4.9 Oxidation – Reduction Reactions

- **Introduction:** Your text uses the reaction between solid sodium metal (Na (s)) and chlorine gas (Cl₂ (g)) as an introduction to the concepts of oxidation and reduction. I would like to start with a different example, the reaction of solid iron metal (Fe (s)) with atmospheric oxygen (O₂ (g)) to form iron (II) oxide (FeO (s)), also known as rust. We can write the equation for this reaction:

\[ 2\text{Fe (s)} + \text{O}_2 \ (g) \rightarrow \text{2FeO (s)} \]

At this point allow me to give you something to memorize that you can use as a foundation for your understanding of the concepts of oxidation and reduction: **Oxidation is what oxygen does.** And we can say, **oxygen is an oxidizing agent.** When oxygen reacts with iron (in the above reaction), it oxidizes the iron.

Now let’s look at the iron (II) oxide. It is a binary ionic compound (You learned this in Chapter 2.) containing iron (II) ions (Fe²⁺) and oxide ions (O²⁻). Since we started with electrically neutral iron and oxygen, we see that the reaction has involved the loss of two electrons from each iron atom and the gain of two electrons by each oxygen atom. If oxidation is what oxygen does, just what was it that oxygen did? The short answer is that it took electrons from iron and kept them for itself. We say that the oxygen oxidized the iron, i. e., the iron became oxidized.

Now we can turn to the example from the text. The reaction is written:

\[ 2\text{Na (s)} + \text{Cl}_2 \ (g) \rightarrow \text{2NaCl (s)} \]

In this reaction, each sodium atom loses one electron, and each chlorine atom gains one. The resulting sodium and chloride ions assemble themselves into a binary ionic compound, much like FeO. In this case we can say that the chlorine oxidized the
sodium, just as the oxygen oxidized the iron. (The biggest difference is that it is not nearly as memorable to say, “Oxidation is what chlorine does.”) Both reactions involve the transfer of electrons, iron to oxygen in the first case, sodium to chlorine in the second. We chemists call reactions like these where electrons are transferred, **oxidation – reduction reactions**. We can also define the shorthand term, **redox reaction**, as an abbreviation for oxidation – reduction reaction.

- **Definitions:** We can define **Oxidation** and **Reduction**:
  - **Oxidation** is a process in which an atom **loses** electrons.
  - **Reduction** is a process in which an atom **gains** electrons.

In the above examples, we can say that the iron and the sodium undergo oxidation, since they lose electrons. And we can say that the oxygen and the chlorine undergo reduction, since they gain electrons.

- **Oxidation – Reduction Reactions That Produce Covalent Products:** When a reaction produces ionic products, it is easy to see whether or not it is a redox reaction. What about a reaction, such as methane burning in oxygen?

\[
\text{CH}_4 (\text{g}) + 2\text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{g})
\]

If oxidation is what oxygen does, then this must be a redox reaction. This being the case, where were the electrons transferred to and from? After all, the products are covalent, so we have no ionic charges to show us where the electrons ended up. We need a new concept, the **oxidation state**.

- **Oxidation States:** The concept of oxidation states (also known as oxidation numbers) gives us a way to track electron transfer, and it is especially useful if the redox reaction produces covalent products. The assignment of oxidation states is a bookkeeping device (but a very useful one) in which the electrons in a covalently bonded molecule or polyatomic ion are arbitrarily assigned to individual atoms.

- **Rules for Assigning Shared Electrons:**
  - **Two Identical Atoms:** For a covalent bond between identical atoms (say, two oxygens or two hydrogens), the shared electrons are divided equally. (This makes sense, because the sharing is equal.)
  - **Two Different Atoms:** In the case of a covalent bond between two different kinds of atoms, the shared electrons
are all assigned to the atom that has the greater attraction for electrons. A good example of how we do this is the water molecule. Here the sharing of bonding electrons is uneven, and these electrons “belong” more to the oxygen than to the hydrogens. So in water we assign all the electrons to the oxygen and none to either hydrogen. Thus, we imagine that each hydrogen atom has lost one electron and bears a charge of +1. And we imagine that the oxygen atom has gained the two electrons and bears a charge of -2. (This doesn’t really happen, but it is a good and useful bookkeeping device.)

