Pearson

19.2: Balancing Oxidation–Reduction Equations

The reactions that create the flow of electric charge within a battery are oxidation–reduction (redox) reactions. Recall from Section 8.9 that *oxidation* is the loss of electrons, and *reduction* is the gain of electrons. Recall also that we identify oxidation–reduction reactions through changes in oxidation states: *oxidation corresponds to an increase in oxidation state, and reduction corresponds to a decrease in oxidation state*. For example, consider the reaction between calcium and water:

$$\underset{0}{Ca(s)} + 2\,\underset{+1\ -2}{H_2O(l)} \longrightarrow \underset{+2\ \ -2\ +1}{Ca(OH)_2(aq)} + \underset{0}{H_2(g)}$$

Reduction

Oxidation

Because calcium increases in oxidation state from 0 to +2, it is oxidized. Because hydrogen decreases in oxidation state from +1 to 0, it is reduced.

> Review assigning oxidation states in Section 8.9.

Balancing redox reactions can be more complicated than balancing other types of reactions because we must balance both the mass (or number of each type of atom) and the *charge*. We can balance redox reactions occurring in aqueous solutions with a special procedure called the *half-reaction method of balancing*. In this procedure, we break down the overall equation into two half-reactions: one for oxidation and one for reduction. We then balance the half-reactions individually and add them together. The steps differ slightly for reactions occurring in acidic and in basic solution. Examples 19.1 and 19.2 demonstrate the method for an acidic solution, and Example 19.3 demonstrates the method for a basic solution.

Example 19.1 Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution

Balance the redox equation.

$$Al(s) + Cu^{2+}(aq) \rightarrow Al^{3+}(aq) + Cu(s)$$

PROCEDURE

Step 1 *Assign oxidation states* to all atoms and identify the substances being oxidized and reduced.

$$\underset{0}{Al(s)} + \underset{+2}{Cu^{2+}(aq)} \longrightarrow \underset{+3}{Al^{3+}(aq)} + \underset{0}{Cu(s)}$$

Reduction

Oxidation

$$\underset{+2}{Fe^{2+}(aq)} + \underset{+7\ -2}{MnO_4^{-}(aq)} \longrightarrow \underset{+3}{Fe^{3+}(aq)} + \underset{+2}{Mn^{2+}(aq)}$$

Reduction

Oxidation

Step 2 *Separate the overall reaction into two half-reactions*: one for oxidation and one for reduction.

Oxidation: $\mathrm{Al}(s) \rightarrow \mathrm{Al}^{3+}(aq)$

Reduction: $\mathrm{Cu}^{2+}(aq) \rightarrow \mathrm{Cu}(s)$

Step 3 *Balance each half-reaction with respect to mass* in the following order:

- Balance all elements other than H and O.
- Balance O by adding H_2O.
- Balance H by adding H^+.

All elements are balanced, so proceed to the next step.

Step 4 *Balance each half-reaction with respect to charge* by adding electrons. (Make the sum of the charges on both sides of the equation equal by adding as many electrons as necessary.)

$\mathrm{Al}(s) \rightarrow \mathrm{Al}^{3+}(aq) + 3\,\mathrm{e}^-$
$2\,\mathrm{e}^- + \mathrm{Cu}^{2+}(aq) \rightarrow \mathrm{Cu}(s)$

Step 5 *Make the number of electrons in both half-reactions equal* by multiplying one or both half-reactions by a small whole number.

$2\left[\mathrm{Al}(s) \rightarrow \mathrm{Al}^{3+}(aq) + 3\,\mathrm{e}^-\right]$
$2\,\mathrm{Al}(s) \rightarrow 2\,\mathrm{Al}^{3+}(aq) + 6\,\mathrm{e}^-$
$3\left[2\mathrm{e}^- + \mathrm{Cu}^{2+}(aq) \rightarrow \mathrm{Cu}(s)\right]$
$6\,\mathrm{e}^- + 3\,\mathrm{Cu}^{2+}(aq) \rightarrow 3\,\mathrm{Cu}(s)$

Step 6 *Add the two half-reactions together*, canceling electrons and other species as necessary.

$$\begin{array}{l} 2\,\mathrm{Al}(s) \longrightarrow 2\,\mathrm{Al}^{3+}(aq) + \cancel{6\,\mathrm{e}^-} \\ \cancel{6\,\mathrm{e}^-} + 3\,\mathrm{Cu}^{2+}(aq) \longrightarrow 3\,\mathrm{Cu}(s) \\ \hline 2\,\mathrm{Al}(s) + 3\,\mathrm{Cu}^{2+}(aq) \longrightarrow \\ \qquad\qquad 2\,\mathrm{Al}^{3+}(aq) + 3\,\mathrm{Cu}(s) \end{array}$$

Step 7 *Verify that the reaction is balanced* with respect to both mass and charge.

