a representative element is the group number for the first two groups and the group number minus 10 (following the long form of periodic table) for the other groups. Thus, it implies that the highest value of oxidation number exhibited by an atom of an element generally increases across the period in the periodic table. In the third period, the highest value of oxidation number changes from 1 to 7 as indicated below in the compounds of the elements.

A term that is often used interchangeably with the oxidation number is the **oxidation state**. Thus in  $\text{CO}_2$ , the oxidation state of carbon is +4, that is also its oxidation number and similarly the oxidation state as well as oxidation number of oxygen is -2. This implies that the oxidation number denotes the oxidation state of an element in a compound.

Group	1	2	13	14	15	16	17
Element	Na	Mg	Al	Si	P	S	Cl
Compound	NaCl	MgSO <sub>4</sub>	AlF <sub>3</sub>	SiCl <sub>4</sub>	P <sub>4</sub> O <sub>10</sub>	SF <sub>6</sub>	HClO
Highest oxidation number state of the group element	+1	+2	+3	+4	+5	+6	+7

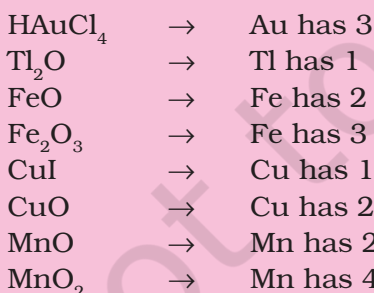
The oxidation number/state of a metal in a compound is sometimes presented according to the notation given by German chemist, Alfred Stock. It is popularly known as **Stock notation**. According to this, the oxidation number is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of the metal in the molecular formula. Thus aurous chloride and auric chloride are written as Au(I)Cl and Au(III)Cl<sub>3</sub>. Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl<sub>2</sub> and Sn(IV)Cl<sub>4</sub>. This change in oxidation number implies change in oxidation state, which in turn helps to identify whether the species is present in oxidised form or reduced form. Thus, Hg<sub>2</sub>(I)Cl<sub>2</sub> is the reduced form of Hg(II)Cl<sub>2</sub>.

### Problem 7.3

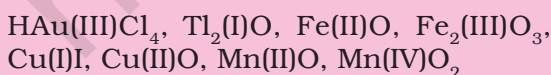
Using Stock notation, represent the following compounds :HAuCl<sub>4</sub>, Tl<sub>2</sub>O, FeO, Fe<sub>2</sub>O<sub>3</sub>, CuI, CuO, MnO and MnO<sub>2</sub>.

### Solution

By applying various rules of calculating the oxidation number of the desired element in a compound, the oxidation number of each metallic element in its compound is as follows:



Therefore, these compounds may be represented as:



The idea of oxidation number has been invariably applied to define oxidation, reduction, oxidising agent (oxidant), reducing agent (reductant) and the redox reaction. To summarise, we may say that:

**Oxidation:** An increase in the oxidation number of the element in the given substance.

**Reduction** : A decrease in the oxidation number of the element in the given substance.

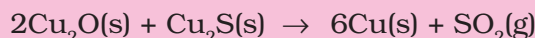
**Oxidising agent:** A reagent which can increase the oxidation number of an element in a given substance. These reagents are called as **oxidants** also.

**Reducing agent:** A reagent which lowers the oxidation number of an element in a given substance. These reagents are also called as **reductants**.

**Redox reactions:** Reactions which involve change in oxidation number of the interacting species.

### Problem 7.4

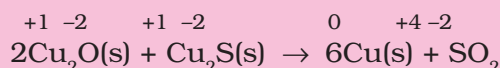
Justify that the reaction:



is a redox reaction. Identify the species oxidised/reduced, which acts as an oxidant and which acts as a reductant.

### Solution

Let us assign oxidation number to each of the species in the reaction under examination. This results into:



We therefore, conclude that in this reaction *copper is reduced* from +1 state to zero oxidation state and *sulphur is oxidised* from -2 state to +4 state. The above reaction is thus a *redox reaction*.