- **Assignment of Oxidation States:**
  - **In Molecules and Polyatomic Ions:** We assign oxidation states (or oxidation numbers) to each individual atom in a molecule or in a polyatomic ion as the charges each atom bears after application of the above rules for assigning shared electrons to individual atoms. Thus in water, the oxidation state of the oxygen atom is -2 and the oxidation state of each hydrogen atom is +1.
  - **In Monatomic Ions:** The oxidation state is the same as the ionic charge. For example, the oxidation state of an oxide ion (O\(^{2-}\)) is -2, and the oxidation state of a hydrogen ion (H\(^+\)) is +1.
  - **Rules for Elements, Monatomic Ions, and Fluorine, Oxygen, and Hydrogen in their compounds:** These rules appear in Table 2 from your text (p. 156). However, the “official” rules for CHM 101 are posted on Marty Wallace’s Website.
Additional Rules: Two important rules that do not appear in Table 4.2 are

a) (Wallace Rule 6): The total oxidation number (summed over all atoms) for a compound (neutral molecule) is 0.
b) (Wallace Rule 7): The total oxidation number on a polyatomic ion is the charge on the ion.

Example Problems: Assign oxidation states to all the atoms in the following compounds and ions:

a) CO₂: We don’t have a rule for carbon, but we do for oxygen, and we know that the total must be 0, because we have a neutral molecule:

<table>
<thead>
<tr>
<th>Atom</th>
<th>OS</th>
<th>#</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>x</td>
<td>1</td>
<td>x</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
<td>2</td>
<td>-4</td>
</tr>
</tbody>
</table>

We add up the oxidation states for the atoms and solve for x, the oxidation state of the carbon:

\[ x - 4 = 0 \]
\[ x = \text{OS}_C = +4 \]
b) \( \text{SF}_6 \): We don’t have a rule for sulfur, but we do for fluorine, and we know that the total must be 0, because we have a neutral molecule:

<table>
<thead>
<tr>
<th>Atom</th>
<th>OS</th>
<th>#</th>
<th>( \Sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>x</td>
<td>1</td>
<td>x</td>
</tr>
<tr>
<td>F</td>
<td>-6</td>
<td>6</td>
<td>-6</td>
</tr>
<tr>
<td>( \text{SF}_6 )</td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

We add up the oxidation states for the atoms and solve for \( x \), the oxidation state of the sulfur:

\[
x - 6 = 0
\]

\[
x = \text{OS}_S = +6
\]

c) \( \text{NO}_3^- \): We don’t have a rule for nitrogen, but we do for oxygen, and we know that the total must be -1, because we have an ion with a charge of -1:

<table>
<thead>
<tr>
<th>Atom</th>
<th>OS</th>
<th>#</th>
<th>( \Sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>x</td>
<td>1</td>
<td>x</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
<td>3</td>
<td>-6</td>
</tr>
<tr>
<td>( \text{NO}_3^- )</td>
<td></td>
<td></td>
<td>-1</td>
</tr>
</tbody>
</table>

We add up the oxidation states for the atoms and solve for \( x \), the oxidation state of the nitrogen:

\[
x - 6 = -1
\]

\[
x = \text{OS}_N = +5
\]

d) \( \text{Fe}_3\text{O}_4 \): We don’t have a rule for iron, but we do for oxygen, and we know that the total must be 0, because we have neutral molecule:

<table>
<thead>
<tr>
<th>Atom</th>
<th>OS</th>
<th>#</th>
<th>( \Sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>x</td>
<td>3</td>
<td>3x</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
<td>4</td>
<td>-8</td>
</tr>
<tr>
<td>( \text{Fe}_3\text{O}_4 )</td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

We add up the oxidation states for the atoms and solve for \( x \), the oxidation state of the nitrogen:

\[
3x - 8 = 0
\]

\[
x = \text{OS}_\text{Fe} = +8/3
\]

