Chapter Outline

- 8.1 Solutions and Their Concentrations
- 8.2 Dilutions
- 8.3 Electrolytes and Nonelectrolytes
- 8.4 Acids, Bases, and Neutralization Reactions
- 8.5 Precipitation Reactions
- **8.6 Oxidation-Reduction Reactions**
- 8.7 Titrations
- 8.8 Ion Exchange
Section 8.6 - Oxidation-Reduction Reactions

Oxidation-Reduction Reactions (Redox):
Characterized by gain or loss of electrons by atoms involved in the reaction.

Oxidation:
Historical definition = gain of oxygen (sometimes with a simultaneous loss of hydrogen)
e.g. \( \text{C}_2\text{H}_6 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \)
Modern definition = loss of electrons

Reduction:
Historical definition = loss of oxygen (sometimes with a simultaneous gain in hydrogen)
e.g. \( \text{Fe}_2\text{O}_3 + 3 \text{CO} \rightarrow 2 \text{Fe} + 3 \text{CO}_2 \)  "oil rig"
Modern definition = gain of electrons

Table 8.4 - Oxidation Number Rules

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred, i.e. applies to both ionic and covalent compounds.

1. The O.N. before a reaction for pure elements = 0 (including diatomics).

2. O.N = the charge on monovalent ions

3. O.N. of fluorine = -1 for all of its compounds
4. O.N. of oxygen = -2 in nearly all of its compounds

\[
\begin{array}{c}
\text{O}^{-2} + 2 \text{e}^- \rightarrow \left(\text{O}^{-2}\right)^{2-}
\end{array}
\]

Exceptions are peroxides (O.N. = -1) and superoxides (O.N. = -1/2), e.g. H₂O₂, KO₂

5. O.N. of hydrogen = +1 in nearly all of its compounds

\[
\begin{array}{c}
\text{H} + \text{H} \rightarrow 2 \text{H}^+ + 2 \text{e}^-
\end{array}
\]

Exception = hydrides, e.g. CaH₂

6. O.N. values of the atoms in a neutral molecule sum up to zero

\[
\begin{array}{c}
\text{CaCl}_2 + 2 + 2(\text{Cl}) = 0 \quad \text{so Cl} = -1
\end{array}
\]

7. O.N. values of the atoms in a polyatomic ion sum up to the charge on the ion

\[
\begin{array}{c}
\text{PO}_4^{3-} + 4(-2) = -3 \quad \text{so P} = +5
\end{array}
\]

---

**Sample Exercise 8.9**

What are the oxidation states for sulfur in (a) S₈, (b) SO₂, (c) Na₂S, and (d) CaSO₄?
Electron Transfer in Redox Reactions

What follows is a method that keeps track of the flow of electrons within the atoms and molecules taking part in a chemical reaction.

\[ \Delta \text{O.N.} = \text{final O.N.} - \text{initial O.N.} \]

<table>
<thead>
<tr>
<th>oxidation</th>
<th>lose ( n ) electrons</th>
<th>( \Delta \text{O.N.} = +n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>reduction</td>
<td>gain ( n ) electrons</td>
<td>( \Delta \text{O.N.} = -n )</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{Pb}^0 & \rightarrow \text{Pb}^{2+} + 2 \text{ e}^- & \Delta \text{O.N.} = (2 - 0) = +2 \\
\text{Cu}^{2+} + 2 \text{ e}^- & \rightarrow \text{Cu}^0 & \Delta \text{O.N.} = (0 - 2) = -2
\end{align*}
\]
What is the net ionic equation for the reaction of zinc metal plus cupric sulfate?