Further,  $\text{Cu}_2\text{O}$  helps sulphur in  $\text{Cu}_2\text{S}$  to increase its oxidation number, therefore,  $\text{Cu(I)}$  is an oxidant; and sulphur of  $\text{Cu}_2\text{S}$  helps copper both in  $\text{Cu}_2\text{S}$  itself and  $\text{Cu}_2\text{O}$  to decrease its oxidation number; therefore, sulphur of  $\text{Cu}_2\text{S}$  is reductant.

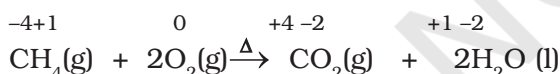
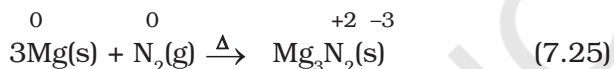
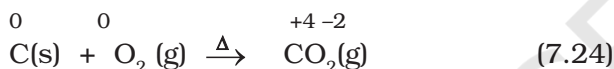
### 7.3.1 Types of Redox Reactions

#### 1. Combination reactions

A combination reaction may be denoted in the manner:

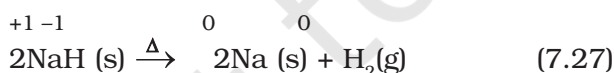
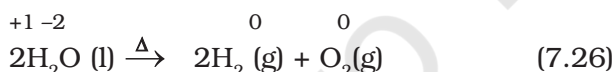


Either A and B or both A and B must be in the elemental form for such a reaction to be a redox reaction. All combustion reactions, which make use of elemental dioxygen, as well as other reactions involving elements other than dioxygen, are redox reactions. Some important examples of this category are:



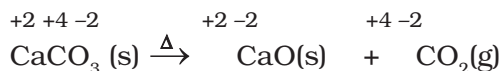
#### 2. Decomposition reactions

Decomposition reactions are the opposite of combination reactions. Precisely, a decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state. Examples of this class of reactions are:



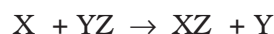
It may carefully be noted that there is no change in the oxidation number of hydrogen in methane under combination reactions and that of potassium in potassium chlorate in reaction (7.28). This may also be noted

here that all decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction.



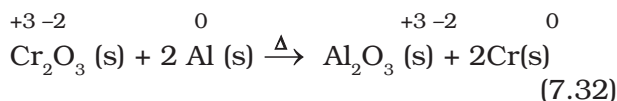
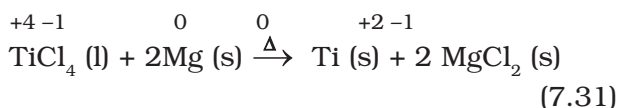
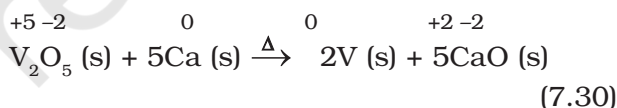
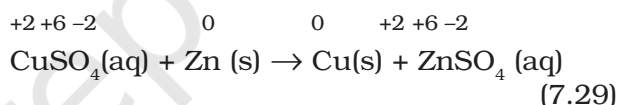
#### 3. Displacement reactions

In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as:



Displacement reactions fit into two categories: metal displacement and non-metal displacement.

**(a) Metal displacement:** A metal in a compound can be displaced by another metal in the uncombined state. We have already discussed about this class of the reactions under section 7.2.1. Metal displacement reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. A few such examples are:

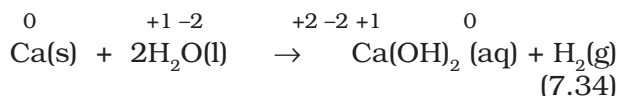
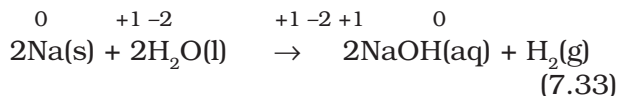


In each case, the reducing metal is a better reducing agent than the one that is being reduced which evidently shows more capability to lose electrons as compared to the one that is reduced.

