Oxidation-Reduction (Redox) Reactions

The terms oxidation and reduction may sound unfamiliar, but we see the results of these processes often in our daily lives. The corrosion of metal structures and monuments, the combustion of fuels, and the processing of photographic film all involve oxidation and reduction. Even the food we eat gets subjected to oxidation and reduction reactions during metabolism, making the food's stored energy available for our use.

Oxidation and Reduction

Originally, **oxidation** was used to describe reactions in which oxygen was added to a reactant. For example, the formation of rust is an oxidation process in which iron metal reacts with oxygen.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Similarly, when methane gas (CH_4) burns, it combines with oxygen to form carbon dioxide and water.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The term **reduction** at first meant the removal of oxygen from a compound. For example, the Fe_2O_3 in iron ore can be reduced to obtain iron metal.

$$2Fe_2O_3(l) + 3C(s) \rightarrow 4Fe(l) + 3CO_2(g)$$

The term reduction comes from the fact that the free metal has a lower mass than its oxide compound.

The words oxidation and reduction are still used to describe the addition or removal of oxygen. However, chemists today use the term in a much broader way. The broader definitions arise from the fact that oxygen tends to gain electrons when it reacts with other substances. As an example, consider the reaction of magnesium with oxygen shown below.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

In this reaction, a magnesium atom (Mg) loses 2 electrons to become a magnesium ion (Mg^{2+}). Similar analysis of other oxidation reactions reveals that substances that are oxidized lose electrons. On the other hand, substances that are reduced gain electrons. Thus, it is useful to define oxidation and reduction in terms of the movements of electrons:

- **oxidation** is the process by which a substance loses one or more electrons
- **reduction** is the process by which a substance gains one or more electrons

The phrase OIL RIG can be used to help remember these definitions: OIL = **O**xidation **I**s **L**oss of electrons; RIG = **R**eduction **I**s **G**ain of electrons.

By defining oxidation and reduction in terms of electrons lost and gained, reactions similar to but not involving oxygen can also be classified as oxidation and reduction reactions. For example:

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$

In this reaction, Mg loses two electrons to become Mg^{2+}. Using the definitions of oxidation and reduction, we say that magnesium is oxidized.

Oxidation and reduction always occur together. If electrons are lost by one substance, they do not simply disappear. Instead, they are gained by another substance. In the above reaction, each Cl atom in Cl_2 gains one electron to form two Cl^- ions. Thus, Mg is oxidized and Cl_2 is reduced.

Because oxidation and reduction occur together, reactions in which electrons are transferred between reactants are called **oxidation-reduction reactions**, or simply **redox reactions**.

Oxidation Number

Many redox reactions are quite complex. It is not always easy to identify the substances that are being oxidized or reduced. In addition, it can be quite difficult to balance redox reactions. Fortunately, chemists have developed a system that helps to solve these problems. This system is based on the concept of oxidation numbers.

The oxidation number of an atom in a substance is determined by the following rules:

1. The oxidation number of an atom in an uncombined element is zero.

2. The oxidation number of any monatomic ion equals its ionic charge.

3. In compounds, the oxidation number of many elements corresponds to the element's position on the periodic table:

   a) Alkali metals are always +1.

   b) Alkaline earth metals are always +2.

   c) Aluminum is always +3.

   d) Fluorine is always –1.

   e) Hydrogen has an oxidation number of +1 when combined with nonmetals and –1 when combined with metals.

   f) Oxygen has an oxidation number of –2 in most compounds and ions. In peroxides, however, oxygen has an oxidation number of –1.

4. The oxidation numbers of elements in compounds are written per atom.

5. The sum of the individual oxidation numbers of all the atoms in the formula for a compound is zero.

6. The sum of the individual oxidation numbers of all the atoms in a polyatomic ion is equal to the charge of the ion.

Notice that oxidation numbers are written with the charge (+ or –) followed by the number, while actual ionic charges are written with the number followed by the charge. For example, the ionic charges of magnesium and chloride ions in the compound $MgCl_2$ are 2+ and 1– respectively. Their oxidation numbers, however, are +2 and –1.

Example 1
What is the oxidation number of each element in potassium dichromate ($K_2Cr_2O_7$)?

Example 2
What is the oxidation number of each element in the compound K_2SO_4 ?

Now we can address the question of how changes in oxidation number are related to oxidation and reduction. When an atom loses an electron (oxidation), it becomes more positive and its oxidation number increases. When an atom gains an electron (reduction), it becomes more negative and its oxidation number decreases. Thus,

- oxidation is said to occur when the oxidation number of an atom increases
- reduction is said to occur when the oxidation number of an atom decreases

We now have three ways to identify oxidation and reduction, as summarized in the table below.

Basis	**Oxidation**	**Reduction**
oxygen	gain of oxygen	loss of oxygen
electrons	loss of electrons	gain of electrons
oxidation number	increase in oxidation number	decrease in oxidation number

Worksheet

1. What is the oxidation number of an atom of each element in

   a) SO_2

   b) $Al(NO_3)_3$

   c) H_2SO_4

   d) $H_2S_2O_7$

   e) SO_3

   f) H_3PO_4

   g) P_4O_6

   h) KH_2PO_4

   i) CuF_2

   j) HNO_3

   k) SO_4^{2-}

   l) $C_{12}H_{22}O_{11}$

   m) PBr_3

   n) $C_2O_4^{2-}$

   o) CO_3^{2-}

   p) H_2O

2. Although the oxidation number of O is usually –2 in its compounds, there are compounds called peroxides in which it is –1. What is the oxidation number of O in the following compounds:

   a) Al_2O_3

   b) BaO_2

   c) H_2O_2

   d) Li_2O

3. Determine the oxidation number for phosphorous in each of the following compounds. Show how you arrived at each answer.

   a) $AlPO_4$

   b) H_3PO_2

   c) $H_4P_2O_7$

   d) Na_2HPO_3

4. Nitrogen forms several oxides (a compound containing only nitrogen and oxygen). Write the chemical formula for the oxide in which nitrogen has an oxidation number of

   a) +1

   b) +2

   c) +3

   d) +4

   e) +5

Answers

1.

a) $S = +4$, $O = -2$

b) $Al = +3$, $N = +5$, $O = -2$

c) $H = +1$, $S = +6$, $O = -2$

d) $H = +1$, $S = +6$, $O = -2$

e) $S = +6$, $O = -2$

f) $H = +1$, $P = +5$, $O = -2$

g) $P = +3$, $O = -2$

h) $K = +1$, $H = +1$, $P = +5$, $O = -2$

i) $Cu = +2$, $F = -1$

j) $H = +1$, $N = +5$, $O = -2$

k) $S = +6$, $O = -2$

l) $C = 0$, $H = +1$, $O = -2$

m) $P = +3$, $Br = -1$

n) $C = +3$, $O = -2$

o) $C = +4$, $O = -2$

p) $H = +1$, $O = -2$

2.

a) –2

b) –1

c) –1

d) –2

3.

a) +5

b) +1

c) +5

d) +3

4.

a) N_2O

b) NO

c) N_2O_3

d) NO_2

e) N_2O_5