Reactants	Products
2 Al	2 Al
3 Cu	3 Cu
6+ Charge	6+ Charge

FOR PRACTICE 19.1 Balance the redox reaction in acidic solution.

$\mathrm{H}^+(aq) + \mathrm{Cr}(s) \rightarrow \mathrm{H}_2(g) + \mathrm{Cr}^{2+}(aq)$

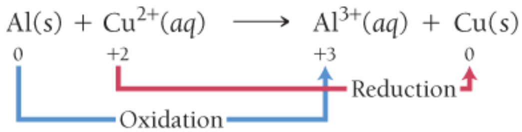
Example 19.2 Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution

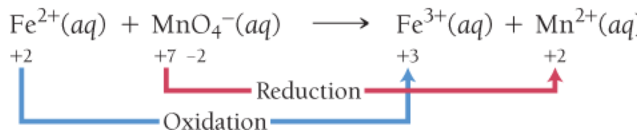
Balance the redox equation.

$$\mathrm{Fe}^{2+}(aq) + \mathrm{MnO_4}^-(aq) \rightarrow \mathrm{Fe}^{3+}(aq) + \mathrm{Mn}^{2+}(aq)$$

PROCEDURE

St[redacted]p 1 *Assign oxidation states* to all atoms and identify the substances being oxidized and reduced.





St[redacted]p 2 *Separate the overall reaction into two half-reactions*: one for oxidation and one for reduction.

Oxidation: $Fe^{2+}\,(aq) \rightarrow Fe^{3+}\,(aq)$

Reduction: $MnO_4^-\,(aq) \rightarrow Mn^{2+}\,(aq)$

St[redacted]p 3 *Balance each half-reaction with respect to mass* in the following order:

- Balance all elements other than H and O.
- Balance O by adding H_2O.
- Balance H by adding H^+.

All elements other than H and O are balanced, so proceed to balance H and O.

$Fe^{2+}\,(aq) \rightarrow Fe^{3+}\,(aq)$
$MnO_4^-\,(aq) \rightarrow Mn^{2+}\,(aq) + 4\,H_2O\,(l)$
$8\,H^+\,(aq) + MnO_4^-\,(aq) \rightarrow Mn^{2+}\,(aq) + 4\,H_2O\,(l)$

St[redacted]p 4 *Balance each half-reaction with respect to charge* by adding electrons. (Make the sum of the charges on both sides of the equation equal by adding as many electrons as necessary.)

$Fe^{2+}\,(aq) \rightarrow Fe^{3+}\,(aq) + 1\,e^-$
$5\,e^- + 8\,H^+\,(aq) + MnO_4^-\,(aq) \rightarrow Mn^{2+}\,(aq) + 4\,H_2O\,(l)$

St[redacted]p 5 *Make the number of electrons in both half-reactions equal* by multiplying one or both half-reactions by a small whole number.

$5\left[Fe^{2+}\,(aq) \rightarrow Fe^{3+}\,(aq) + 1\,e^-\right]$
$5\,Fe^{2+}\,(aq) \rightarrow 5\,Fe^{3+}\,(aq) + 5\,e^-$
$5\,e^- + 8\,H^+\,(aq) + MnO_4^-\,(aq) \rightarrow Mn^{2+}\,(aq) + 4\,H_2O\,(l)$

St[redacted]p 6 *Add the two half-reactions together*, canceling electrons and other species as necessary.

$$5\,Fe^{2+}(aq) \longrightarrow 5\,Fe^{3+}(aq) + \cancel{5\,e^-}$$
$$\cancel{5\,e^-} + 8\,H^+(aq) + MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$
$$5\,Fe^{2+}(aq) + 8\,H^+(aq) + MnO_4^-(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

St[redacted]p 7 *Verify that the reaction is balanced* with respect to both mass and charge.

Reactants	Products
5 Fe	5 Fe
8 H	8 H
1 Mn	1 Mn
4 O	4 O
17+ Charge	17+ Charge

FOR PRACTICE 19.2 Balance the redox reaction in acidic solution.

