Oxidation-reduction reactions, also called redox reactions, involve the transfer of electrons from one species to another. These kinds of reactions are at the heart of energy producing devices such as batteries and fuel cells. They are also involved in many electrochemical processes by which we obtain useful materials.

**Learning Objectives**

- Know the definitions of oxidation, reduction, oxidizing agent, and reducing agent
- Know the systematic procedure for balancing redox reactions by the ion-electron method

**Success Criteria**

- Be able to separate a redox reaction into an oxidation and a reduction half reaction
- Be able to balance any skeletal redox reaction by the ion-electron method

**Electron Transfer Reactions**

A reaction in which one species transfers electrons to another is called an **oxidation-reduction reaction**, also called a **redox reaction**. For example, we can think of the reaction of metallic iron with chlorine gas to form ionic iron(III) chloride as the net transfer of six electrons from two iron atoms to three chlorine molecules:

<table>
<thead>
<tr>
<th>Multiplier</th>
<th>Half Reaction</th>
<th>Direction of Electrons</th>
<th>REDOX Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>(Fe^0 \rightarrow Fe^{3+} + 3e^–)</td>
<td>electrons &quot;pushed&quot;</td>
<td>oxidation</td>
</tr>
<tr>
<td>3</td>
<td>((Cl_2^0 + 2e^– \rightarrow 2Cl^–))</td>
<td>electrons &quot;pulled&quot;</td>
<td>reduction</td>
</tr>
</tbody>
</table>

Adding the scaled reactants and scaled products results in

\[
[2Fe^0 + 3 Cl_2^0 + \cancel{6 e^+} \rightarrowarrow 2Fe^{3+} + \cancel{6e^-} + 2Cl^-]
\]

and canceling electrons results in the final redox reacton is then

\[
[2Fe(s) + 3Cl_2(g) \rightarrowarrow 2Fe^{3+} +6Cl^-] \]

In essence, the Fe "pushes" electrons and the Cl₂ "pulls" electrons, thereby effecting electron transfer. On this basis, we have the following definitions:

- **Oxidation** - loss of electrons by a substance
- **Reduction** - gain of electrons by a substance

As this example shows, we can separate the overall redox reaction into two **half reactions**, one for the oxidation and
Oxidation and reduction always involve transfer of electrons. Therefore, there is never oxidation without reduction and vice versa in a redox reaction. Oxidizing something must cause something else to be reduced and vice versa. Therefore, the substance oxidized is seen to be the agent of the other substance’s reduction, and the substance reduced is seen to be the agent of the other substance’s oxidation. This leads to the following definitions:

- **Oxidizing agent (oxidant)** - a substance that causes another substance to be oxidized and is itself reduced.
- **Reducing agent (reductant)** - a substance that causes another substance to be reduced and is itself oxidized.

In these terms, all redox reactions take on the general form

\[Ox_1 + Red_2 \rightarrow Red_1 + Ox_2\]

In this general representation, Ox\(_1\) and Ox\(_2\) are oxidizing agents (oxidants), and Red\(_1\) and Red\(_2\) are reducing agents (reductants). Thus, when Ox\(_1\) reacts with Red\(_2\), it becomes its reduced species, Red\(_1\), while at the same time Red\(_2\) becomes its oxidized species, Ox\(_2\). The process of \(\text{Ox}_1 \rightarrow \text{Red}_1\) is a reduction that might require, say, \(n\) electrons. Thus we could write this as the reduction half reaction

\[\text{Ox}_1 + ne^– \rightarrow \text{Red}_1 \label{half1}\]

Likewise, the process of \(\text{Red}_2 \rightarrow \text{Ox}_2 + me^–\) is an oxidation that might require, say, \(m\) electrons. Thus we could write this as the oxidation half reaction

\[\text{Red}_2 \rightarrow \text{Ox}_2 + me^– \label{half2}\]

To write the balanced redox reaction, we want to put these two half reactions (Equations \(\ref{half1}\) and \(\ref{half2}\)) together in such a way that no net electrons show on either side of the overall reaction equation. Assuming that \(n \neq m\), we will need to multiply the reduction half reaction by the factor \(m\) and the oxidation half reaction by the factor \(n\), so that on addition the total number of electrons on both sides cancel out. Thus, we will bring our two half reactions together as follows:

