Worksheet 25 - Oxidation/Reduction Reactions

Oxidation number rules:

**Elements** have an oxidation number of 0

**Group I** and **II** – In addition to the elemental oxidation state of 0, Group I has an oxidation state of +1 and Group II has an oxidation state of +2.

**Hydrogen** – usually +1, except when bonded to Group I or Group II, when it forms hydrides, -1.

**Oxygen** – usually -2, except when it forms a O-O single bond, a peroxide, when it is -1.

**Fluorine** is always -1. Other halogens are usually -1, except when bonded to O.

1. **Assign oxidation numbers** to each of the atoms in the following compounds:

   - \( \text{Na}_2\text{CrO}_4 \)  
     - Na = +1  
     - O = -2  
     - Cr = +6

   - \( \text{K}_2\text{Cr}_2\text{O}_7 \)  
     - K = +1  
     - O = -2  
     - Cr = +6

   - \( \text{CO}_2 \)  
     - O = -2  
     - C = +4

   - \( \text{CH}_4 \)  
     - H = +1  
     - C = -4

   - \( \text{HClO}_4 \)  
     - O = -2  
     - H = +1  
     - Cl = +7

   - \( \text{MnO}_2 \)  
     - O = -2  
     - Mn = +4

   - \( \text{SO}_3^{2-} \)  
     - O = -2  
     - S = +4

   - \( \text{SF}_4 \)  
     - F = -1  
     - S = +4

   a. What is the range of oxidation states for **carbon**? -4 to +4

   b. Which compound has C in a +4 state? \( \text{CO}_2 \)

   c. Which compound has C in a -4 state? \( \text{CH}_4 \)
2. Nitrogen has 5 valence electrons (Group V). It can gain up to 3 electrons (-3), or lose up to 5 (+5) electrons. Fill in the missing names or formulas and assign an oxidation state to each of the following nitrogen containing compounds:

<table>
<thead>
<tr>
<th>name</th>
<th>formula</th>
<th>oxidation state of N</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>NH₃</td>
<td>-3</td>
</tr>
<tr>
<td>nitrogen</td>
<td>N₂</td>
<td>0</td>
</tr>
<tr>
<td>nitrite</td>
<td>NO₂⁻</td>
<td>+3</td>
</tr>
<tr>
<td>nitrate</td>
<td>NO₃⁻</td>
<td>+5</td>
</tr>
<tr>
<td>dinitrogen monoxide</td>
<td>N₂O</td>
<td>+1</td>
</tr>
<tr>
<td>nitrogen dioxide</td>
<td>NO₂</td>
<td>+4</td>
</tr>
<tr>
<td>hydroxylamine</td>
<td>NH₂OH</td>
<td>-1</td>
</tr>
<tr>
<td>nitrogen monoxide</td>
<td>NO</td>
<td>+2</td>
</tr>
<tr>
<td>hydrazine</td>
<td>N₂H₄</td>
<td>-2</td>
</tr>
</tbody>
</table>

3. During chemical reactions, the oxidation state of atoms can change. This occurs when compounds gain or lose electrons, or when the bonds to an atom change. This is illustrated by the reaction between nitrogen and hydrogen to make ammonia:

\[ \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g}) \]

a. Assign oxidation numbers to each of the atoms in this reaction.

\[ \text{N (in N}_2) = 0 \quad \text{in NH}_3 = -3 \]
\[ \text{H (in H}_2) = 0 \quad \text{H (in NH}_3) = +1 \]

When an oxidation number increases, that species has been oxidized.

b. Which reactant undergoes an increase in its oxidation number? \[ \text{H}_2 \]

When an oxidation number decreases, that species has been reduced.

c. Which reactant undergoes a decrease in its oxidation number? \[ \text{N}_2 \]
The species that is oxidized is called the **reducing agent** because it gives up an electron, so that another species can gain an electron (be reduced).

d. What is the reducing agent in this reaction? $H_2$

The species that is reduced is called the **oxidizing agent** because it takes an electron away from another group, raising that group’s oxidation number.

e. What is the oxidizing agent in this reaction? $N_2$

4. In each of the following reactions, assign oxidation numbers to all of the elements and identify the oxidizing and reducing agents and the change in oxidation number.

