Learning Objectives

- Categorize reactions by type: synthesis, decomposition, single replacement, double replacement, and combustion.
- Given a redox reaction equation, identify the element being oxidized, the one being reduced, and any spectator ions.
- Write balanced equations for single replacement, double replacement, and combustion reactions.

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity.

**Decomposition Reactions**

A decomposition reaction is a type of chemical reaction in which one reactant yields two or more products. The general form for a decomposition reaction is:

\[ AB \rightarrow A + B \]

Consider the decomposition of calcium carbonate:

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]

- calcium carbonate
- calcium oxide
- carbon dioxide

**Synthesis Reactions**

A synthesis reaction is a type of chemical reaction in which two or more simple substances combine to form a more complex product. The reactants may be elements or compounds, while the product is always a compound. The general equation for a synthesis reaction is:

\[ A + B \rightarrow AB \]

For example, the synthesis of hydrochloric acid from hydrogen and chlorine:

\[ 2\text{Cl} + \text{H}_2 \rightarrow 2\text{HCl} \]
Oxidation-Reduction Reactions

Earth’s atmosphere contains about 20% molecular oxygen, O$_2$, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term oxidation was originally used to describe chemical reactions involving O$_2$, but its meaning has evolved to refer to a broad and important reaction class known as oxidation-reduction (redox) reactions. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$\text{\ce{2Na(s)+Cl2(g)\rightarrow 2NaCl(s)}}$$

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a half-reaction:

$$\begin{align*}
\text{\ce{2Na(s)\rightarrow 2Na+}(s)+2e-}} \\
\text{\ce{Cl2(g)+2e-\rightarrow 2Cl-}(s)}
\end{align*}$$

These equations show that Na atoms lose electrons while Cl atoms (in the Cl$_2$ molecule) gain electrons, the “s” subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

- **oxidation** = loss of electrons
- **reduction** = gain of electrons

In this reaction, then, sodium is oxidized and chlorine undergoes reduction. Viewed from a more active perspective, sodium functions as a reducing agent (reductant), since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an oxidizing agent (oxidant), as it effectively removes electrons from (oxidizes) sodium.

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding \(\text{\ce{NaCl}}\):

$$\text{\ce{H2(g)+Cl2(g)\rightarrow 2HCl(g)}}$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called oxidation number has been defined. The oxidation number (or oxidation state) of an element in a compound is the charge its atoms would possess if the compound was ionic. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion’s charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:
   ◦ Hydrogen: +1 when combined with nonmetals, −1 when combined with metals
   ◦ Oxygen: −2 in most compounds, sometimes −1 (so-called peroxides, \(\text{\textit{ice(\text{O}_2^2-\text{-j)}}}\)), very rarely \((-\dfrac{1}{2})\) (so-called superoxides, \(\text{\textit{ice\{O}_2^2\text{-j}}\)), positive values when combined with F (values vary)
   ◦ Halogens: −1 for F always, −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)

4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

Example \(\PageIndex{3}\): Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

a. \(\text{H}_2\text{S}\)
b. \(\text{\textit{ice(SO}_3^2-\text{-j)}}\)
c. \(\text{Na}_2\text{SO}_4\)

Solution

(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound’s formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

\[
\text{\textit{ice\{charge\: on\: H}_2\text{S}\}=0=(2\times +1)+(1\times x)}
\]

\[
x=0-(2\times +1)=-2
\]

(b) Guideline 3 suggests the oxidation number for oxygen is −2.

Using this oxidation number and the ion’s formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

\[
\text{\textit{ice\{charge\: on\: SO}_3^2-\text{-j)}}=-2=(3\times -2)+(1\times x)
\]

\[
x=-2-(3\times -2)=+4
\]

(c) For ionic compounds, it’s convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

\[
\text{\textit{ice\{charge\: on\: SO}_4^2-\text{-j)}}=-2=(4\times -2)+(1\times x)
\]
\( (x=-2-(4\times-2)=+6) \)

Exercise \( \text{PageIndex}(3) \)

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

a. \( \text{KNO}_3 \)

b. \( \text{AlH}_3 \)

c. \( \text{N}_{4}^+ \)

d. \( \text{H}_2\text{PO}_4^- \)

