Work in groups on these problems. You should try to answer the questions without referring to your textbook. If you get stuck, try asking another group for help.

“The most striking feature of this process is the ease with which a doubly or triply charged ion gives up a third or forth electron. We know that this process takes place at the enormously high temperatures in the center of a star, but it is at first a little surprising to find it happening so readily at room temperature.”

Ronald W. Gurney

Introduction

In 1884, Svante Arrhenius, a young Swedish scientist, published his doctoral dissertation in which he described his measurements on the electrical conductivity of salt solutions. In his dissertation, he presented ideas on why the electrical conductivity of water increases greatly when a salt is dissolved in it. Three years later, he published a detailed paper in which he explained his theory of ionic dissociation. Arrhenius assumed that a solution of sodium chloride contained sodium and chloride ions. When electrodes are connected to a battery and placed into the solution, the sodium ions are attracted to the cathode (the negative electrode) and move in that direction. The chloride ions are attracted to the anode (the positive electrode) and move in that direction. This motion of ions through the solution provides the mechanism by which the solution conducts an electrical current.

Arrhenius and other scientists also noticed that the electrolysis of dilute aqueous solutions of electrolytes produced oxygen and hydrogen gases at the electrodes. Hydrogen gas was produced at the cathode, and oxygen gas was produced at the anode. They eventually concluded that the chemical reaction at the cathode involved a gain of electrons while the reaction at the anode involved the loss of electrons.

Chemical reactions in which there is a transfer of electrons from one substance to another are known as oxidation–reduction reactions, or redox reactions. In this unit you will examine the oxidation–reduction process and use the oxidation state and oxidation number concepts to identify redox reactions and to keep track of electrons transferred in a reaction.

Oxidation State

Formal charge is a measure of the charge accumulation on an atom in a bonding situation. It is useful to use the formal charge concept when describing the electron distribution in molecular compounds. The concept is also helpful in describing resonance structure of molecules and ions. When dealing with redox reactions, formal charge is not as useful because there is a substantial shift in electron density, with electrons transferred from one substance to another. We therefore use the concept of oxidation state to keep track of electron location in redox reactions.
Oxidation state is defined as the charge on an atom in bonding situation if all of the bonded electrons go to the most electronegative atom. The Lewis structure of a molecule or ion can be helpful in determining the oxidation state of an atom in a bonding situation. The oxidation state of an atom is represented by a positive or negative number called its oxidation number. Chemists have developed rules used to assign oxidation numbers. The following rules will help you determine the oxidation state of an atom or ion:

1. A free atom has an oxidation number of zero. It is not sharing, gaining, or losing electrons.
2. Polyatomic elements have an oxidation number of zero for each atom. Elements such as \( \text{H}_2, \text{O}_2, \) and \( \text{P}_4 \) share electrons equally among all atoms in the molecule.
3. The sum of the oxidation numbers in a neutral molecule is zero.
4. A monoatomic ion has an oxidation number equal to its charge. For example, the oxidation number of the oxygen in the oxide ion, \( \text{O}^{2-} \), is –2.
5. The sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.

Let’s examine the oxidation numbers of some common elements. Notice the periodic trend among the main-group elements.

**Hydrogen** Hydrogen has an electronegativity value slightly below that of carbon, so when it forms compounds with nonmetals, it usually has an oxidation state of +1. When hydrogen is bonded with metals, it has an oxidation state of –1 because most metals have electronegativity values less than that of hydrogen. Compounds in which hydrogen is in the –1 oxidation state are called hydrides.

**Group 1A Elements** Alkali metals have very low electronegativity values. When they combine with other atoms, they always lose an electron which gives them an oxidation state of +1.

**Group 2A Elements** Alkaline earth metals have low electronegativity values. When they form compounds, they give up their two electrons, leaving the ions with an oxidation state of +2. A typical example is magnesium oxide, \( \text{MgO} \), in which the oxidation state of magnesium is +2.