Oxidizing Agent = oxidizes something else while being reduced (Cu^{2+} → Cu^{0})

Reducing Agent = reduces something else while being oxidized (Zn → Zn^{2+})
Sample Exercise 8.10:
Identifying Oxidizing and Reducing Agents and Determining Number of Electrons Transferred

Energy released by the reaction of hydrazine and dinitrogen tetroxide is used to orient and maneuver spacecraft and to propel rockets into space. Identify the elements that are oxidized and reduced, the oxidizing agent, and the reducing agent, and determine the number of electrons transferred in the balanced chemical equation.

\[
2 \text{N}_2\text{H}_4(g) + \text{N}_2\text{O}_4(g) \rightarrow 3 \text{N}_2(g) + 4 \text{H}_2\text{O}(g)
\]

\[
\begin{align*}
\text{O.N.} &= 0 - (-2) = +2 \\
\text{lost electrons} &\quad \text{oxidation} \\
\text{O.N.} &= (0 - 4) = -4 \\
\text{gained electrons} &\quad \text{reduction}
\end{align*}
\]
Net number of electrons transferred during the reaction:

\[ \Delta \text{O.N.} = (\# \text{molecules}) \times (\# \text{atoms in molecule}) \times \Delta \text{O.N.} \]

\[ \Delta \text{O.N. from previous slide} \]

\[ 2 \times 2 \times +2 = +8 \] (oxidation)

\[ 2 \text{N}_2\text{H}_4(g) + \text{N}_2\text{O}_4(g) \rightarrow 3 \text{N}_2(g) + 4 \text{H}_2\text{O}(g) \]

\[ 1 \times 2 \times -4 = -8 \] (reduction)

\[ \Delta \text{O.N. from previous slide} \]

So the net number of electrons flowing is 8

---

**Balancing Redox Reactions in Acid and Base**
*(We’re going to use a simpler method than the book called the Method of Half Reactions)*

**Examples of Half Reactions:**
copper wire immersed in a silver nitrate solution:

\[
\text{Cu(s)} + 2 \text{AgNO}_3(aq) \rightarrow \text{Cu(NO}_3)_2(aq) + 2 \text{Ag(s)}
\]

\[ \Delta \text{O.N. Cu} = +2 - (0) = +2 \] oxidation

\[ \Delta \text{O.N. Ag} = 0 - (1) = -1 \] reduction

The half-reactions are:

**ox:** Cu(s) → Cu⁴⁺(aq) + 2 e⁻

**red:** Ag⁺(aq) + e⁻ → Ag(s)

---

(a) Cu(s)

(b) Ag(s)

AgNO₃(aq) (clear soln)

Cu(NO₃)₂(aq) (blue soln)
Examples of Half Reactions (cont’d):
copper wire immersed in a silver nitrate solution:

The total reaction is obtained by adding the half reactions together, after balancing electrons -

\[ \text{ox: } \text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \]
\[ \text{red: } \left[ \text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag(s)} \right] \times 2 \]
\[ \text{ox: } \text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \]
\[ \text{red: } 2 \text{Ag}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{Ag(s)} \]

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

The next topic is how to balance a redox reaction that occurs in acid or base.

---

Procedure for balancing a redox reaction in acid or base.

1. Determine the oxidation numbers for the reactants and compare to the products.
2. Write the oxidation and reduction half-reactions **without electrons (yet)**
3. Balance everything but oxygen and hydrogen
4. Balance oxygen by adding water
5. Balance hydrogen by adding (a) H\(^+\) in acidic solutions, (b) in basic solutions, continue as if in acidic solution, but at the end each H\(^+\) ion will be neutralized by adding OH\(^-\) ions
6. Balance charge by adding electrons; for the oxidation half-reaction, the electrons will be on the right, for the reduction half-reaction, the electrons will appear on the left
7. Make sure the number of electrons in each half-reaction are the same. Then add the half reactions together
8. Make sure that the equation is balanced for mass and for charge

**NOTE:** sometimes you have to cancel H\(_2\)O's that are on each side, as well as H\(^+\) or OH\(^-\)
Sample Exercise 8.11
Balancing Redox Equations I: Acidic Solutions

Microorganisms called denitrifying bacteria that grow in waterlogged soil convert NO\textsubscript{3} ions into N\textsubscript{2}O gas as they feed on dead plant tissue (empirical formula = CH\textsubscript{2}O), converting it into CO\textsubscript{2} and H\textsubscript{2}O. Write a balanced net ionic equation describing this conversion of dissolved nitrates to N\textsubscript{2}O gas. Assume the reaction occurs in slightly acidic water.

