



11083CH08

UNIT 8

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.

8.1 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:



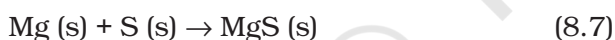
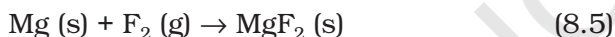
In reactions (8.1) and (8.2), the elements magnesium and sulphur are oxidised on account of addition of oxygen to them. Similarly, methane is oxidised owing to the addition of oxygen to it.



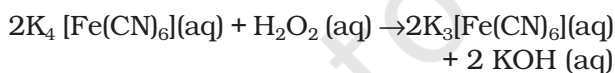
A careful examination of reaction (8.3) in which hydrogen has been replaced by oxygen prompted chemists to reinterpret oxidation in terms of removal of hydrogen from it and, therefore, the scope of term oxidation was broadened to include the removal of hydrogen from a substance. The following illustration 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 (8.1 to 8.4), 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 (8.5 to 8.7) 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 :

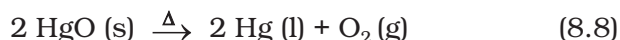


is interpreted as oxidation due to the removal of electropositive element potassium from potassium ferrocyanide before it changes to potassium ferricyanide. To summarise, the term “**oxidation**” is defined as the **addition of oxygen/electronegative element to a substance or removal of hydrogen/electropositive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

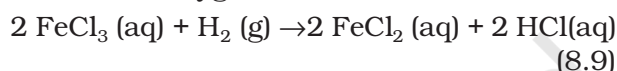
In the beginning, reduction was considered as removal of oxygen from a compound. However, the term **reduction** has

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

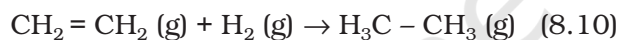
According to the definition given above, the following are the examples of reduction processes:



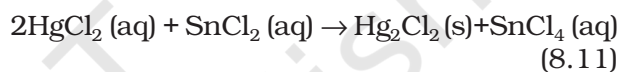
(removal of oxygen from mercuric oxide)



(removal of electronegative element, chlorine from ferric chloride)



(addition of hydrogen)

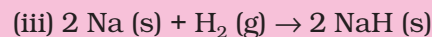
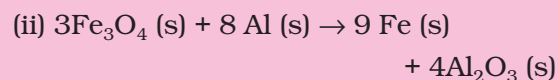
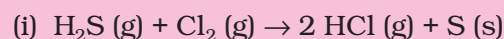


(addition of mercury to mercuric chloride)

In reaction (8.11) 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 8.1

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



Solution

(i) H_2S 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

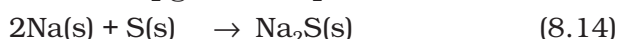
(Fe₃O₄) is reduced because oxygen has been removed from it.

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

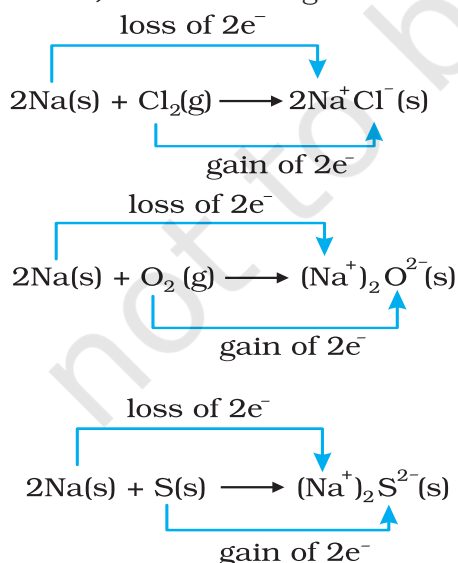
Reaction (iii) chosen here prompts us to think in terms of another way to define redox reactions.

8.2 REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER REACTIONS

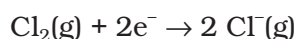
We have already learnt that the reactions



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⁺Cl⁻(s), (Na⁺)₂O²⁻(s), and (Na⁺)₂S²⁻(s). Development of charges on the species produced suggests us to rewrite the reactions (8.12 to 8.14) 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 8.12 to 8.14 **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 (8.12 to 8.14) 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

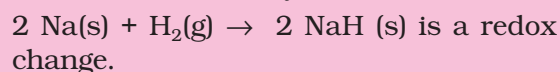
Oxidation: Loss of electron(s) by any species.

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

Oxidising agent: Acceptor of electron(s).

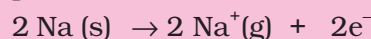
Reducing agent: Donor of electron(s).

