Reactions in aqueous solutions
Redox reactions
Redox reactions

- In precipitation reactions, cations and anions come together to form an insoluble ionic compound.

- In neutralization reactions, $H^+$ ions and $OH^-$ ions come together to form $H_2O$ molecules.

- In a third kind of reaction electrons are transferred from one reactant to another. Such reactions are called either oxidation-reduction reactions or redox reactions.
Redox reactions

One of the most familiar redox reactions is corrosion of a metal.
In some cases corrosion is limited to the surface of the metal, with the green coating that forms on copper roofs and statues. In other instances the corrosion goes deeper, eventually compromising the structural integrity of the metal. Iron rusting is an important example.
Redox reactions

Corrosion is the conversion of a metal into a metal compound by a reaction between the metal and some substance in its environment. When a metal corrodes, each metal atom loses electrons and so forms a cation, which can combine with an anion to form an ionic compound.

The green coating on some buildings contains Cu\(^{2+}\) combined with carbonate and hydroxide anions, rust contains Fe\(^{3+}\) combined with oxide and hydroxide anions, and oxidized silver contains Ag\(^{+}\) combined with sulfide anions.
Oxidation Vs Reduction

Oxidation

When an ion become more positively charged (it loses electrons), we say that it has been oxidized. **Loss of electrons by a substance is called oxidation.** The term oxidation is used because the first reactions of this sort to be studied were reactions with oxygen.

![Oxidation and Reduction Diagram](image)

Many metals react directly with $O_2$ in air to form metal oxides. In these reactions the metal loses electrons to oxygen, forming an ionic compound of the metal ion and oxide ion.

The familiar example of rusting involves the reaction between iron metal and oxygen in the presence of water. In this process Fe is oxidized (loses electrons) to form $Fe^{3+}$.

$$4 \text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$$
Oxidation Vs Reduction

Many metals, such as the alkali and alkaline earth metals, react quickly upon exposure to air.

E.g. The bright metallic surface of calcium tarnishes as CaO(s) forms in the reaction.

\[
2 \text{ Ca}(s) + \text{O}_2 (g) \rightarrow 2\text{CaO}(s)
\]

In this reaction Ca is oxidized to Ca\(^{2+}\) and neutral O\(_2\) is transformed to O\(^{2-}\) ions.

![Diagram showing the oxidation and reduction process with calcium metal and oxygen gas forming calcium oxide.](image)
Oxidation Vs Reduction

Reduction
When an atom, ion, or molecule becomes more negatively charged (gains electrons), we say that it is reduced.

The gain of electrons by a substance is called reduction. When one reactant loses electrons (when it is oxidized), another reactant must gain them. In other words, **oxidation of one substance must be accompanied by reduction of some other substance.**
Oxidation States rules (a review)

Each atom is assigned an oxidation number.
For monatomic ions the oxidation number is the same as the charge.
We use the following rules for assigning oxidation numbers:

1. For an atom in its elemental form, the oxidation number is always zero

2. For any monatomic ion the oxidation number equals the ionic charge.

3. Nonmetals usually have negative oxidation numbers
   a. The oxidation number of oxygen is usually -2 in both ionic and molecular compounds.
   b. The oxidation number of hydrogen is usually +1 when bonded to nonmetals and -1 when bonded to metals.
   c. The oxidation number of fluorine is -1 in all compounds. The other halogens have an oxidation number of -1 in most binary compounds. When combined with oxygen, as in oxyanions, however, they have positive oxidation states.

4. The sum of the oxidation numbers of all atoms in a neutral compound is zero.

5. The sum of the oxidation numbers in a polyatomic ion equals the charge of the ion.
Oxidation of Metals by Acids and Salts

The reaction between a metal and either an acid or a metal salt conforms to the general pattern

\[ A + BX \rightarrow AX + B \]

Examples:

\[ \text{Zn} \,(s) + 2 \text{HBr} \,(aq) \rightarrow \text{ZnBr}_2 \,(aq) + \text{H}_2 \,(g) \]
\[ \text{Mn} \,(s) + \text{Pb(NO}_3)_2 \,(aq) \rightarrow \text{Mn(NO}_3)_2 \,(aq) + \text{Pb} \,(s) \]

These reactions are called displacement reactions because the ion in solution is displaced (replaced) through oxidation of an element.
Many metals undergo displacement reactions with acids, producing salts and hydrogen gas. For example, magnesium metal reacts with hydrochloric acid to form magnesium chloride and hydrogen.