1. Determine the oxidation numbers for the reactants and compare to the products.

\[
\begin{align*}
\text{Given:} & \quad \text{NO}_3^- (\text{aq}) + \text{CH}_2\text{O(s)} \rightarrow \text{N}_2\text{O(g)} + \text{CO}_2(g) + \text{H}_2\text{O(l)}
\end{align*}
\]

\[\Delta \text{O.N.} \quad C = +4 - 0 = +4 \quad \text{oxidation} \]
\[\Delta \text{O.N.} \quad N = 0 - 5 = -4 \quad \text{reduction} \]

2. Write the oxidation and reduction half-reactions \textit{without electrons (yet)}

\[
\begin{align*}
\text{ox:} & \quad \text{CH}_2\text{O(s)} \rightarrow \text{CO}_2(g) \\
\text{red:} & \quad \text{NO}_3^- (\text{aq}) \rightarrow \text{N}_2\text{O(g)}
\end{align*}
\]

3. Balance everything but oxygen and hydrogen

\[
\begin{align*}
\text{ox:} & \quad \text{CH}_2\text{O(s)} \rightarrow \text{CO}_2(g) \\
\text{red:} & \quad 2 \text{NO}_3^- (\text{aq}) \rightarrow \text{N}_2\text{O(g)}
\end{align*}
\]

4. Balance oxygen by adding water

\[
\begin{align*}
\text{ox:} & \quad H_2\text{O} + \text{CH}_2\text{O(s)} \rightarrow \text{CO}_2(g) \\
\text{red:} & \quad 2 \text{NO}_3^- (\text{aq}) \rightarrow \text{N}_2\text{O(g)} + 5 H_2\text{O}
\end{align*}
\]
5. Balance hydrogen by adding (a) $H^+$ in acidic solutions, (b) in basic solutions, continue as if in acidic solution, but at the end each $H^+$ ion will be neutralized by adding $OH^-$ ions

\[
\text{ox: } \text{H}_2\text{O} + \text{CH}_2\text{O(s)} \rightarrow \text{CO}_2(g) + 4 \text{ H}^+(aq) \\
\text{red: } 10 \text{ H}^+(aq) + 2 \text{ NO}_3^-(aq) \rightarrow \text{N}_2\text{O(g)} + 5 \text{ H}_2\text{O}
\]

6. Balance charge by adding electrons; for the oxidation half-reaction, the electrons will be on the right, for the reduction half-reaction, the electrons will appear on the left

\[
\text{ox: } \text{H}_2\text{O} + \text{CH}_2\text{O(s)} \rightarrow \text{CO}_2(g) + 4 \text{ H}^+(aq) + 4 e^- \\
\text{red: } 8 e^- + 10 \text{ H}^+(aq) + 2 \text{ NO}_3^-(aq) \rightarrow \text{N}_2\text{O(g)} + 5 \text{ H}_2\text{O}
\]

7. Make sure the number of electrons in each half-reaction are the same. Then add the half reactions together

\[
\text{ox: } \left[ \text{H}_2\text{O} + \text{CH}_2\text{O(s)} \rightarrow \text{CO}_2(g) + 4 \text{ H}^+(aq) + 4 e^- \right] \times 2 \\
\text{red: } 8 e^- + 10 \text{ H}^+(aq) + 2 \text{ NO}_3^-(aq) \rightarrow \text{N}_2\text{O(g)} + 5 \text{ H}_2\text{O} \\
\text{Net: } 2\text{H}_2\text{O} + 2\text{CH}_2\text{O(s)} + 10\text{H}^+(aq) + 2\text{NO}_3^-(aq) \rightarrow 2\text{CO}_2(g) + 8\text{H}^+(aq) + \text{N}_2\text{O(g)} + 5\text{H}_2\text{O}
\]