This looks strange. How can we have fractional charges on the iron atoms? Our resolution is to say
that two of the iron atoms are in oxidation states of +3, and the third is in an oxidation state of +2. Or we could simply say that 8 electrons were transferred from elementary iron to oxygen in the reaction that formed the Fe₃O₄.

\[ 3\text{Fe (s)} + 4\text{O}_2 (g) \rightarrow \text{Fe}_3\text{O}_4 (s) \]

- **Characteristics of Oxidation – Reduction Reactions:** Now we can state that an oxidation – reduction reaction is a reaction in which electrons are transferred. Sometimes the transfer is explicitly obvious, as when two elements react to form an ionic product:

\[ 2\text{Na (s)} + \text{Cl}_2 (g) \rightarrow 2\text{NaCl (s)} \]

But when the products are covalent, the electron transfer, if there is any, is not so clear. That is where oxidation states are useful, as in the combustion of methane in air:

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \]

If we look at the oxidation states of the individual atom types on each side of this reaction, we see that the carbon atom loses 8 electrons (in changing oxidation states from −4 to +4) and that the 4 oxygen atoms together gain 8 electrons (in changing oxidation states from 0 to −2). (The hydrogens do not participate in this electron transfer.)

- **Definitions:** We summarize Section 4.9 by defining some important terms. Let us first recall that:
  - **Oxidation** is what oxygen does.
  - **Oxygen** is an oxidizing agent.

Now we can define:

- **Oxidation** is an increase in oxidation state (a loss of electrons).
- **Reduction** is a decrease in oxidation state (a gain of electrons).

In the reaction of sodium metal with chlorine gas:
sodium is oxidized (as the electron donor, it loses electrons), and chlorine is reduced (as the electron acceptor, it gains electrons), but be careful. Chlorine is the **oxidizing agent** because it oxidizes the sodium, and sodium is the **reducing agent** because it reduces chlorine.

Now we should add one more statement about the role of oxygen when it is involved in a redox reaction:

- **After doing what it does, oxygen ends up reduced.**

The three statements about oxygen bear repetition:

1. **Oxidation is what oxygen does.**
2. **Oxygen is an oxidizing agent.**
3. **After doing what it does, oxygen ends up reduced.**

Figure 4.20 from the text is a good summary of a generic oxidation – reduction process:
• **Revisiting the Oxidation of Methane in Oxygen:** Let us return to the oxidation of methane in oxygen:

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)
\]

<table>
<thead>
<tr>
<th>Oxidized</th>
<th>Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>loses electrons</td>
<td>gains electrons</td>
</tr>
<tr>
<td>oxidation state increases</td>
<td>oxidation state decreases</td>
</tr>
<tr>
<td>reducing agent</td>
<td>oxidizing agent</td>
</tr>
</tbody>
</table>

**FIGURE 4.20**
A summary of an oxidation-reduction process, in which M is oxidized and X is reduced.

Now we can say
Carbon is oxidized. There has been an increase in its oxidation state. It has lost electrons.

Oxygen is reduced. There has been a decrease in its oxidation state. It has gained electrons.

Methane (CH₄) is the reducing agent.

Oxygen (O₂) is the oxidizing agent.

Note that the oxidizing and reducing agents are whole molecules found among the reactants.

Sample Exercise 4.17 (pp. 160-1) Powdered aluminum metal and pulverized iodine crystals are mixed, and a reaction between them is triggered with a drop of water. The reaction is vigorous. The mixture erupts in flames and some of the excess I₂ vaporizes as a purple cloud of smoke. The equation for the chemical reaction is:

$$2\text{Al (s)} + 3\text{I}_2 (s) \rightarrow 2\text{AlI}_3 (s)$$

Identify the atoms that are oxidized and reduced and identify the oxidizing and reducing agents.