**Aluminum** The Group 3A elements have variable oxidation states, but aluminum almost always has an oxidation number of +3. Boron also commonly has a +3 oxidation state.

**Carbon** The oxidation state concept is rarely applied to carbon compounds because they typically have a great variety of single, double, and triple bonds, and combinations thereof. Oxidation number are applied, however in compounds in which carbon is combined with only one other element. When carbon combines with an element that has a greater electronegativity than itself, it will lose its electrons and have a positive oxidation state. Carbon has a +2 oxidation state in \( \text{CO} \) and a +4 oxidation state in \( \text{CO}_2 \). When carbon combines with less electronegative elements, it will gain electrons. Carbon has an oxidation state of –4 in \( \text{CH}_4 \).

**Nitrogen** The electronegativity value for nitrogen is 3.0, and its oxidation state can vary widely, depending on the atom it combines with. When nitrogen combines with a less electronegative element such as hydrogen or a metal, its oxidation state is –3, as is the case with \( \text{NH}_3 \). When nitrogen combines with a more electronegative element, its oxidation state will be positive, varying from +2, as in \( \text{NO} \), to +5, as in \( \text{HNO}_3 \).
Oxygen  The term oxidation originally meant combination with oxygen to form an oxide. Oxygen, with an electronegativity of 3.5, almost always gains electrons when it forms a compound. Molecular oxygen compounds normally have two covalent bonds, and the bonding electrons are strongly held by the oxygen atom. Therefore oxygen has a oxidation state of –2 in most of its compounds.

Fluorine  Fluorine has the highest electronegativity of all elements (with the exception of the noble gases), with a value of 4.0, and therefore it always gains an electron and has an oxidation state of –1. The other halogens frequently have an oxidation state of –1 as well, but since electronegativity decreases down a group on the periodic table, they can have multiple oxidation states.

The Transition Metals

The elements in the d- and f-blocks of the periodic table are called the transition elements. Since they are all metals, they are also referred to as transition metals. Within this group of metals are two inner groups called the lanthanide and actinide series.

Many transition metal compounds do not obey the octet rule, and the metals therefore have variable oxidation states. Manganese, for example, has oxidation states ranging from +2 to +7. Iron commonly has oxidation states of +2 and +3. The oxidation state of a transition metal can usually be determined from a knowledge of the oxidation states of the other elements in the compound. In CuO, copper has an oxidation state of +2 because oxygen is –2 and the sum of the oxidation numbers must be zero. In KMnO₄, potassium is +1 and oxygen is –2, therefore (±1) + ? + [4 x (–2)] = 0, and manganese must be +7.

Oxidizing and Reducing Agents

Chemists often use the terms oxidizing agent and reducing agent to describe the reactants in redox reactions. Since oxidation is the loss of electrons, an oxidizing agent is any substance that can cause a loss of electrons in another substance in a chemical reaction. The oxidizing agent gains electrons, and its oxidation number decreases. Reduction is a gain of electrons, therefore a reducing agent is a substance than can cause another substance to gain electrons. The reducing agent loses electrons, and its oxidation number increases.

Consider the reaction of iron(III) oxide and carbon monoxide:

\[ \text{Fe}_2\text{O}_3 + 3 \text{CO} \rightarrow 2 \text{Fe} + 3 \text{CO}_2 \]

1. The oxidation state of oxygen is –2 in all compounds, therefore oxygen is neither oxidized or reduced.
2. The oxidation state of iron decreases from +3 in \text{Fe}_2\text{O}_3 to zero in the uncombined element Fe. Therefore, iron gains electrons and \text{Fe}_2\text{O}_3 is the oxidizing agent.
3. Iron is reduced.
4. The oxidation state of carbon increases from +2 in CO to +4 in \text{CO}_2. Therefore, carbon loses electrons and CO is the reducing agent.
5. Carbon is oxidized.

Worksheets

- Oxidation-Reduction Reaction: Worksheet 1