**NOTE:** sometimes you have to cancel $\text{H}_2\text{O}$'s that are on each side, as well as $\text{H}^+$ or $\text{OH}^-$

\[
2\text{H}_2\text{O} + 2\text{CH}_2\text{O(s)} + 10\text{H}^+(aq) + 2\text{NO}_3^-(aq) \rightarrow 2\text{CO}_2(g) + 8\text{H}^+(aq) + \text{N}_2\text{O(g)} + 5\text{H}_2\text{O} \\
2\text{CH}_2\text{O(s)} + 10\text{H}^+(aq) + 2\text{NO}_3^-(aq) \rightarrow 2\text{CO}_2(g) + 8\text{H}^+(aq) + \text{N}_2\text{O(g)} + \text{3H}_2\text{O} \\
2\text{CH}_2\text{O(s)} + 2\text{H}^+(aq) + 2\text{NO}_3^-(aq) \rightarrow 2\text{CO}_2(g) + \text{N}_2\text{O(g)} + \text{3H}_2\text{O}
\]
8. Make sure that the equation is balanced for mass and for charge

\[ 2\text{CH}_2\text{O}(s) + 2\text{H}^+(aq) + 2\text{NO}_3^-(aq) \rightarrow 2\text{CO}_2(g) + \text{N}_2\text{O}(g) + 3\text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>H</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>O</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>N</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Mass: C = 2  H = 6  O = 8  N = 2

Charge: \(2(+1) + 2(-1) = 0\)

---

**Homework Problem 98(c)**

**Balancing Redox Equations II: Basic Solutions**

Permanganate ion is used in water purification to remove oxidizable substances. Complete and balance the reaction for the removal of sulfite ion.

1. Determine the oxidation numbers for the reactants and compare to the products.

\[ \text{(+7)} (-2) \quad \text{(+4)} (-2) \quad \text{(+4)} (-2) \quad \text{(+6)} (-2) \]

\[ \text{MnO}_4^-(aq) + \text{SO}_3^{2-}(aq) \rightarrow \text{MnO}_2(s) + \text{SO}_4^{2-}(aq) \]

\[ \Delta \text{O.N.} \quad \text{S} = +6 - (+4) = +2 \quad \text{oxidation} \]

\[ \Delta \text{O.N.} \quad \text{Mn} = +4 - (+7) = -3 \quad \text{reduction} \]

2. Write the oxidation and reduction half-reactions *without electrons (yet)*

\[ \text{ox:} \quad \text{SO}_3^{2-}(aq) \rightarrow \text{SO}_4^{2-}(aq) \]

\[ \text{red:} \quad \text{MnO}_4^-(aq) \rightarrow \text{MnO}_2(s) \]
3. Balance everything but oxygen and hydrogen

\[
\begin{align*}
\text{ox:} & \quad \text{SO}_3^{2-}(aq) & \rightarrow & \quad \text{SO}_4^{2-}(aq) \\
\text{red:} & \quad \text{MnO}_4^{-}(aq) & \rightarrow & \quad \text{MnO}_2(s)
\end{align*}
\]
S and Mn are already balanced

4. Balance oxygen by adding water

\[
\begin{align*}
\text{ox:} & \quad \text{H}_2\text{O} + \text{SO}_3^{2-}(aq) & \rightarrow & \quad \text{SO}_4^{2-}(aq) \\
\text{red:} & \quad \text{MnO}_4^{-}(aq) & \rightarrow & \quad \text{MnO}_2(s) + 2\text{H}_2\text{O}
\end{align*}
\]

5. Balance hydrogen by adding (a) H⁺ in acidic solutions, (b) in basic solutions, continue as if in acidic solution, but at the end each H⁺ ion will be neutralized by adding OH⁻ ions

\[
\begin{align*}
\text{ox:} & \quad \text{H}_2\text{O} + \text{SO}_3^{2-}(aq) & \rightarrow & \quad \text{SO}_4^{2-}(aq) + 2\text{H}⁺(aq) \\
\text{red:} & \quad 4\text{H}⁺(aq) + \text{MnO}_4^{-}(aq) & \rightarrow & \quad \text{MnO}_2(s) + 2\text{H}_2\text{O}
\end{align*}
\]