We start by listing the oxidation states of the various atoms in the reaction:

<table>
<thead>
<tr>
<th>Atom</th>
<th>in</th>
<th>Oxidation State</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Al (s)</td>
<td>0</td>
<td>free element</td>
</tr>
<tr>
<td>I</td>
<td>I₂ (s)</td>
<td>0</td>
<td>free element</td>
</tr>
<tr>
<td>Al</td>
<td>AlI₃ (s)</td>
<td>+3</td>
<td>ionic charge is 3+</td>
</tr>
<tr>
<td>I</td>
<td>AlI₃ (s)</td>
<td>−1</td>
<td>ionic charge is −</td>
</tr>
</tbody>
</table>

With this information, we can write the answers:

- Aluminum atoms are oxidized. Their oxidation state changes from 0 to +3 as each atom loses 3 electrons.
- Iodine atoms are reduced. Their oxidation state changes from 0 to −1 as each atom gains 1 electron.
- Aluminum (Al (s)) is the reducing agent.
- Iodine (I₂ (s)) is the oxidizing agent.

Sample Exercise 4.18 (pp. 161-2) The production of metallic lead from its ore, galena (PbS (s)) is a two step process. The first step is the conversion (roasting) of the galena to produce lead (II) oxide:
\[ 2\text{PbS (s)} + 3\text{O}_2 (g) \rightarrow 2\text{PbO (s)} + 2\text{SO}_2 (g) \]

The (lead (II)) oxide is then treated with carbon monoxide (CO \((g)\)) to produce free lead:

\[ \text{PbO (s)} + \text{CO (g)} \rightarrow \text{Pb (s)} + \text{CO}_2 (g) \]

Identify the atoms that are oxidized and reduced and identify the oxidizing and reducing agents in both steps.

We start by listing the oxidation states of the various atoms in the first step:

<table>
<thead>
<tr>
<th>Atom in</th>
<th>Oxidation State</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>(+2)</td>
<td>ionic charge is 2+</td>
</tr>
<tr>
<td>S</td>
<td>(-2)</td>
<td>ionic charge is 2—</td>
</tr>
<tr>
<td>O</td>
<td>(0)</td>
<td>free element</td>
</tr>
<tr>
<td>Pb</td>
<td>(+2)</td>
<td>ionic charge is 2+</td>
</tr>
<tr>
<td>O</td>
<td>(-2)</td>
<td>(rule 4)</td>
</tr>
<tr>
<td>O</td>
<td>(-2)</td>
<td>(rule 4)</td>
</tr>
<tr>
<td>S</td>
<td>(+4)</td>
<td>to balance O</td>
</tr>
</tbody>
</table>

With this information, we can write the answers for the first stage:

- Sulfur atoms are oxidized. Their oxidation state changes from \(-2\) to \(+4\) as each atom loses 6 electrons.
- Oxygen atoms are reduced. Their oxidation state changes from \(0\) to \(-2\) as each atom gains 2 electron.
- Lead (II) sulfide (\(\text{PbS (s)}\)) is the reducing agent.
- Oxygen (\(\text{O}_2 (g)\)) is the oxidizing agent.

Now we list the oxidation states of the various atoms in the second step:

<table>
<thead>
<tr>
<th>Atom in</th>
<th>Oxidation State</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>(+2)</td>
<td>ionic charge is 2+</td>
</tr>
<tr>
<td>O</td>
<td>(-2)</td>
<td>(rule 4)</td>
</tr>
<tr>
<td>O</td>
<td>(-2)</td>
<td>(rule 4)</td>
</tr>
<tr>
<td>C</td>
<td>(+2)</td>
<td>to balance O</td>
</tr>
<tr>
<td>Pb</td>
<td>(0)</td>
<td>free element</td>
</tr>
</tbody>
</table>
4.10 Balancing Oxidation – Reduction Reactions: Let us preview the second example (pp. 163-5) from the text to get an idea of what kind of problem this can be. The reaction is between iron (II) ions (Fe$^{2+}$) and permanganate ions (MnO$_4^-$) in acid solution to form iron (III) ions (Fe$^{3+}$) and manganese (II) ions (Mn$^{2+}$). The initial unbalanced equation is:

$$\text{MnO}_4^- (aq) + \text{Fe}^{2+} (aq) \rightarrow \text{Mn}^{2+} (aq) + \text{Fe}^{3+} (aq)$$