a. $4 \text{Fe} + 3 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3$

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
</tr>
<tr>
<td>Fe</td>
<td>+3</td>
</tr>
<tr>
<td>change in oxidation number</td>
<td></td>
</tr>
<tr>
<td>oxidizing agent</td>
<td>O$_2$ 0 $\rightarrow$ -2</td>
</tr>
<tr>
<td>reducing agent</td>
<td>Fe 0 $\rightarrow$ +3</td>
</tr>
</tbody>
</table>

b. $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \rightarrow 2 \text{CrO}_4^{2-} + \text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>+6</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
</tr>
<tr>
<td>H</td>
<td>+1</td>
</tr>
<tr>
<td>change in oxidation number</td>
<td></td>
</tr>
<tr>
<td>oxidizing agent</td>
<td>no change in any oxidation numbers;</td>
</tr>
<tr>
<td>reducing agent</td>
<td>not a redox reaction</td>
</tr>
</tbody>
</table>

c. $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$

*Think of this as $\text{NH}_4^+$ and $\text{NO}_2^-$

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-3</td>
</tr>
<tr>
<td>N</td>
<td>+1</td>
</tr>
<tr>
<td>H</td>
<td>+3</td>
</tr>
<tr>
<td>H</td>
<td>+1</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
</tr>
<tr>
<td>change in oxidation number</td>
<td></td>
</tr>
<tr>
<td>oxidizing agent</td>
<td>NH$_4$NO$_2$</td>
</tr>
<tr>
<td>reducing agent</td>
<td>NH$_4$NO$_2$</td>
</tr>
</tbody>
</table>

*The nitrogens are in different states*

d. $\text{P}_4 + 10 \text{Cl}_2 \rightarrow 4 \text{PCl}_5$

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0</td>
</tr>
<tr>
<td>Cl</td>
<td>0</td>
</tr>
<tr>
<td>change in oxidation number</td>
<td></td>
</tr>
<tr>
<td>oxidizing agent</td>
<td>Cl$_2$ 0 $\rightarrow$ -1</td>
</tr>
<tr>
<td>reducing agent</td>
<td>P$_4$ 0 $\rightarrow$ +5</td>
</tr>
</tbody>
</table>

e. $2 \text{Cr}^{3+} + \text{H}_2\text{O} + 6\text{ClO}_3^- \rightarrow \text{Cr}_2\text{O}_7^{2-} + 6\text{ClO}_2 + 2\text{H}^+$

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>+5</td>
</tr>
<tr>
<td>Cl</td>
<td>+4</td>
</tr>
<tr>
<td>Cl</td>
<td>+3</td>
</tr>
<tr>
<td>Cr</td>
<td>+3</td>
</tr>
<tr>
<td>Cr</td>
<td>+1</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
</tr>
<tr>
<td>H</td>
<td>+1</td>
</tr>
<tr>
<td>change in oxidation number</td>
<td></td>
</tr>
<tr>
<td>oxidizing agent</td>
<td>ClO$_3^-$ +5 $\rightarrow$ +4</td>
</tr>
<tr>
<td>reducing agent</td>
<td>Cr$_3^+$ +3 $\rightarrow$ +6</td>
</tr>
</tbody>
</table>
Balancing Redox Reactions

Oxidation/Reduction (Redox) reactions can be balanced using the oxidation state changes, as seen in the previous example. However, there is an easier method, which involves breaking a redox reaction into two half-reactions. This is best shown by working an example.

Hydrobromic acid will react with permanganate to form elemental bromine and the manganese(II) ion. The unbalanced, net reaction is shown below,

\[ \text{Br}^- + \text{MnO}_4^- \rightarrow \text{Br}_2 + \text{Mn}^{2+} \]

5. Break this into two half-reactions, one involving bromine and the other involving manganese.

<table>
<thead>
<tr>
<th>Bromine half-reaction</th>
<th>Manganese half-reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br(^-) → Br(_2)</td>
<td>MnO(_4)^- → Mn(^{2+})</td>
</tr>
</tbody>
</table>