6. Balance charge by adding electrons; for the oxidation half-reaction, the electrons will be on the right, for the reduction half-reaction, the electrons will appear on the left

\[
\begin{align*}
\text{ox:} & \quad \text{H}_2\text{O} + \text{SO}_3^{2-}(aq) & \rightarrow & \quad \text{SO}_4^{2-}(aq) + 2\text{H}⁺(aq) + 2 \text{e}⁻ \\
\text{red:} & \quad 3 \text{e}⁻ + 4\text{H}⁺(aq) + \text{MnO}_4^{-}(aq) & \rightarrow & \quad \text{MnO}_2(s) + 2\text{H}_2\text{O}
\end{align*}
\]

7. Make sure the number of electrons in each half-reaction are the same. Then add the half reactions together

\[
\begin{align*}
\text{ox:} & \quad \left[ \text{H}_2\text{O} + \text{SO}_3^{2-}(aq) \rightarrow \quad \text{SO}_4^{2-}(aq) + 2\text{H}⁺(aq) + 2 \text{e}⁻ \right] \times 3 \\
\text{red:} & \quad \left[ 3 \text{e}⁻ + 4\text{H}⁺(aq) + \text{MnO}_4^{-}(aq) \rightarrow \quad \text{MnO}_2(s) + 2\text{H}_2\text{O} \right] \times 2
\end{align*}
\]

\[
\text{Net:} \quad 3\text{H}_2\text{O} + 3\text{SO}_3^{2-}(aq) + 8\text{H}⁺(aq) + 2\text{MnO}_4^{-}(aq) \rightarrow \\
3\text{SO}_4^{2-}(aq) + 6\text{H}⁺(aq) + 2\text{MnO}_2(s) + 4\text{H}_2\text{O}
\]
NOTE: sometimes you have to cancel H₂O’s that are on each side, as well as H⁺ or OH⁻

\[ 2\text{H}_2\text{O} + 3\text{SO}_3^{2-}(aq) + 8\text{H}^+(aq) + 2\text{MnO}_4^-(aq) \rightarrow 3\text{SO}_4^{2-}(aq) + 6\text{H}^+(aq) + 2\text{MnO}_2(s) + 4\text{H}_2\text{O} \]

\[ 3\text{SO}_3^{2-}(aq) + 8\text{H}^+(aq) + 2\text{MnO}_4^-(aq) \rightarrow 3\text{SO}_4^{2-}(aq) + 8\text{H}^+(aq) + 2\text{MnO}_2(s) + \text{H}_2\text{O} \]

\[ 3\text{SO}_3^{2-}(aq) + 2\text{H}_2\text{O}(l) + 2\text{MnO}_4^-(aq) \rightarrow 3\text{SO}_4^{2-}(aq) + 2\text{MnO}_2(s) + 2\text{OH}^- (aq) \]

8. Make sure that the equation is balanced for mass and for charge

\[ 3\text{SO}_3^{2-}(aq) + \text{H}_2\text{O}(l) + 2\text{MnO}_4^-(aq) \rightarrow 3\text{SO}_4^{2-}(aq) + 2\text{MnO}_2(s) + 2\text{OH}^- (aq) \]

<table>
<thead>
<tr>
<th>Mass:</th>
<th>S = 3</th>
<th>S = 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O = 18</td>
<td>O = 18</td>
</tr>
<tr>
<td></td>
<td>H = 2</td>
<td>H = 2</td>
</tr>
<tr>
<td></td>
<td>Mn = 2</td>
<td>Mn = 2</td>
</tr>
</tbody>
</table>

| Charge: | 3(-2) + 2(-1) = -8 | 3(-2) + 2(-1) = -8 |

✓