## Assigning Oxidation Numbers

Oxidation numbers are a bookkeeping system used by chemists to describe redox reactions. A redox reaction is a chemical reaction in which changes in oxidation numbers occur.

In many cases oxidation numbers assigned may be identical to the simple monatomic ion charge on the ion. Do not assume that Cl is always -1 , (valence charge). This depends on the application of the assignment of the rules. Transition elements will have various oxidation numbers depending on the compound that they are in.
One must always follow the rules for assigning oxidation numbers as listed below.

1. Oxidation numbers must equal the charge on the molecule, formula unit or ion. For example, $\mathrm{SO}_{4}^{-2}$ indicates the total of the oxidation numbers is equal to -2 . A polyatomic total ion charge equals the oxidation number.
2. The oxidation number of any free element (an element not combined chemically with a different element) is zero. This is not altered by the complexity of its molecules, e.g. $\mathrm{O}_{2}$.
3. Metals in Groups 1A. 2 A and Al have $+1,+2,+3$ oxidation numbers, respectively.
4. H and F in compounds have +1 and -1 oxidation numbers, respectively.
5. Oxygen has a -2 oxidation number.
6. Group 7A has a -1 oxidation number.
7. Group 6A has a -2 oxidation number.
8. Group 5A has a -3 oxidation number.
9. When there is a conflict between two of these rules, the rule with the lower number has priority.

It is important to note that these rules have a priority of application (i.e. rule 4 supersedes rule 5 as in following assignment of oxidation numbers).

$$
\mathrm{O}_{2} \mathrm{~F}_{2} \quad \mathrm{~F}=-1
$$

- The sum of oxidation numbers in a compound must equal zero.
- Therefore, O must $=+1$ so that $\mathrm{O}_{2} \mathrm{~F}_{2}(+2-2)=0$.

If you utilize the oxidation set of rules to determine the oxidation numbers in a binary compound (contains only 2 elements) and are unable to identify specific oxidation numbers, make the following assumptions:

1. The left side of the element will be the positive oxidation number.
2. The sum total of the oxidation numbers will equal zero, a neutral molecule, or the charge of the ion.
3. Treat the problem as an algebraic equation such that the sum of the charges will equal each other and then solve for a set of numbers that will give you whole values for the oxidation numbers.
4. If the compound is a ternary compound, it may be possible that the oxidation numbers will be a fraction or zero, e.g. HOF. In HOF, the values are: $\mathrm{H}=+1, \mathrm{~F}=-1, \mathrm{O}=0$.
5. Examine compound $\mathrm{Cr} \mathrm{Cl}_{3}$.
a. Cl is from Group 7. It has an oxidation number of -1 (Rule 6). Solve for Cr .
b. $\mathrm{CrCl}_{3}=0$
c. $\mathrm{Cr}+3 \mathrm{Cl}=0$

$$
\begin{aligned}
\mathrm{Cr} & =-3 \mathrm{Cl} \\
\mathrm{Cl} & =-1 \quad \mathrm{Cr}=+3
\end{aligned}
$$

2. Examine compound $\mathrm{Cr}_{2} \mathrm{~S}_{3}$.
a. Assume $\mathrm{Cr}^{+}$and $\mathrm{S}=-2$ (Rule 7)
b. $\mathrm{Cr}_{2} \mathrm{~S}_{3}=0$
c. $2 \mathrm{Cr}+3 \mathrm{~S}=0$
$2 \mathrm{Cr}=-3 \mathrm{~S}$
$2 \mathrm{Cr}=+6$
$\mathrm{Cr}=+3$

$$
\begin{aligned}
& \mathrm{S}=-2 \\
& \mathrm{Cr}=+3
\end{aligned}
$$

3. Treat a poly atomic compound as a binary compound if you have multiple unknown oxidation potentials. The compound is $\mathrm{Co}_{2}\left(\mathrm{SO}_{4}\right)_{3}$.
a. Assume Co is positive and $\left(\mathrm{SO}_{4}\right)$ is negative. Rule 1: $\mathrm{SO}_{4}=-2$
b. $\mathrm{Co}_{2}\left(\mathrm{SO}_{4}\right)_{3}=0$ (Rule 1)
c. $2 \mathrm{Co}+3\left(\mathrm{SO}_{4}\right)=0$
$\mathrm{SO}_{4}=-2$ (From polyatomic ion chart)(Rule 1)
$\mathrm{Co}=+3$
d. $\mathrm{SO}_{4}=-2$
$1 \mathrm{~S}+4 \mathrm{O}=-2$
$1 \mathrm{~S}+4(-2)=-2$
$1 \mathrm{~S}+-8=-2$
$S=+6$
4. For compound $\left(\mathrm{NH}_{4}\right)_{2}\left(\mathrm{SO}_{4}\right)$ : list all the oxidation numbers for each element.

Follow the rules for assigning oxidation numbers. In this case apply Rule 1 twice, it has a higher priority. The compound can be broken into two polyatomic ions, one positive and one negative. Apply Rule 1 to each.

$$
2\left(\mathrm{NH}_{4}\right)+\left(\mathrm{SO}_{4}\right)=0
$$

The polyatomic ion table indicates these values which are also oxidation numbers per Rule 1.

$$
\begin{array}{ll}
\mathrm{NH}_{4}=+1 & \\
\mathrm{SO}_{4}=-2 & \\
& \\
\mathrm{~N}+4 \mathrm{H}=+1 & \mathrm{~N}=-3 \\
\mathrm{~S}+4 \mathrm{O}=-2 & \mathrm{~S}=+6
\end{array}
$$

Sample Problems:
Assign oxidation numbers to the elements in the following:
a. $\mathrm{ClO}_{4}^{-}$
b. $\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}$
c. $\mathrm{MnO}_{2}$
d. $\mathrm{H}_{2} \mathrm{O}_{2}$

## Answer Key

a. $\quad \mathrm{ClO}_{4}-$ :

$$
\mathrm{Cl}=+7, \quad \mathrm{O}=-2
$$

b. $\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}$ :

$$
\mathrm{O}=-2, \mathrm{~N}=+5, \mathrm{Ca}=+2
$$

c. $\mathrm{MnO}_{2}$ :
$\mathrm{O}=-2, \mathrm{Mn}=+4$
d. $\mathrm{H}_{2} \mathrm{O}_{2}$ :
$\mathrm{H}=+1, \quad \mathrm{O}=-1$