$Cu\,(s) + NO_3^-\,(aq) \rightarrow Cu^{2+}\,(aq) + NO_2\,(aq)$

Interactive Worked Example 19.2 **Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution**

When a redox reaction occurs in basic solution, we balance the reaction in a similar manner, except that we add an extra step to neutralize any H^+ with OH^-. The H^+ and the OH^- combine to form H_2O as demonstrated in Example 19.3.

Example 19.3 Balancing Redox Reactions Occurring in Basic Solution

Balance the equation occurring in basic solution.

$$I^-\,(aq) + MnO_4^-\,(aq) \rightarrow I_2\,(aq) + MnO_2\,(s)$$

SOLUTION To balance redox reactions occurring in basic solution, follow the half-reaction method outlined in Examples 19.1 and 19.2, but add an extra step to neutralize the acid with OH^- as shown in Step 3 of this example.

1. Assign oxidation states.

$$\underset{-1}{I^-}(aq) + \underset{+7\ -2}{MnO_4^-}(aq) \longrightarrow \underset{0}{I_2}(aq) + \underset{+4\ -2}{MnO_2}(s)$$

Reduction

Oxidation

2. Separate the overall reaction into two half-reactions.

Oxidation: $I^-\,(aq) \rightarrow I_2\,(aq)$

Reduction: $MnO_4^-\,(aq) \rightarrow MnO_2\,(s)$

3. Balance each half-reaction with respect to mass:

- Balance all elements other than H and O.
- Balance O by adding H_2O.
- Balance H by adding H^+.
- Neutralize H^+ by adding enough OH^- to neutralize each H^+. Add the same number of OH^- ions to each side of the equation.

$$\begin{cases} 2\,I^-(aq) \longrightarrow I_2(aq) \\ MnO_4^-(aq) \longrightarrow MnO_2(s) \end{cases}$$

$$\begin{cases} 2\,I^-(aq) \longrightarrow I_2(aq) \end{cases}$$

$$MnO_4^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

$$\begin{cases} 2\,I^-(aq) \longrightarrow I_2(aq) \\ 4\,H^+(aq) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l) \end{cases}$$

$$\begin{cases} 2\,I^-(aq) \longrightarrow I_2(aq) \\ \underbrace{4\,H^+(aq) + 4\,OH^-(aq)}_{4\,H_2O(l)} + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l) + 4\,OH^-(aq) \end{cases}$$

4. Balance each half-reaction with respect to charge.

$$2\,I^-(aq) \rightarrow I_2(aq) + 2\,e^-$$
$$4\,H_2O(l) + MnO_4^-(aq) + 3\,e^- \rightarrow MnO_2(s) + 2\,H_2O(l) + 4\,OH^-(aq)$$

5. Make the number of electrons in both half-reactions equal.

$$3\left[2\,I^-(aq) \rightarrow I_2(aq) + 2\,e^-\right]$$
$$6\,I^-(aq) \rightarrow 3\,I_2(aq) + 6\,e^-$$
$$2\left[4\,H_2O(l) + MnO_4^-(aq) + 3\,e^- \rightarrow MnO_2(s) + 2\,H_2O(l) + 4\,OH^-(aq)\right]$$
$$8\,H_2O(l) + 2\,MnO_4^-(aq) + 6\,e^- \rightarrow 2\,MnO_2(s) + 4\,H_2O(l) + 8\,OH^-(aq)$$

6. Add the half-reactions together.

$$6\,I^-(aq) \rightarrow 3\,I_2(aq) + \cancel{6\,e^-}$$
$$4\,\cancel{8}\,H_2O(l) + 2\,MnO_4^-(aq) + \cancel{6\,e^-} \rightarrow 2\,MnO_2 + \cancel{4\,H_2O(l)} + 8\,OH^-(aq)$$
$$6\,I^-(aq) + 4\,H_2O(l) + 2\,MnO_4^-(aq) \rightarrow 3\,I_2(aq) + 2\,MnO_2(s) + 8\,OH^-(aq)$$

7. Verify that the reaction is balanced.

Reactants	Products
6 I	6 I
8 H	8 H
2 Mn	2 Mn
12 O	12 O
8− Charge	8− Charge

FOR PRACTICE 19.3 Balance the following redox reaction occurring in basic solution.

$$ClO^-(aq) + Cr(OH)_4^-(aq) \rightarrow CrO_4^{2-}(aq) + Cl^-(aq)$$

Interactive Worked Example 19.3 **Balancing Redox Reactions Occurring in Basic Solution**