17.1: Oxidation-reduction Reactions

We find it useful to classify reactions according to the type of change that the reagents undergo. Many classification schemes exist, often overlapping one another. The three most commonly used classifications are acid–base reactions, substitution reactions, and oxidation–reduction reactions.

Acids and bases can be defined in several ways, the most common being the Brønsted-Lowry definition, in which acids are proton donors and bases are proton acceptors. The Brønsted-Lowry definition is particularly useful for reactions that occur in aqueous solutions. A prototypical example is the reaction of acetic acid with hydroxide ion to produce the acetate ion and water.

$$CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$$

Here acetic acid is the proton donor, hydroxide ion is the proton acceptor. The products are also an acid and a base, since water is a proton donor and acetate ion is a proton acceptor.

When we talk about substitution reactions, we focus on a particular substituent in a chemical compound. The original compound is often called the substrate. In a substitution reaction, the original substituent is replaced by a different chemical moiety. A prototypical example is the displacement of one substituent on a tetrahedral carbon atom by a more nucleophilic group, as in the reaction of methoxide ion with methyl iodide to give dimethyl ether and iodide ion.

$$CH_3I + CH_3O^- \rightarrow CH_3OCH_3 + I^-$$

We could view a Brønsted-Lowry acid-base reaction as a substitution reaction in which one group (the acetate ion in the example above) originally bonded to a proton is replaced by another (hydroxide ion). Whether we use one classification scheme or another to describe a particular reaction depends on which is better suited to our immediate purpose.

In acid-base reactions and substitution reactions, we focus on the transfer of a chemical moiety from one chemical environment to another. In a large and important class of reactions we find it useful to focus on the transfer of one or more electrons from one chemical moiety to another. For example, copper metal readily reduces aqueous silver ion. If we place a piece of clean copper wire in an aqueous silver nitrate solution, reaction occurs according to the equation

$$2Ag^+ + Cu^0 \rightarrow 2Ag^0 + Cu^{2+}$$

We have no trouble viewing this reaction as the transfer of two electrons from the copper atom to the silver ions. In consequence, a cupric ion, formed at the copper surface, is released into the solution. Two atoms of metallic silver are deposited at the copper surface. Reactions in which electrons are transferred from one chemical moiety to another are called ***oxidation–reduction*** reactions, or ***redox*** reactions, for short.

We define oxidation as the loss of electrons by a chemical moiety. Reduction is the gain of electrons by a chemical moiety. Since a moiety can give up electrons only if they have some place to go, oxidation and reduction are companion processes. Whenever one moiety is oxidized, another is reduced. In the reduction of silver ion by copper metal, it is easy to see that silver ion is gaining electrons and copper metal is losing them. In other reactions, it is not always so easy to see which moieties are gaining and losing electrons, or even that electron transfer is actually involved. As an adjunct to our ideas about oxidation and reduction, we develop a scheme for formally assigning electrons to the atoms in a molecule or ion. This is called the ***oxidation state*** formalism and comprises a series of rules for assigning a number, which we call the oxidation state (or oxidation number), to every atom in the molecule. When we adopt this scheme, the redox character of a reaction is determined by which atoms increase their oxidation state and which decrease their oxidation state as a consequence of the reaction. Those whose oxidation state increases lose electrons and are ***oxidized***, while those whose oxidation state decreases gain electrons and are ***reduced***.

A process of electron loss is called an oxidation because reactions with elemental oxygen are viewed as prototypical examples of such processes. Since many observations are correlated by supposing that oxygen atoms in compounds are characteristically more electron-rich than the atoms in elemental oxygen, it is useful to regard a reaction of a substance with oxygen as a reaction in which the atoms of the substance surrender electrons to oxygen atoms. It is then a straightforward generalization to say that a substance is oxidized whenever it loses electrons, whether oxygen atoms or some other chemical moiety takes up those electrons. So, for example, the reaction of sodium metal with oxygen in a dry environment produces sodium oxide, Na_2O, in which the sodium is usefully viewed as carrying a positive charge. (The oxidation state of sodium is 1+; the oxidation state of oxygen is 2–.)

The conversion of a metal oxide to the corresponding metal is described as reducing the oxide. Since converting a metal oxide to the metal reverses the change that occurs when we oxidize it, generalization of this idea leads us to apply the term reduction to any process in which a chemical moiety gains electrons. It is a fortunate coincidence that a reduction process is one in which the oxidation number of an atom becomes smaller (more negative) and is therefore reduced, in the sense of being decreased.

Another feature of oxidation–reduction reactions, and one that relates to the utility of viewing these reactions in terms of electron gain and loss, emerges when we observe the reaction of aqueous silver ions with copper metal closely. As the reaction proceeds, the aqueous solution becomes blue as cupric ions accumulate. Long needle-like crystals of silver metal grow out from the copper surface. The simplest mechanism that we can imagine for the growth of well-formed silver crystals is that silver ions from the solution plate out on the surface of the growing silver crystal, accepting an electron from the metallic crystal as they do so. The silver metal acquires this electron from the copper metal, with which it is in contact, but at a large (on an atomic scale) distance from the site at which the new atom of silver is deposited. Evidently the processes of electron loss and gain that characterize an overall reaction can occur at different locations, if there is a suitable process for moving the electron from one location to the other.