The oxidation number of Mg changes from 0 to +2, an increase that indicates the atom has lost electrons and has therefore been oxidized. The oxidation number of H in the acid decreases from +1 to 0, indicating that this ion has gained electrons and has therefore been reduced. Chlorine has an oxidation number of both before and after the reaction, indicating that it is neither oxidized nor reduced. In fact, the Cl ions are spectator ions, dropping out of the net ionic equation:

$$\text{Mg} + 2 \text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2$$

Metals can also be oxidized by aqueous solutions of various salts. Iron metal, for example, is oxidized to $\text{Fe}^{2+}$ by aqueous solutions of such as $\text{Ni(NO}_3)_2$:

$$\text{Molecular equation:}$$

$$\text{Fe} + \text{Ni(NO}_3)_2 \rightarrow \text{Fe(NO}_3)_2 + \text{Ni}$$

$$\text{Net ionic equation:}$$

$$\text{Fe} + \text{Ni}^{2+} \rightarrow \text{Fe}^{2+} + \text{Ni}$$

The oxidation of Fe to $\text{Fe}^{2+}$ in this reaction is accompanied by the reduction of $\text{Ni}^{2+}$ to $\text{Ni}$. Remember: Whenever one substance is oxidized, another substance must be reduced.
Many metals undergo displacement reactions with acids, producing salts and hydrogen gas. For example, magnesium metal reacts with hydrochloric acid to form magnesium chloride and hydrogen:

$$\text{Mg}(s) + 2 \text{HCl} \,(aq) \rightarrow \text{MgCl}_2 \,(aq) + \text{H}_2 \,(g)$$

The oxidation number of Mg changes from 0 to +2, an increase that indicates the atom has lost electrons and has therefore been oxidized. The oxidation number of H\(^+\) in the acid decreases from +1 to 0, indicating that this ion has gained electrons and has therefore been reduced. Chlorine has an oxidation number of -1 both before and after the reaction, indicating that it is neither oxidized nor reduced. In fact the Cl\(^-\) ions are spectator ions, dropping out of the net ionic equation:

$$\text{Mg}(s) + 2 \text{H}^+ \,(aq) \rightarrow \text{Mg}^{2+} \,(aq) + \text{H}_2 \,(g)$$
Oxidation of Metals by Acids and Salts

Metals can also be oxidized by aqueous solutions of various salts. Iron metal, for example, is oxidized to Fe$^{2+}$ by aqueous solutions of Ni$^{2+}$ such as Ni(NO$_3$)$_2$ (aq):

\[
\text{Molecular equation} \quad \text{Fe}(s) + \text{Ni(NO}_3\text{)}_2 (aq) \rightarrow \text{Fe(NO}_3\text{)}_2 (aq) + \text{Ni} (s)
\]

\[
\text{Ionic equation} \quad \text{Fe}(s) + \text{Ni}^{2+} (aq) \rightarrow \text{Fe}^{2+} (aq) + \text{Ni} (s)
\]

The oxidation of Fe to Fe$^{2+}$ is accompanied by the reduction of Ni$^{2+}$ to Ni.

Whenever one substance is oxidized, another substance must be reduced.
Predicting redox reactions - the Activity Series

We can predict whether a metal will be oxidized either by an acid or a salt as different metals vary in the ease with which they are oxidized. Zn is oxidized by aqueous solutions of Cu\(^{2+}\) but Ag is not. Zn, therefore, loses electrons more readily than Ag; that is, Zn is easier to oxidize than Ag.

Experimentally we can create a list of metals arranged in order of decreasing ease of oxidation is called an activity series.

Any metal on the list can be oxidized by the elements below it. E.g., Cu is above Ag in the series. Thus, copper metal is oxidized by silver ions:

\[
\text{Cu(s)} + 2\text{Ag}^+ (aq) \rightarrow \text{Cu}^{2+} (aq) + 2\text{Ag (s)}
\]

The oxidation of copper to copper ions is accompanied by the reduction of silver ions to silver metal. The silver metal is evident on the surface of the copper wire.