**Table \[\text{PageIndex}(2)\]: General Redox Reaction Balancing**

<table>
<thead>
<tr>
<th>Multiplier</th>
<th>Half Reaction</th>
<th>Direction of Electrons</th>
<th>REDOX Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m)</td>
<td>(\text{Ox}_1 + ne^– \rightarrow \text{Red}_1)</td>
<td>electrons &quot;pushed&quot;</td>
<td>reduction</td>
</tr>
<tr>
<td>(n)</td>
<td>(\text{Red}_2 \rightarrow \text{Ox}_2 + me^–)</td>
<td>electrons &quot;pulled&quot;</td>
<td>oxidation</td>
</tr>
</tbody>
</table>

Adding the scaled reactants and scaled products along with canceling the electrons results in to balanced redox reaction

\[m\text{Ox}_1 + n\text{Red}_2 \rightarrow m\text{Red}_1 + n\text{Ox}_2\]

Notice that by multiplying the first half reaction by \(m\) and the second by \(n\), we balanced the overall redox reaction in terms of a transfer of \(nm\) electrons, but those electrons do not show in the final balanced equation. This should always...
be the case for a balanced redox reaction.

Redox also causes a change in the oxidation numbers of the reductant and oxidant. In a reduction, one element in a species experiences a lowering of its oxidation number, while in an oxidation the opposite occurs. This is demonstrated by expanding Table \(\PageIndex{1}\).

**Table \(\PageIndex{3}\): Redox Reaction Example**

<table>
<thead>
<tr>
<th>Multiplier</th>
<th>Half Reaction</th>
<th>Change in Oxidation Number</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>(\text{Fe}^0 \rightarrow \text{Fe}^{3+} + 3e^-)</td>
<td>Fe oxidation number increases (0 \rightarrow +3)</td>
<td>Oxidation</td>
</tr>
<tr>
<td>3</td>
<td>(\text{Cl}_2^0 + 2e^- \rightarrow 2\text{Cl}^-)</td>
<td>Cl oxidation number decreases (0 \rightarrow -1)</td>
<td>Reduction</td>
</tr>
</tbody>
</table>

The two half reactions in Table \(\PageIndex{1}\) also illustrate another important feature of balancing redox reactions. Notice that in each half reaction there is a balance both in the numbers of atoms of each kind and in the overall charge on each side. For example, in the oxidation

\[\text{Fe}^0 \rightarrow \text{Fe}^{3+} + 3e^-\]

we have one iron atom on each side, but also the zero charge on the left is balanced by the \(3 + (3^-)\) sum on the right from the \(\text{Fe}^{3+}\) ion and the three negative electrons. Likewise, in the reduction

\[\text{Cl}_2^0 + 2e^- \rightarrow 2\text{Cl}^-\]

the \(-2\) charge on the left from the two electrons is balanced by the \((2)(-1)\) charge on the right from the two chloride ions.

In every half reaction and every overall redox equation there must be both a mass balance and a charge balance.

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**Q1**

For each of the following, separate the skeletal (unbalanced) equation into two half reactions. For each half reaction, balance the elements (mass balance), and then add electrons to the right or left side to make a net charge balance. Identify which half reaction is the oxidation and which is the reduction. Then, multiply each half reaction by an appropriate factor so that the two multiplied half reactions add together to make a balanced redox equation.

a. \((\text{Hg}_2^{2+} + \text{S}_2\text{O}_3^{2-} \rightarrow \text{Hg} + \text{S}_4\text{O}_6^{2-})\)

b. \((\text{Al} + \text{Cr}^{3+} \rightarrow \text{Al}^{3+} + \text{Cr}^{2+})\)

c. \((\text{Au}^{3+} + \text{I}^- \rightarrow \text{Au} + \text{I}_2)\)

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**Balancing Redox Equations by the Ion-Electron Method**

There are two principal methods for balancing redox equations:
• oxidation state method
• ion-electron method.

The latter is easier to use with redox reactions in aqueous solution and if necessary can be adapted to many situations that are not in aqueous solution. Our primary interest will be in aqueous-solution redox; therefore, we will use the ion-electron method. One of the major advantages of this method is that it makes it completely unnecessary to assign individual oxidation numbers.

To balance a redox equation by the ion-electron method, carry out the following steps in this sequence:

1. **Separate the skeletal equation into two half reactions.** One half reaction will be a reduction and the other will be an oxidation. It is not necessary at this stage to identify which is which.

2. **Balance each half reaction separately.** Balance atoms on each side of a half reaction by inspection. If the reaction occurs in acidic medium, you may add H$_2$O and/or H$^+$ to balance oxygen and/or hydrogen. If the reaction occurs in basic medium, you may add H$_2$O and/or OH$^-$ to balance oxygen and/or hydrogen. Do not add any other new species (e.g., O$_2$, H$_2$) unless already a part of the skeletal half reaction.