6. First balance the bromine half-reaction first.
   a. Balance the bromine atoms of the reaction
      \[ 2\text{Br}^- \rightarrow 1\text{Br}_2 \]
   b. Now balance charge by adding electrons (e\(^-\))
      \[ 2\text{Br}^- \rightarrow 1\text{Br}_2 + 2\text{e}^- \]

This half-reaction is producing/consuming electrons. This is an oxidation/reduction half-reaction. Confirm this by assigning oxidation numbers to the bromine species.

\[ \text{Br}^- = -1 \quad \text{Br}_2 = 0 \quad \text{(oxidation state increases; oxidation)} \]

7. Next, balance the manganese half-reaction.
   a. Balance the manganese atoms of the half-reaction
      \[ 1\text{MnO}_4^- \rightarrow 1\text{Mn}^{2+} \]
   b. Next, balance oxygen by adding water molecules (H\(_2\)O)
      \[ 1\text{MnO}_4^- \rightarrow 1\text{Mn}^{2+} + 4\text{H}_2\text{O} \]
c. Next, balance hydrogen by adding protons (\(H^+\))

\[8H^+ + \underline{1} \text{MnO}_4^- \rightarrow \underline{1} \text{Mn}^{2+} + 4\text{H}_2\text{O}\]

d. Finally, balance charge by adding electrons (\(e^-\)).

\[5e^- + 8H^+ + \underline{1} \text{MnO}_4^- \rightarrow \underline{1} \text{Mn}^{2+} + 4\text{H}_2\text{O}\]

This half-reaction is producing/consuming electrons. This is a oxidation/reduction half-reaction. Confirm this by assigning oxidation numbers to the manganese atoms.

\[
\begin{align*}
\text{MnO}_4^- &= +7 \\
\text{Mn}^{2+} &= +2
\end{align*}
\]

+7 \(\rightarrow\) 2 is a reduction

Notice that the number of electrons equals the change in oxidation number.

8. Now put the two half-reactions together. The number of electrons produced must equal the number of electrons consumed.

\[2 \text{Br}^- \rightarrow \text{Br}_2 + 2e^- \quad 5e^- + 8H^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}\]

multiply this half-reaction by \(5\) multiply this half-reaction by \(2\)

\[
\begin{align*}
10 \text{Br}^- & \rightarrow 5 \text{Br}_2 + 10e^- \\
10e^- + 16H^+ + 2\text{MnO}_4^- & \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O}
\end{align*}
\]

Add the two half-reactions, canceling out species that appear on both sides (including electrons) 10 e\(^-\) appear on both sides. Cancel those out to obtain

\[
\begin{align*}
10\text{Br}^- + 16H^+ + 2\text{MnO}_4^- & \rightarrow 5\text{Br}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}
\end{align*}
\]

Which compound is the oxidizing agent? \(\text{MnO}_4^-\) (gets reduced)

Which compound is the reducing agent? \(\text{Br}^-\) (gets oxidized)

Notice that there are protons (\(H^+\)) present in the reactants. This indicates that the reaction is carried out in an acidic solution. To carry this out in a basic solution, simply add enough hydroxide ions (\(\text{OH}^-\)) to each side of the equation to neutralize the protons. The product of the neutralization reaction will be water.

Add 16 \(\text{OH}^-\) to each side. On the left side, 16 \(H^+ + 16 \text{OH}^- = 16\text{H}_2\text{O}\)

The overall balanced reaction under basic conditions is:

\[
\begin{align*}
10\text{Br}^- + 2\text{MnO}_4^- + 16\text{H}_2\text{O} & \rightarrow 5\text{Br}_2 + 2\text{Mn}^{2+} + 8\text{OH}^- + 8\text{H}_2\text{O} \\
10\text{Br}^- + 2\text{MnO}_4^- + 8\text{H}_2\text{O} & \rightarrow 5\text{Br}_2 + 2\text{Mn}^{2+} + 8\text{OH}^-
\end{align*}
\]
Now, balance the redox reaction between methanol and dichromate, which produces methanal and chromium (III), as shown below:

\[
\begin{align*}
-2 & +1 & -2 & +1 & +6 & -2 & 0 & +1 & -2 & +3 \\
\text{CH}_3\text{OH} + \text{Cr}_2\text{O}_7^{2-} & \rightarrow \text{CH}_2\text{O} + \text{Cr}^{3+}
\end{align*}
\]

