DETERMINING OXIDATION STATES

The determination of oxidation states is based on knowing which elements can have only one oxidation state other than the elemental state and which elements are able to form more than one oxidation state other than the elemental state. Let's look at some of the "rules" for determining the oxidation states.

1. The oxidation state of an element is always zero.
2. For metals, the charge of the ion is the same as the oxidation state. The following metals form only one ion: Group IA, Group IIA, Group IIIA (except Tl), Zn$^{2+}$, Cd$^{2+}$.
3. For monatomic anions and cations, the charge is the same as the oxidation state.
4. Oxygen in a compound is -2, unless a peroxide is present. The oxidation state of oxygen in peroxide ion, O$_2^2-$, is -1.
5. For compounds containing polyatomic ions, use the overall charge of the polyatomic ion to determine the charge of the cation.

Here is a convenient method for determining oxidation states. Basically, you treat the charges in the compound as a simple algebraic expression. For example, let's determine the oxidation states of the elements in the compound, KMnO$_4$. Applying rule 2, we know that the oxidation state of potassium is +1. We will assign "x" to Mn for now, since manganese may be of several oxidation states. There are 4 oxygens at -2 apiece. The overall charge of the compound is zero:

\[
\begin{align*}
K &\quad Mn &\quad O_4 \\
+1 &\quad x &\quad 4(-2)
\end{align*}
\]

The algebraic expression generated is:

\[
1 + x - 8 = 0
\]

Solving for x gives the oxidation state of manganese:

\[
x - 7 = 0 \\
x = +7
\]

\[
\begin{align*}
K &\quad Mn &\quad O_4 \\
+1 &\quad +7 &\quad 4(-2)
\end{align*}
\]

Suppose the species under consideration is a polyatomic ion. For example, what is the oxidation state of chromium in dichromate ion, (Cr$_2$O$_7^{2-}$)? As before, assign the oxidation state for oxygen, which is known to be -2. Since the oxidation state for chromium is not known, and two chromium atoms are present, assign the algebraic value of 2x for chromium:

\[
\begin{align*}
Cr_2 &\quad O_7^{2-} \\
2x &\quad 7(-2)
\end{align*}
\]

Set up the algebraic equation to solve for x. Since the overall charge of the ion is -2, the expression is set equal to -2 rather than 0:

\[
2x + 7(-2) = -2
\]

Solve for x:

\[
2x - 14 = -2 \\
2x = 12 \\
x = +6
\]

Each chromium in the ion has an oxidation state of +6.
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Let's do one last example, where a polyatomic ion is involved. Suppose you need to find the oxidation state of all atoms in Fe₂(CO₃)₃. Here two atoms, iron and carbon, have more than one possible oxidation state. What happens if you don't know the oxidation state of carbon in carbonate ion? In fact, knowledge of the oxidation state of carbon is unnecessary. What you need to know is the charge of carbonate ion (-2). Set up an algebraic expression while considering just the iron ion and the carbonate ion:

$$\text{Fe}_2(\text{CO}_3)_3$$

$$2x \cdot 3(-2)$$

$$2x - 6 = 0$$

$$2x = 6$$

$$x = 3$$

Each iron ion in the compound has an oxidation state of +3.

Next consider the carbonate ion independent of the iron(III) ion:

$$\text{C} \quad \text{O}_3^{2-}$$

$$x \cdot 3(-2)$$

$$x - 6 = -2$$

$$x = +4$$

The oxidation state of carbon is +4 and each oxygen is -2.

Determining the Oxidizing Agent and Reducing Agent

Now that you know how to determine oxidation states, you can figure out the oxidizing agent and reducing agent in a oxidation-reduction reaction. First, let's define oxidizing agent and reducing agent. An oxidizing agent is a substance that causes another substance to be oxidized. It oxidizes another substance by removing the electrons from that substance. The oxidizing agent gains the electrons it is removing from the substance oxidized, thus it becomes reduced. This means the oxidation number of the oxidizing agent becomes less positive. A reducing agent is a substance that causes another substance to be reduced. It reduces another substance by giving away its own electrons to the substance reduced. Thus, the reducing agent loses these electrons and is oxidized. This means the oxidation number of the reducing agent becomes more positive. Using a number line may be helpful in identifying the substances reduced or oxidized and thus whether they are oxidizing agents or reducing agents, respectively.

oxidation number decreased, substance reduced

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<td>-5 -4 -3 -2 -1 0</td>
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oxidation number increased, substance oxidized

Let's look at a redox reaction and identify the substance oxidized, substance reduced, the oxidizing agent and the reducing agent:

$$\text{Cu(s)} + 4 \text{HNO}_3 (aq) \rightarrow \text{Cu(NO}_3)_2 (aq) + 2 \text{NO}_2 (g) + 2 \text{H}_2\text{O (l)}$$

First, determine the oxidation states for each of the atoms in the reactants and products. Elemental copper, Cu(s), has an oxidation state of zero (0).
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For nitric acid, HNO₃:

\[
\begin{align*}
H & \quad N & \quad O_3 \\
+1 & \quad x & \quad 3(-2) \\
1 + x - 6 &= 0 \\
x &= +5 \\
\text{so, } H &= +1, \ N = +5, \ O = -2
\end{align*}
\]

For copper(II) nitrate, Cu(NO₃)₂:

Copper is +2, since two nitrates are each -1.

Nitrate ion:

\[
\begin{align*}
N & \quad O_3 \quad 1^- \\
& \quad x & \quad 3(-2) \\
x - 6 &= -1 \\
x &= +5 \\
\text{so, } Cu &= +2, \ N = +5, \ O = -2
\end{align*}
\]

For nitrogen dioxide, NO₂:

\[
\begin{align*}
N & \quad O_2 \\
x & \quad 2(-2) \\
x - 4 &= 0 \\
x &= +4 \\
\text{so, } N &= +4, \ O = -2
\end{align*}
\]

For water, H₂O:

\[
\begin{align*}
H_2 & \quad O \\
2(+1) & \quad -2 \\
\text{so } H &= +1, \ O = -2
\end{align*}
\]

Next identify the compounds that have changed oxidation states. In this case, copper has changed from having an oxidation state of 0 to +2. Using the number line, one can see that the oxidation number has increased, so copper has been oxidized. Since copper has been oxidized, it is the reducing agent. Copper reduced nitric acid (as we shall see momentarily), by giving away its own electrons to the nitrogen in nitric acid. Since the copper lost these electrons, was oxidized. Similarly, the nitrogen in nitric acid changed from +5 to +4 in nitrogen dioxide. Using the number line, one can see that the oxidation number of nitrogen has decreased, so nitric acid has been reduced (by copper). Since the nitric acid has been reduced, it is the oxidizing agent. Nitric acid has "ripped off" the electrons from the copper to oxidize the copper, thus, in gaining those electrons, it was reduced. These "arguments" seem circular, yet it reinforces that fact that an oxidation cannot occur without also having a reduction.

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