Answer a

N, +5

Answer b

Al, +3

Answer c

N, −3

Answer d

P, +5

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. Oxidation-reduction (redox) reactions are those in which one or more elements involved undergo a change in oxidation number. While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist as shown below. Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

\[
\begin{align}
\text{oxidation} &= \text{increase in oxidation number} \\
\text{reduction} &= \text{decrease in oxidation number}
\end{align}
\]

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl\(_2\) to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H\(_2\) to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl\(_2\) to −1 in HCl). Single-replacement reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

\[
\text{Zn}(s)+2\text{HCl}(aq)\rightarrow \text{ZnCl}_2(aq)+\text{H}_2(g)
\]

Metallic elements may also be oxidized by solutions of other metal salts; for example:
\[
\text{Cu}(s) + 2\text{AgNO}_3(aq) \rightarrow \text{Cu(NO}_3)_2(aq) + 2\text{Ag}(s)
\]

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting \( \text{Cu}^{2+} \) ions dissolve in the solution to yield a characteristic blue color (Figure \( \PageIndex{4} \)).

![Figure](a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

**Example \( \PageIndex{4} \): Describing Redox Reactions**

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

a. \( \text{ZnCO}_3(s) \rightarrow \text{ZnO}(s) + \text{CO}_2(g) \)

b. \( 2\text{Ga}(l) + 3\text{Br}_2(l) \rightarrow 2\text{GaBr}_3(s) \)

c. \( \text{H}_2\text{O}_2(aq) \rightarrow \text{H}_2\text{O}(l) + \text{O}_2(g) \)

d. \( \text{BaCl}_2(aq) + \text{K}_2\text{SO}_4(aq) \rightarrow \text{BaSO}_4(s) + 2\text{KCl}(aq) \)

e. \( \text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \)

**Solution**

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

a. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

b. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(\( l \)) to +3 in GaBr\(_3\)(s). The reducing agent is Ga(\( l \)). Bromine is reduced, its oxidation number decreasing from 0 in Br\(_2\)(\( l \)) to −1 in GaBr\(_3\)(s). The oxidizing agent is Br\(_2\)(\( l \)).

c. This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called **disproportionation reaction**). Oxygen is oxidized, its oxidation number increasing from −1 in H\(_2\)O\(_2\)(aq) to 0 in O\(_2\)(g). Oxygen is also reduced, its oxidation number decreasing from −1 in H\(_2\)O\(_2\)(aq) to −2 in H\(_2\)O(\( l \)). For disproportionation reactions, the same substance functions as an oxidant and a reductant.

d. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

e. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in C\(_2\)H\(_4\)(g) to +4 in CO\(_2\)(g). The reducing agent (fuel) is C\(_2\)H\(_4\)(g). Oxygen is reduced, its oxidation number decreasing from 0 in O\(_2\)(g) to −2 in H\(_2\)O(\( l \)). The oxidizing agent is O\(_2\)(g).

**Exercise \( \PageIndex{4} \)**

This equation describes the production of tin(II) chloride:

\[
\text{Sn}(s) + 2\text{HCl}(g) \rightarrow \text{SnCl}_2(s) + \text{H}_2(g)
\]
Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

**Answer**

Yes, a single-replacement reaction. Sn(s) is the reductant, HCl(g) is the oxidant.

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**Combustion Reactions**

Several subclasses of redox reactions are recognized, including combustion reactions in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. This is the basic structure of a combustion reaction in which oxygen from air is the oxidizing agent:

\[
\text{fuel} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

Note that the equation must be balanced based on the type of fuel being burnt.

Solid rocket-fuel reactions such as the one depicted below are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

\[
\text{10Al(s)} + \text{6NH}_4\text{ClO}_4(s) \rightarrow \text{4Al}_2\text{O}_3(s) + \text{2AlCl}_3(s) + \text{12H}_2\text{O}(g) + \text{3N}_2(g)
\]

Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.
Precipitation Reactions and Solubility Rules

A precipitation reaction is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as double displacement, double replacement, or metathesis reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and gravimetric methods for determining the composition of matter (see the last module of this chapter).