First, separate this into two half-reactions

\[
\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} \quad \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}
\]

Then, balance the redox active species.

\[
\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} \quad \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}
\]

Then, balance oxygens with H2O

\[
\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} \quad \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

Balance hydrogen with H+.

\[
\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + 2\text{H}^+ \quad 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

Balance charge with electrons.

\[
\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \quad 6\text{e}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

Equalize the number of electrons lost and gained

\[
2 \text{ total e}^-; \text{ multiply by 3 to get 6} \quad 6 \text{ total e}^-; \text{ multiply by 1 to get 6}
\]

Combine the two equations to get...

\[
3\text{CH}_3\text{OH} + 6\text{e}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 3\text{CH}_2\text{O} + 6\text{H}^+ + 6\text{e}^- + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

Simplify by canceling out all the electrons and 6H+ from each side...

\[
3\text{CH}_3\text{OH} + 8\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 3\text{CH}_2\text{O} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

This indicates that the reaction must be carried out in an **acidic** solution.

To carry it out in a **basic** solution, just add enough OH- to neutralize the acid, H+.

Add 8 OH- to each side of the equation. On the left, the H+ and OH- form H2O.

\[
3\text{CH}_3\text{OH} + 8\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 8\text{OH}^- \rightarrow 3\text{CH}_2\text{O} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 8\text{OH}^-  \\
3\text{CH}_3\text{OH} + 8\text{H}_2\text{O} + \text{Cr}_2\text{O}_7^{2-} \rightarrow 3\text{CH}_2\text{O} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 8\text{OH}^-
\]

Cancel out water molecules that appear on both sides (7 total)...  

\[
3\text{CH}_3\text{OH} + \text{H}_2\text{O} + \text{Cr}_2\text{O}_7^{2-} \rightarrow 3\text{CH}_2\text{O} + 2\text{Cr}^{3+} + 8\text{OH}^-
\]
Balance the following redox-reaction which takes place in basic solutions.

$$\begin{align*}
\text{Zn (s)} + \text{NO}_2^- & \rightarrow \text{NH}_3 + \text{Zn(OH)}_4^{2-} \\
4\text{H}_2\text{O} + \text{Zn} & \rightarrow \text{Zn(OH)}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \\
7\text{H}^+ + 6\text{e}^- + \text{NO}_2^- & \rightarrow \text{NH}_3 + 2\text{H}_2\text{O}
\end{align*}$$

(multiply by 3) (multiply by 1)

Combine the two equations to get...

$$\begin{align*}
12\text{H}_2\text{O} + 3\text{Zn} + 7\text{H}^+ + 6\text{e}^- + \text{NO}_2^- & \rightarrow 3\text{Zn(OH)}_4^{2-} + 12\text{H}^+ + 6\text{e}^- + \text{NH}_3 + 2\text{H}_2\text{O} \\
10\text{H}_2\text{O} + 3\text{Zn} + \text{NO}_2^- & \rightarrow 3\text{Zn(OH)}_4^{2-} + 5\text{H}^+ + \text{NH}_3
\end{align*}$$

Add 5 OH\(^{-}\) to each side (b/c there are currently 5H\(^{+}\) on the right-hand side) to create basic conditions...

$$\begin{align*}
10\text{H}_2\text{O} + 3\text{Zn} + \text{NO}_2^- + 5\text{OH}^- & \rightarrow 3\text{Zn(OH)}_4^{2-} + 5\text{H}^+ + \text{NH}_3 + 5\text{OH}^- \\
10\text{H}_2\text{O} + 3\text{Zn} + \text{NO}_2^- + 5\text{OH}^- & \rightarrow 3\text{Zn(OH)}_4^{2-} + 5\text{H}_2\text{O} + \text{NH}_3
\end{align*}$$

Simplify the expression by eliminating extra water:

$$\begin{align*}
5\text{H}_2\text{O} + 3\text{Zn} + \text{NO}_2^- + 5\text{OH}^- & \rightarrow 3\text{Zn(OH)}_4^{2-} + \text{NH}_3
\end{align*}$$