Upon balancing, the equation becomes:

$$\text{MnO}_4^- (aq) + 5\text{Fe}^{2+} (aq) + 8\text{H}^+ (aq) \rightarrow \text{Mn}^{2+} (aq) + 5\text{Fe}^{3+} (aq) + 4\text{H}_2\text{O} (aq)$$

How on earth do we actually balance an equation like this? Is there a system we can use?

- The Half – Reaction Method for Balancing Oxidation – Reduction Reactions in Aqueous Solution
  - The good news is: yes, there is a system. Consider the redox reaction between cerium (IV) ion and tin (II) ion, for which the unbalanced equation is:

$$\text{Ce}^{4+} (aq) + \text{Sn}^{2+} (aq) \rightarrow \text{Ce}^{3+} (aq) + \text{Sn}^{4+} (aq)$$

The key to the system is to separate the reaction into two half-reactions. One of them is for the species that becomes reduced:

$$\text{Ce}^{4+} (aq) \rightarrow \text{Ce}^{3+} (aq)$$

The other is for the species that becomes oxidized:
Sn\(^{2+}\) (aq) ——>Sn\(^{4+}\) (aq)

Each half – reaction is then balanced separately. Then they can be recombined to form the final balanced equation for the redox reaction.

- **The Half – Reaction Method, Step-by-Step:**
  - Write separate equations for the oxidation and reduction half – reactions. We just did this for the cerium (IV) ion – tin (II) ion reaction.
  - For each half – reaction:
    - a) Balance all the elements except hydrogen and oxygen.
    - b) Balance oxygen using H\(_2\)O.
    - c) Balance hydrogen using H\(^+\).
    - d) Balance the charge using electrons.
      
      Steps 2a, 2b, & 2c are not necessary for the cerium (IV) ion – tin (II) ion reaction. Step 2d gives us:
      
      \[
e^{-} + \text{Ce}^{4+} (aq) ——> \text{Ce}^{3+} (aq)
\]
      
      And:
      
      \[
      \text{Sn}^{2+} (aq) ——>\text{Sn}^{4+} (aq) + 2e^{-}
      \]
  - If necessary, multiply one or both half – reactions by a suitable integer to equalize the numbers of electrons transferred in the two half – reactions. In our example, we multiply the half – reaction involving cerium by 2 so that two electrons are transferred in each half – reaction:
      
      \[
      2e^{-} + 2\text{Ce}^{4+} (aq) ——> 2\text{Ce}^{3+} (aq)
      \]
  - Add the half – reactions back together and cancel identical species. We have only electrons to cancel in the cerium (IV) ion – tin (II) ion reaction.
      
      \[
      2e^{-} (aq) + 2\text{Ce}^{4+} + \text{Sn}^{2+} (aq) ——> 2\text{Ce}^{3+} (aq) + \text{Sn}^{4+} (aq) + 2e^{-}
      \]
      
      \[
      2\text{Ce}^{4+} + \text{Sn}^{2+} (aq) ——> 2\text{Ce}^{3+} (aq) + \text{Sn}^{4+} (aq)
      \]
  - Check that the elements and the charges are balanced. We have 2 cerium atoms, 1 tin atom, and net
charges of 10+ on either side of the final equation. It is balanced.