Problem 8.2 Justify that the reaction :



Solution

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



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 H_2 , O_2 , Cl_2 , O_3 , P_4 , 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 Na^+ ion has an oxidation number of +1, Mg^{2+} ion, +2, Fe^{3+} ion, +3, Cl^- ion, -1, 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., H_2O_2 , Na_2O_2), each oxygen atom is assigned an oxidation number of -1, in superoxides (e.g., KO_2 , RbO_2) each oxygen atom is assigned an oxidation number of $-(\frac{1}{2})$. The second exception appears rarely, i.e. when oxygen is bonded to fluorine. In such compounds e.g., oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_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 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 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 ₄ | AlF ₃ | SiCl ₄ | P ₄ O ₁₀ | SF ₆ | HClO ₄ |
| 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)Cl₃. Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl₂ and Sn(IV)Cl₄. 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, Hg₂(I)Cl₂ is the reduced form of Hg(II) Cl₂.

Problem 8.3

Using Stock notation, represent the following compounds :HAuCl₄, Tl₂O, FeO, Fe₂O₃, CuI, CuO, MnO and MnO₂.

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:

| | | |
|--------------------------------|---|----------|
| HAuCl ₄ | → | Au has 3 |
| Tl ₂ O | → | Tl has 1 |
| FeO | → | Fe has 2 |
| Fe ₂ O ₃ | → | Fe has 3 |
| CuI | → | Cu has 1 |
| CuO | → | Cu has 2 |
| MnO | → | Mn has 2 |
| MnO ₂ | → | Mn has 4 |

Therefore, these compounds may be represented as:

HAu(III)Cl₄, Tl₂(I)O, Fe(II)O, Fe₂(III)O₃, Cu(I)I, Cu(II)O, Mn(II)O, Mn(IV)O₂.

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.

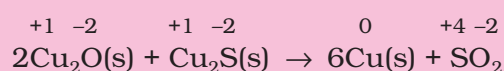
Problem 8.4

Justify that the reaction:

$2\text{Cu}_2\text{O}(\text{s}) + \text{Cu}_2\text{S}(\text{s}) \rightarrow 6\text{Cu}(\text{s}) + \text{SO}_2(\text{g})$
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*.

Solution

In reaction (a), the compound nitric oxide is formed by the combination of the elemental substances, nitrogen and oxygen; therefore, this is an example of combination redox reactions. The reaction (b) involves the breaking down of lead nitrate into three components; therefore, this is categorised under decomposition redox reaction. In reaction

(c), hydrogen of water has been displaced by hydride ion into dihydrogen gas. Therefore, this may be called as displacement redox reaction. The reaction (d) involves disproportionation of NO_2 (+4 state) into NO_2^- (+3 state) and NO_3^- (+5 state). Therefore reaction (d) is an example of disproportionation redox reaction.

The Paradox of Fractional Oxidation Number

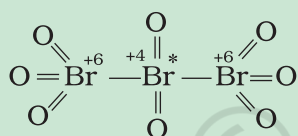
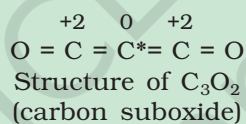
Sometimes, we come across with certain compounds in which the oxidation number of a particular element in the compound is in fraction. Examples are:

C_3O_2 [where oxidation number of carbon is (4/3)],

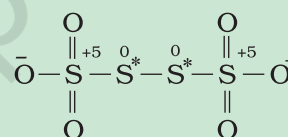
Br_3O_8 [where oxidation number of bromine is (16/3)]

and $\text{Na}_2\text{S}_4\text{O}_6$ (where oxidation number of sulphur is 2.5).

We know that the idea of fractional oxidation number is unconvincing to us, because electrons are never shared/transferred in fraction. Actually this fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is present in different oxidation states. Structure of the species C_3O_2 , Br_3O_8 and $\text{S}_4\text{O}_6^{2-}$ reveal the following bonding situations:



Structure of Br_3O_8 (tribromooctaoxide)



Structure of $\text{S}_4\text{O}_6^{2-}$ (tetrathionate ion)

The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in C_3O_2 , two carbon atoms are present in +2 oxidation state each, whereas the third one is present in zero oxidation state and the average is 4/3. However, the realistic picture is +2 for two terminal carbons and zero for the middle carbon. Likewise in Br_3O_8 , each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality, is 16/3. In the same fashion, in the species $\text{S}_4\text{O}_6^{2-}$, each of the two extreme sulphurs exhibits oxidation state of +5 and the two middle sulphurs as zero. The average of four oxidation numbers of sulphurs of the $\text{S}_4\text{O}_6^{2-}$ is 2.5, whereas the reality being +5, 0, 0 and +5 oxidation number respectively for each sulphur.

We may thus, in general, conclude that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only. Further, whenever we come across with fractional oxidation state of any particular element in any species, we must understand that this is the average oxidation number only. In reality (revealed by structures only), the element in that particular species is present in more than one whole number oxidation states. Fe_3O_4 , Mn_3O_4 , Pb_3O_4 are some of the other examples of the compounds, which are mixed oxides, where we come across with fractional oxidation states of the metal atom. However, the oxidation states may be in fraction as in O_2^+ and O_2^- where it is $+1/2$ and $-1/2$ respectively.