### Activity Series of Metals in Aqueous Solution

<table>
<thead>
<tr>
<th>Metal</th>
<th>Oxidation reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>Li (s) \rightarrow Li(^{2+}) (aq) + e(^-)</td>
</tr>
<tr>
<td>Potassium</td>
<td>K (s) \rightarrow K(^{+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba (s) \rightarrow Ba(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca (s) \rightarrow Ca(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na (s) \rightarrow Na(^{+}) (aq) + e(^-)</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg(s) \rightarrow Mg(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al(s) \rightarrow Al(^{3+}) (aq) + 3e(^-)</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn(s) \rightarrow Mn(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn(s) \rightarrow Zn(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr(s) \rightarrow Cr(^{3+}) (aq) + 3e(^-)</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe(s) \rightarrow Fe(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co(s) \rightarrow Co(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni(s) \rightarrow Ni(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn(s) \rightarrow Sn(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb(s) \rightarrow Pb(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td><strong>Hydrogen</strong></td>
<td>H(_2)(g) \rightarrow 2H(^{+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu(s) \rightarrow Cu(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag(s) \rightarrow Ag(^{+}) (aq) + e(^-)</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg(l) \rightarrow Hg(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt(s) \rightarrow Pt(^{2+}) (aq) + 2e(^-)</td>
</tr>
<tr>
<td>Gold</td>
<td>Au(s) \rightarrow Au(^{3+}) (aq) + 3e(^-)</td>
</tr>
</tbody>
</table>
Predicting redox reactions - the Activity Series

Only metals above hydrogen in the activity series are able to react with acids to form H₂. For example, Ni reacts with HCl(aq) to form H₂:

\[ \text{Ni}(s) + 2\text{HCl (aq)} \rightarrow \text{NiCl (aq)} + \text{H}_2 (s) \]

Because elements below hydrogen in the activity series are not oxidized by H⁺, Cu does not react with HCl(aq).
PRACTICE EXERCISE

• Will an aqueous solution of iron(II) chloride oxidize magnesium metal? If so, write the balanced molecular and net ionic equations for the reaction.

Solution

Two substances (an aqueous salt, FeCl₂, and a metal, Mg)

A reaction occurs if the reactant that is a metal in its elemental form (Mg) is located above the reactant that is a metal in its oxidized form (Fe²⁺) in the “Activity Series of Metals in Aqueous Solution” Table.

If the reaction occurs, the Fe²⁺ ion in FeCl₂ is reduced to Fe, and the Mg is oxidized to Mg²⁺.

Because Mg is above Fe in the table, the reaction occurs. To write the formula for the salt produced in the reaction, we must remember the charges on common ions. Magnesium is always present in compounds as Mg²⁺; the chloride ion is Cl⁻. The magnesium salt formed in the reaction is MgCl₂, meaning the balanced molecular equation is:

\[
\text{Mg (s)} + \text{FeCl}_2 \,(aq) \rightarrow \text{MgCl}_2 \,(aq) + \text{Fe (s)}
\]

Both FeCl₂ and MgCl₂ are soluble strong electrolytes and can be written in ionic form, which shows us that Cl⁻ is a spectator ion in the reaction. The net ionic equation is:

\[
\text{Mg (s)} + \text{Fe}^{2+} \,(aq) \rightarrow \text{Mg}^{2+} \,(aq) + \text{Fe (s)}
\]

The net ionic equation shows that Mg is oxidized and Fe²⁺ is reduced in this reaction.

• Which of the following metals will be oxidized by Pb(NO₃)₂: Zn, Cu, Fe?

Answers:
Zn and Fe
PRACTICE EXERCISE

Determine the oxidation number for the indicated element in each of the following substances:

a) S in SO₂
b) C in COCl₂
c) Mn in KMnO₄
d) Br in HBrO
e) As in As₄
f) O in K₂O₂

Which element is oxidized and which is reduced in the following reactions?

a) N₂ (g) + 3 H₂ (g) → 2 NH₃ (g)
b) 3Fe(NO₃)₂ (aq) + 2 Al (s) → 3 Fe (s) + 2Al(NO₃)₃ (aq)
c) Cl₂ (aq) + 2 NaI (aq) → I₂ (aq) + 2 NaCl (aq)
d) PbS (s) + 4 H₂O₂ (aq) → PbSO₄ (s) + 4 H₂O (l)

Write balanced molecular and net ionic equations for the reactions of

a) manganese with sulfuric acid in aqueous solution
b) chromium with hydrobromic acid
c) tin with hydrochloric acid
d) aluminum with formic acid (HCOOH)

Using the activity series table, write balanced chemical equations for the following reactions. If no reaction occurs, simply write NR.

a) Iron metal is added to a solution of copper(II) nitrate
b) zinc metal is added to a solution of magnesium sulfate
c) hydrobromic acid is added to tin metal
d) hydrogen gas is bubbled through an aqueous solution of nickel(II) chloride
e) aluminum metal is added to a solution of cobalt(II) sulfate.