- **Balancing the Iron (II) – Permanganate Reaction** (pp. 163-5): Now we return to the problem of balancing the reaction between iron (II) ions (Fe2+) and permanganate ions (MnO4—) in acid solution to form iron (III) ions (Fe3+) and manganese (II) ions (Mn2+). The initial unbalanced equation is:

\[
\text{MnO}_4^- (aq) + \text{Fe}^{2+} (aq) \rightarrow \text{Mn}^{2+} (aq) + \text{Fe}^{3+} (aq)
\]

This separates into the half – reactions:

\[
\text{MnO}_4^- (aq) \rightarrow \text{Mn}^{2+} (aq)
\]

For reduction, and:

\[
\text{Fe}^{2+} (aq) \rightarrow \text{Fe}^{3+} (aq)
\]

For oxidation. Since Mn and Fe are already balanced, we do not need to apply step 2a. Proceeding to step 2b, we balance the oxygens in the reduction half - reaction:

\[
\text{MnO}_4^- (aq) \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O} (l)
\]

Now we have hydrogens (step 2c) that need balancing:

\[
\text{MnO}_4^- (aq) + 8\text{H}^+ (aq) \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O} (l)
\]

This achieves full element balance in both half – reactions. Now we must balance the charge with electrons in each half – reaction (step 2d):

\[
5\text{e}^- + \text{MnO}_4^- (aq) + 8\text{H}^+ (aq) \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O} (l)
\]

\[
\text{Fe}^{2+} (aq) \rightarrow \text{Fe}^{3+} (aq) + \text{e}^-
\]

We can check that these numbers of electrons are correct by looking at changes in oxidation states. Manganese starts with an oxidation state of +7 and ends at +2, a difference of 5 that is consistent with it gaining 5 electrons. Iron starts at +3 and ends at +2, consistent with each iron losing 1 electron.

Now we apply step 3 and equalize the electrons between the two half - reactions:

\[
5\text{e}^- + \text{MnO}_4^- (aq) + 8\text{H}^+ (aq) \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O} (l)
\]

\[
5\text{Fe}^{2+} (aq) \rightarrow 5\text{Fe}^{3+} (aq) + 5\text{e}^-
\]
The two half-reactions are now ready to be recombined (step 4):

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

The 5 electrons on each side cancel to give us our final result:

\[ MnO_4^- (aq) + 8H^+ (aq) + 5Fe^{2+} (aq) \rightarrow Mn^{2+} (aq) + 4H_2O (l) + 5Fe^{3+} (aq) \]

We check for balance. Each side has 1 manganese, 4 oxygens, 8 hydrogens, 5 irons, and a net charge of 17+. It is balanced.

- **Sample Exercise 4.19** (pp. 165-6): Potassium dichromate (K₂Cr₂O₇) can be dissolved in water to produce a bright orange solution. It is a powerful oxidizing agent that can be reduced to blue-violet chromium (III) ions (Cr³⁺ (aq)) by a suitable reducing agent, such as ethyl alcohol (C₂H₅OH). Assuming acidic conditions (presence of H⁺ (aq) ions), balance the following reaction, using the half-reaction method:

\[ H^+ (aq) + Cr_2O_7^{2-} (aq) + C_2H_5OH (aq) \rightarrow Cr^{3+} (aq) + CO_2 (g) + H_2O (l) \]

We will work this example on the whiteboard.

- **Balancing Redox Reactions in Basic Media:** We can use the same basic half-reaction procedure we just learned for acidic media, but we need to make some adjustments in the end.
  - Use the half-reaction method as specified for acidic solutions to obtain a balanced redox equation as if H⁺ (aq) ions were present.
  - To both sides of this equation add a number of OH⁻ (aq) ions that matches the number of H⁺ (aq) ions in the equation. This will “create” OH⁻ (aq) ions on the side of the equation originally lacking H⁺ (aq) ions, and will allow us to combine OH⁻ (aq) ions with all the H⁺ (aq) ions to form H₂O (l).
  - Eliminate the H⁺ (aq) ions and OH⁻ (aq) ions on the side where both are present, forming H₂O (l) molecules in their place. Then cancel H₂O (l) molecules as appropriate.
  - Check that elements and charges are balanced.
Sample Exercise 4.20 (pp. 167-8): An aqueous solution containing cyanide ion (CN⁻ (aq)) is capable of dissolving metallic silver (Ag (s)). The process involves oxygen gas (O₂ (g)) and the unbalanced (redox) reaction is written:

\[ \text{Ag (s)} + \text{CN}^- (aq) + \text{O}_2 (g) \rightarrow \text{Ag(CN)}_2^- (aq) \]

Assume the reaction takes place in basic media (containing OH⁻ (aq) ions).

