Red-Ox reactions and Oxidation states

Red-ox is short for oxidation reduction reaction. The two always go together. It is not possible to have a reduction reaction without an oxidation reaction.

A red-ox reaction is a reaction in which the oxidation states of some of the atoms change. (oxidation what?)

**Oxidation number** is a formalized way of keeping track of oxidation state.

When molecules form electrons are rarely shared equally.

e.g. CF$_4$ is held together by covalent bonds. Even though the electrons are shared, the electrons are not shared equally. Fluorine attracts electrons more strongly than carbon, so the electrons spend more time near the fluorine. Chemists have invented an accounting method to keep track of the electrons.

The atom that more strongly attracts the electron is "given" the electron. The more electronegative atom is the one that strongly attract the electrons.

  in CF$_4$ the oxidation number of the C is +4

  the oxidation number of each of the F's is -1.

In reality, the electron is not given to the fluorine or removed from the carbon. So, the carbon does not really have a +4 charge, nor do each of the F's have a -1 charge. However, the F's of CF$_4$ are more negative than a fluorine in F$_2$, and the carbon is more positive than the C's in graphite or diamond.

So, if an oxidation number is not always the actual charge why use oxidation numbers?
Because if these simple rules are used for all molecules then chemists can use oxidation numbers to determine where all the electrons are going, and it works.

**Here are the rules for determining the oxidation number of an atom.**
Elements: (including all allotropes) have an oxidation number = 0.

In an ionic compound:
  Monoatomic ions: oxidation number is the same as charge.
  Polyatomic ions are treated as molecules since they are molecules.

When occurring in a molecule (other than an allotropic form of the element)
  H always has a +1 oxidation number.
  F always has a -1 oxidation number.
  O always has a -2 oxidation number, except when bonded to a F or another O in a molecule.
  Cl has a -1 oxidation number, except when bonded to a F or an O.
  Br has a -1 oxidation number, except when bonded to a F, a Cl, or an O.
  S has a sometimes has a -2 oxidation number, except when bonded to a F, a Cl, a Br, or an O.

What we are really saying is that for nonmetals the oxidation number of an atom will be the same as the charge on the ion that the element forms so long as the atom is not bonded to a more electronegative element.

The electronegativity of an element is a measure of the element's ability to attract the electrons which are in a bond.

Earlier we said the fluorine in CF$_4$ has and oxidation number of -1. Fluorine is assigned the oxidation number of -1 because it attracts the electrons in the bond more strongly than the carbon does. Thus, fluorine appears to have an extra electron, -1 oxidation number.
F is the most electronegative element on the periodic table. Followed by O, then N and Cl.

In general the electronegativity of an element increases as one goes up a family.

electronegativity increases in the order: I < Br < Cl < F.

Also, electronegativity increases as one goes across the table.

electronegativity increases in the order: B < C < N < O < F.

When determining oxidation numbers the element with the higher electronegativity wins the electron tug-of-war so it is assumed to have complete ownership of the electron for the purpose (porpoise?) of determining oxidation numbers.

For metals the atom is assigned an oxidation number equal to the charge on the metal ion. Since we do not talk about metal-metal bonds in general chemistry we will not have to worry about metals competing for electrons.

For a neutral compound : the sum of the oxidation numbers must be 0.
For a polyatomic ion: the sum of the oxidation numbers must equal the charge of the ion.

**A Red-ox reaction**

The obvious reaction:

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

\[
\begin{array}{ccc}
0 & 0 & +1 & -1 \\
\end{array}
\]

Another fairly obvious reaction:

\[ 4 \text{Fe}_\text{(s)} + 3 \text{O}_2 \text{(g)} \rightarrow 2 \text{Fe}_2\text{O}_3 \text{(s)} \]

\[
\begin{array}{ccc}
0 & 0 & (+3)2 & (-2)3 \\
\end{array}
\]

Less obvious, but similar to rusting...combustion:

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

\[
\begin{array}{ccc}
-4 & 0 & +4 & (-2)2 & (+1)2 & -2 \\
\end{array}
\]

Combustion is a redox reaction.

This is an important revelation. Typically, methane is burned, the heat which is produced during the combustion reaction is converted to mechanical energy, and the mechanical energy is converted to electrical energy. However, combustion is just a reaction that moves
8 e-'s from a C atom to 4 O atoms. If the e-'s can be siphoned off the chemical energy can be converted to electrical energy directly. In fact, this is the basis for fuel cells.

NASA uses the reaction of H$_2$ with O$_2$ for two forms of energy.

The main engines of the shuttle burn H$_2$ in pure O$_2$ the heat from the reaction produces rapidly expanding gases and thrust.

The shuttle produces electricity using fuel cells that convert the chemical energy of H$_2$ and O$_2$ directly to electrical energy.

Cars which convert gasoline to electrical energy using fuel cells are being developed. The electrical energy powers electrical motors. Fuel cells would eliminate some of the problems associated with battery powered electrical cars; limited range and long recharge times. while also elimination some of the problems with internal combustion engines. Fuel cells have advantages over internal combustion engines; the fuel cells produce fewer by products—carbon monoxide, hydrocarbons, nitrogen dioxide, sulfur dioxide—and fuel cells are more efficient than combustion engines. However, fuel cells have some severe disadvantages. Currently fuel cells do not handle hydrocarbons well. The hydrocarbons must be converted to H$_2$ and the H$_2$ is then sent to the fuel cell. A great deal of energy is lost in the hydrocarbon to hydrogen conversion. Also, recent advances in hybrid engines are making today’s fuel cells less competitive.