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its solubility, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be soluble. A substance will precipitate when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be insoluble, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in the text chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (Table \(\PageIndex{1}\)).

\[\text{Table } \PageIndex{1}: \text{ Solubilities of Common Ionic Compounds in Water}\]

<table>
<thead>
<tr>
<th>Soluble compounds</th>
<th>Exceptions to these solubility rules include</th>
</tr>
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</table>

• group 1 metal cations ($\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Rb}^+$, and $\text{Cs}^+$) and ammonium ion ($\text{NH}_4^+$)
• the halide ions ($\text{Cl}^-$, $\text{Br}^-$, and $\text{I}^-$)
• the acetate ($\text{C}_2\text{H}_3\text{O}_2^-$), bicarbonate ($\text{HCO}_3^-$), nitrate ($\text{NO}_3^-$), and chlorate ($\text{ClO}_3^-$) ions
• the sulfate ($\text{SO}_4^{2-}$) ion

**Insoluble compounds** contain

• carbonate ($\text{CO}_3^{2-}$), chromate ($\text{CrO}_4^{2-}$), phosphate ($\text{PO}_4^{3-}$), and sulfide ($\text{S}_2^-$) ions
• hydroxide ion ($\text{OH}^-$)

**Exceptions** to these insolubility rules include

• compounds of these anions with group 1 metal cations and ammonium ion
• hydroxides of group 1 metal cations and $\text{Ba}^{2+}$

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

$$\ce{2KI(aq) + Pb(NO3)2(aq) \rightarrow PbI2(s) + 2KNO3(aq)}$$

This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:

$$\ce{Pb^2+(aq) + 2I-(aq) \rightarrow PbI2(s)}$$

Lead iodide is a bright yellow solid that was formerly used as an artist’s pigment known as iodine yellow (Figure \(\PageIndex{1}\)). The properties of pure $\text{PbI}_2$ crystals make them useful for fabrication of X-ray and gamma ray detectors.
The solubility guidelines in Table \(\PageIndex{1}\) may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium fluoride will yield a solution containing \(\text{Ag}^+\), \(\text{NO}_3^-\), \(\text{Na}^+\), and \(\text{F}^-\) ions. Aside from the two ionic compounds originally present in the solutions, \(\text{AgNO}_3\) and \(\text{NaF}\), two additional ionic compounds may be derived from this collection of ions: \(\text{NaNO}_3\) and \(\text{AgF}\). The solubility guidelines indicate all nitrate salts are soluble but that \(\text{AgF}\) is one of the exceptions to the general solubility of fluoride salts. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

\[
\text{NaF}(aq)+\text{AgNO}_3(aq)\rightarrow \text{AgF}(s)+\text{NaNO}_3(aq)\hspace{20px}\text{(molecular)}
\]
\[
\text{Ag}^+(aq)+\text{F}^-(aq)\rightarrow \text{AgF}(s)\hspace{20px}\text{(net\ionic)}
\]

Example \(\PageIndex{1}\): Predicting Precipitation Reactions

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

a. potassium sulfate and barium nitrate
b. lithium chloride and silver acetate
c. lead nitrate and ammonium carbonate

Solution
(a) The two possible products for this combination are KNO₃ and BaSO₄. The solubility guidelines indicate BaSO₄ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is
\[
\ce{Ba^{2+}(aq) + SO_{4}^{2-}(aq) \rightarrow BaSO_4(s)}
\]

(b) The two possible products for this combination are LiC₂H₃O₂ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is
\[
\ce{Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)}
\]

(c) The two possible products for this combination are PbCO₃ and NH₄NO₃. The solubility guidelines indicate PbCO₃ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is
\[
\ce{Pb^{2+}(aq) + CO_{3}^{2-}(aq) \rightarrow PbCO_3(s)}
\]

Steps for Writing Displacement Reactions

1. Figure out what the reactants and products will be.
   - The cations will switch places in the products for double replacement reactions.
   - The element will replace the cation in the reacting compound and result in a new product for single replacement reactions.

2. Make sure that all of the compound formulas are correctly written based on the oxidation state of the elements involved.

3. Balance the equation.

Summary

Chemical reactions are classified according to similar patterns of behavior. Redox reactions involve a change in oxidation number for one or more reactant elements. Precipitation reactions involve the formation of one or more insoluble products. A synthesis reaction is a type of chemical reaction in which two or more simple substances combine to form a more complex product. A decomposition reaction is a type of chemical reaction in which one reactant yields two or more products.