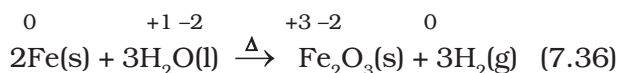
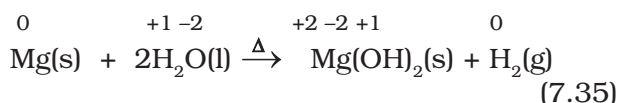
**(b) Non-metal displacement:** The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.



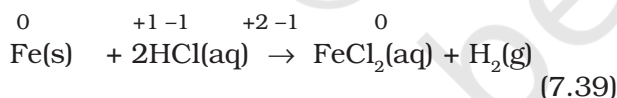
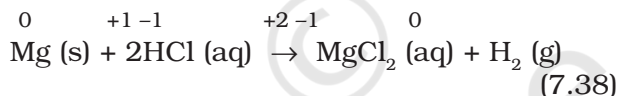
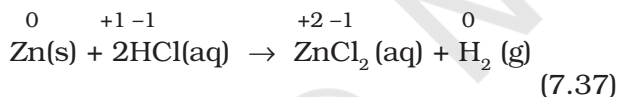
All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants, will displace hydrogen from cold water.



Less active metals such as magnesium and iron react with steam to produce dihydrogen gas:



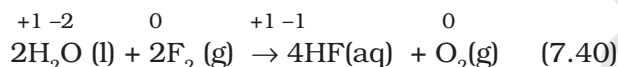
Many metals, including those which do not react with cold water, are capable of displacing hydrogen from acids. Dihydrogen from acids may even be produced by such metals which do not react with steam. Cadmium and tin are the examples of such metals. A few examples for the displacement of hydrogen from acids are:



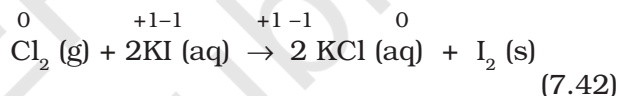
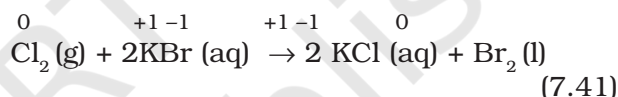
Reactions (7.37 to 7.39) are used to prepare dihydrogen gas in the laboratory. Here, the reactivity of metals is reflected in the rate of hydrogen gas evolution, which is the slowest for the least active metal Fe, and the fastest for the most reactive metal, Mg. Very less active metals, which may occur in the native state such as silver (Ag), and gold (Au) do not react even with hydrochloric acid.

In section (7.2.1) we have already discussed that the metals – zinc (Zn), copper (Cu) and silver (Ag) through tendency to lose electrons show their reducing activity in the order  $\text{Zn} >$

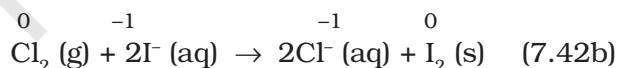
$\text{Cu} > \text{Ag}$ . Like metals, activity series also exists for the halogens. The power of these elements as oxidising agents decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it attacks water and displaces the oxygen of water :



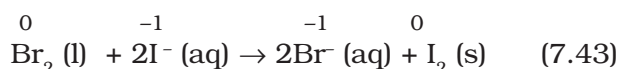
It is for this reason that the displacement reactions of chlorine, bromine and iodine using fluorine are not generally carried out in aqueous solution. On the other hand, chlorine can displace bromide and iodide ions in an aqueous solution as shown below:



As  $\text{Br}_2$  and  $\text{I}_2$  are coloured and dissolve in  $\text{CCl}_4$ , can easily be identified from the colour of the solution. The above reactions can be written in ionic form as:



Reactions (7.41) and (7.42) form the basis of identifying  $\text{Br}^-$  and  $\text{I}^-$  in the laboratory through the test popularly known as 'Layer Test'. It may not be out of place to mention here that bromine likewise can displace iodide ion in solution:



The halogen displacement reactions have a direct industrial application. The recovery of halogens from their halides requires an oxidation process, which is represented by:

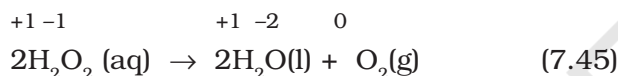


here X denotes a halogen element. Whereas chemical means are available to oxidise  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , as fluorine is the strongest oxidising

agent; there is no way to convert  $F^-$  ions to  $F_2$  by chemical means. The only way to achieve  $F_2$  from  $F^-$  is to oxidise electrolytically, the details of which you will study at a later stage.

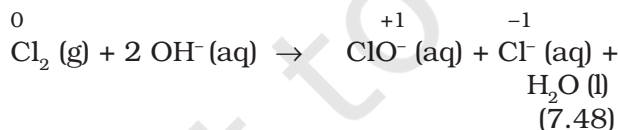
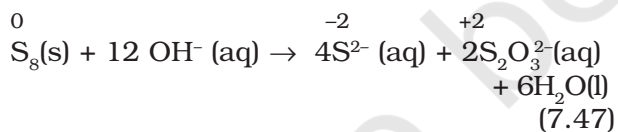
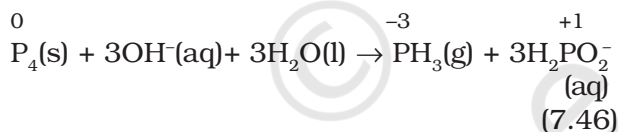
#### 4. Disproportionation reactions

Disproportionation reactions are a special type of redox reactions. In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state; and both higher and lower oxidation states of that element are formed in the reaction. The decomposition of hydrogen peroxide is a familiar example of the reaction, where oxygen experiences disproportionation.



Here the oxygen of peroxide, which is present in  $-1$  state, is converted to zero oxidation state in  $O_2$  and decreases to  $-2$  oxidation state in  $H_2O$ .

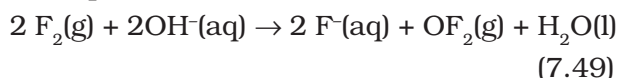
Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below :



The reaction (7.48) describes the formation of household bleaching agents. The hypochlorite ion ( $ClO^-$ ) formed in the reaction oxidises the colour-bearing stains of the substances to colourless compounds.

It is of interest to mention here that whereas bromine and iodine follow the same trend as exhibited by chlorine in reaction (7.48),

fluorine shows deviation from this behaviour when it reacts with alkali. The reaction that takes place in the case of fluorine is as follows:



(It is to be noted with care that fluorine in reaction (7.49) will undoubtedly attack water to produce some oxygen also). This departure shown by fluorine is not surprising for us as we know the limitation of fluorine that, being the most electronegative element, it cannot exhibit any positive oxidation state. This means that among halogens, fluorine does not show a disproportionation tendency.

#### Problem 7.5

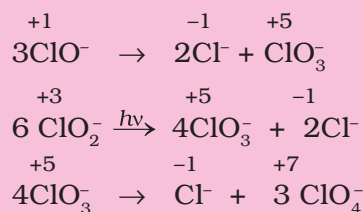
Which of the following species, do not show disproportionation reaction and why ?



Also write reaction for each of the species that disproportionates.

#### Solution

Among the oxoanions of chlorine listed above,  $ClO_4^-$  does not disproportionate because in this oxoanion chlorine is present in its highest oxidation state that is,  $+7$ . The disproportionation reactions for the other three oxoanions of chlorine are as follows:



#### Problem 7.6

Suggest a scheme of classification of the following redox reactions

- $N_2(g) + O_2(g) \rightarrow 2NO(g)$
- $2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$
- $NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$
- $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$