3. **Balance the net charge across each half reaction by adding electrons to the side with the more positive net ionic charge.** If by this process electrons are added on the left side of a half reaction, the half reaction is a reduction. If electrons are added to the right side, the half reaction is an oxidation. (If you add electrons to the same side in both half reactions, something is wrong!)

4. **Multiply both half-reactions by appropriate whole number factors, so that the number of electrons is the same in both half reactions and will cancel when the two are added together.**

5. **Add the two multiplied half reactions together to obtain the overall redox equation.**

6. **Check the balance.** No electrons should appear in the overall redox equation. Not only should there be an element-by-element balance across the equation, but also the net charge (the sum of both ionic charges and electron charges) on both sides of the equation should be equal.

Note that this procedure does not involve assigning oxidation numbers. Nonetheless, if oxidation numbers are assigned to the balanced equation, it will always occur that the reduction involves lowering an oxidation state of some element, and the oxidation involves raising an oxidation state of some element. The following examples illustrate the ion-electron procedure, starting from the skeletal equation in either acidic or basic solution.

**Example 1: Balancing in Acid Solutions**

Balance \(\text{NO}_3^– + \text{Fe}^{2+} \rightarrow \text{HNO}_2 + \text{Fe}^{3+}\) in acid aqueous solution.

The fact that this reaction occurs in acid aqueous solution suggest that water or \((\text{H}^+)) may be involved in the reaction. This is not a requirement from the question of course. The protonation of a species \((\text{NO}_3^- \text{\rightarrow HNO}_2)) further suggest this.

<table>
<thead>
<tr>
<th>Multiplier</th>
<th>Half Reaction</th>
<th>Change in Oxidation Number</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>((\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-)))</td>
<td>Fe oxidation number increases (( +2 \text{\rightarrow +3})))</td>
<td>Oxidation</td>
</tr>
<tr>
<td>3</td>
<td>((2e^- + 3 \text{H}^+ + \text{NO}_3^- \rightarrow \text{HNO}_2))</td>
<td>N oxidation number decreases (( +5)))</td>
<td>Reduction</td>
</tr>
</tbody>
</table>

**Table \(\text{(PageIndex(4))}: Redox Reaction Example**
Adding these half reactions together and canceling electrons results in

\[2 \text{Fe}^{2+} + 3 \text{H}^+ + \text{NO}_3^- \rightarrow 2 \text{Fe}^{3+} + \text{HNO}_2 + \text{H}_2\text{O} \]

To make the oxygen balance in the \(\text{NO}_3^-/\text{HNO}_2\) reduction half reaction, we added \((\text{H}_2\text{O})\) to the right and then added \((3 \text{H}^+)\) to make the hydrogen balance. These are the only allowable species to use in acid medium.

**Example 2: Balancing in Basic Solutions I**

Balance \(\text{NiO}_2 + \text{Cd} \rightarrow \text{Ni(OH)}_2 + \text{Cd(OH)}_2\) in basic aqueous solution. This is a "NiCad" secondary battery reaction.

The fact that this reaction occurs in basic aqueous solution suggest that water or \((\text{OH}^-)\) may be involved in the reaction. This is not a requirement from the question of course.

**Table \((\text{PageIndex}[5])\): Redox Reaction Example**

<table>
<thead>
<tr>
<th>Multiplier</th>
<th>Half Reaction</th>
<th>Change in Oxidation Number</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(2 \text{OH}^- + \text{Cd} \rightarrow \text{Cd(OH)}_2 + 2 \text{e}^-)</td>
<td>Fe oxidation number increases (+2 \rightarrow +3)</td>
<td>Oxidation</td>
</tr>
<tr>
<td>1</td>
<td>(2 \text{e}^- + 2 \text{H}_2\text{O} + \text{NiO}_2 \rightarrow \text{Ni(OH)}_2 + 2 \text{OH}^-)</td>
<td>Ni oxidation number decreases (+5 \rightarrow +3)</td>
<td>Reduction</td>
</tr>
</tbody>
</table>

Adding these half reactions together and canceling electrons results in

\[[\text{NiO}_2 + \text{Cd} + \text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2 + \text{Cd(OH)}_2 ]\]

Because this is in base, we can only add \(\text{H}_2\text{O}\) and/or \(\text{OH}^-\) to make the oxygen and hydrogen balances. The need to add \(\text{OH}^-\) in the \(\text{Cd/Cd(OH)}_2\) half reaction is straightforward. In the \(\text{NiO}_2/\text{Ni}\) half reaction, think of \(\text{H}_2\text{O}\) as an acid neutralizing basic \(\text{NiO}_2\). Thus, we add two \(\text{H}_2\text{O}\) to the left to neutralize the two \(\text{O}^{2-}\) ions of \(\text{NiO}_2\), and then we add two \(\text{OH}^-\) to the right side to complete the balance.