First we balance the reaction, assuming temporarily that H⁺ (aq) ions are present. The oxidation half-reaction is:

\[ \text{Ag (s)} + \text{CN}^- (aq) \rightarrow \text{Ag(CN)}_2^- (aq) \]

Silver is already balanced, so we balance C and N:

\[ \text{Ag (s)} + 2\text{CN}^- (aq) \rightarrow \text{Ag(CN)}_2^- (aq) \]

There are no oxygens or hydrogens, so we balance the charge with electrons:

\[ \text{Ag (s)} + 2\text{CN}^- (aq) \rightarrow \text{Ag(CN)}_2^- (aq) + \text{e}^- \]

We check the number of electrons by noting that the oxidation state of silver changes from 0 to +1, consistent with the loss of 1 electron.

Now we balance the reduction half-reaction:

\[ \text{O}_2 (g) \rightarrow \]

We need 2 waters to balance oxygen:

\[ \text{O}_2 (g) \rightarrow 2\text{H}_2\text{O (l)} \]

Now we need 4 H⁺ (aq) ions to balance hydrogen:

\[ \text{O}_2 (g) + 4\text{H}^+ (aq) \rightarrow 2\text{H}_2\text{O (l)} \]

And 4 electrons to balance the charge:

\[ 4\text{e}^- + \text{O}_2 (g) + 4\text{H}^+ (aq) \rightarrow 2\text{H}_2\text{O (l)} \]

We check this number of electrons by noting that the oxidation state of oxygen changes from 0 to -2. Thus we need 2 electrons for each of the 2 oxygen atoms.

We need to multiply the oxidation half-reaction by 4 to equalize electrons in the two half-reactions:

\[ 4\text{Ag (s)} + 8\text{CN}^- (aq) \rightarrow 4\text{Ag(CN)}_2^- (aq) + 4\text{e}^- \]

Now we recombine the two half reactions and cancel the electrons:

\[ 4\text{e}^- + 4\text{Ag (s)} + 8\text{CN}^- (aq) + \text{O}_2 (g) + 4\text{H}^+ (aq) \rightarrow \]
\[4\text{Ag(CN)}_2^-(aq) + 2\text{H}_2\text{O}(l) + 4\text{e}^-\]

\[4\text{Ag}(s) + 8\text{CN}^-(aq) + \text{O}_2(g) + 4\text{H}^+(aq) \rightarrow 4\text{Ag(CN)}_2^-(aq) + 2\text{H}_2\text{O}(l)\]

Now we add OH\(^-\) (aq) ions to both sides of the balanced equation. We need 4 of them to combine with the 4 H\(^+\) (aq) ions on the left hand side:

\[4\text{Ag}(s) + 8\text{CN}^-(aq) + \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{OH}^-(aq) \rightarrow 4\text{Ag(CN)}_2^-(aq) + 2\text{H}_2\text{O}(l) + 4\text{OH}^-(aq)\]

We combine the H\(^+\) (aq) ions with the OH\(^-\) (aq) ions on the left hand side to form water:

\[4\text{Ag}(s) + 8\text{CN}^-(aq) + \text{O}_2(g) + 4\text{H}_2\text{O}(l) \rightarrow 4\text{Ag(CN)}_2^-(aq) + 2\text{H}_2\text{O}(l) + 4\text{OH}^-(aq)\]

Finally we cancel 2 waters on each side:

\[4\text{Ag}(s) + 8\text{CN}^-(aq) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{Ag(CN)}_2^-(aq) + 4\text{OH}^-(aq)\]

Checking for balance, we count 4 Ag, 8 C, 8 N, 4 O, 4 H, and net charges of \(-8\) on each side of the equation. The equation is balanced.

**4.11 Stoichiometry of Redox Reactions:** I have good news for you. You already know enough about working stoichiometry problems so that you don’t need to learn anything new.