Balancing oxygen and hydrogen in basic redox reactions sometimes can be difficult, because both \(\text{OH}^-\) and \(\text{H}_2\text{O}\) contain both elements. A trick to get around this is to balance any troublesome half-reaction or the entire redox reaction first as if it were in acid, using \(\text{H}^+\) and \(\text{H}_2\text{O}\). Then, the acid-balanced equation is converted to its form in basic medium by adding the same number of \(\text{OH}^-\) to both sides of the equation that would be needed to "neutralize" any \(\text{H}^+\) in the acid-balanced equation. Combine \(\text{H}^+\) and \(\text{OH}^-\) pairs to become \(\text{H}_2\text{O}\); i.e., \((\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O})\). The following example shows this technique for a redox reaction to be balanced in base.
Example 3: Balancing in Basic Solutions II

Balance \(I^– + MnO_4^{2–} \rightarrow IO_3^{–} + MnO_2\) in basic aqueous solution.

We will balance this in acid first, then "neutralize" any \(H^+ \) to convert the redox reaction to basic conditions.

<table>
<thead>
<tr>
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<th>Half Reaction</th>
<th>Change in Oxidation Number</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(3 H_2O + I^– \rightarrow IO_3^{–} + 6 H^+ + 6e^{–})</td>
<td>I oxidation number increases ((-1 \rightarrow +5))</td>
<td>Oxidation</td>
</tr>
<tr>
<td>1</td>
<td>(2e^{–} + 2 H_2O + NiO_2 \rightarrow Ni(OH)_2 + 2 OH^–)</td>
<td>Ni oxidation number decreases ((+4 \rightarrow +2))</td>
<td>Reduction</td>
</tr>
</tbody>
</table>

Adding these half reactions together and canceling electrons results in

\[6 H^+ + I^– + 3 MnO_4^{2–} \rightarrow IO_3^{–} + 3 MnO_2 + 3 H_2O\]

but this is writing as if in acid. We can add six \(OH^-\) ions to each side.

\[\cancel{6OH^- + 6 H^+} + I^– + 3 MnO_4^{2–} \rightarrow IO_3^{–} + 3 MnO_2 + \cancel{3 H_2O} + 6OH^- \text{\label{Ex3}}\]

This neutralizes the hydronium ions on the reactant side of the equation to generate water (via \(H^+ + OH^- \rightarrow H_2O\)), which is partially canceled by the water in the products. Equation \(\text{\ref{Ex3}}\) is the balanced redox reaction in basic solution.

\[3 H_2O + I^– + 3 MnO_4^{2–} \rightarrow IO_3^{–} + 3 MnO_2 + 6 OH^- \text{\label{Ex3}}\]

On the left, the six added \(OH^-\) ions are combined with the six \(H^+\) ions of the acid-balanced equation to make 6 H_2O. Three of these cancel with the 3 H_2O on the right in the acid-balanced equation. Thus, we have a net of 3 H_2O on the left in the base-balanced equation. All six \(OH^-\) ions added on the right appear in the net redox reaction in base.

Q2

Use the ion-electron method to complete and balance the following skeletal redox equations, occurring in either acidic or basic aqueous solution, as indicated. Identify the oxidation and reduction half reactions in each case.

a. In acidic aqueous solution: \(\text{Cu} + NO3^{–} \rightarrow \text{Cu}^{2+} + N_2O_4\)

b. In acidic aqueous solution: \(\text{XeO}_3 + BrO_3^{–} \rightarrow \text{Xe} + BrO_4^{–}\)

c. In acidic aqueous solution: \(\text{MnO}_4^{–} + CH_3OH \rightarrow \text{Mn}^{2+} + HCO_2H\)

d. In acidic aqueous solution: \(\text{Cr}_2O_7^{2–} + I_2 \rightarrow \text{Cr}^{3+} + IO_3^{–}\)

e. In basic aqueous solution: \(\text{Pb(OH)}_4^{2–} + ClO^{–} \rightarrow \text{PbO}_2 + Cl^{–}\)

f. In basic aqueous solution: \(\text{SO}_2 + MnO_4^{4–} \rightarrow \text{SO}_4^{2–} + MnO_2\)