Oxidation Numbers

When a covalent bond forms between two atoms with different electronegativities the shared electrons in the bond lie closer to the more electronegative atom:

- The **oxidation number** of an atom is the charge that results when the electrons in a covalent bond are assigned to the more electronegative atom
- It is the charge an atom would possess ***if*** the bonding were ionic

In HCl (above) the oxidation number for the hydrogen would be +1 and that of the Cl would be -1

in oxidation numbers we write the sign first to distinguish them from ionic (electronic) charges

Oxidation numbers do not refer to real charges on the atoms, except in the case of actual ionic substances.

Oxidation numbers can be determined using the following rules:

1. ***The oxidation number for an element in its elemental form is 0*** (holds true for isolated atoms and elemental substances which bond identical atoms: e.g. Cl2, etc)

2. ***The oxidation number of a monoatomic ion is the same as its charge*** (e.g. oxidation number of Na+ = +1, and that of S2- is -2)

3. ***In binary compounds (two different elements) the element with greater electronegativity is assigned a negative oxidation number equal to its charge in simple ionic compounds of the element*** (e.g. in the compound PCl3 the chlorine is more electronegative than the phosphorous. In simple ionic compounds Cl has an ionic charge of 1-, thus, its oxidation state is -1)

4. ***The sum of the oxidation numbers is zero for an electrically neutral compound and equals the overall charge for an ionic species***.

5. ***Alkali metals exhibit only an oxidation state of +1 in compounds***

6. ***Alkaline earth metals exhibit only an oxidation state of +2 in compounds***

PCl_3

The chlorine is more electronegative and so its oxidation number is set to -1. The overall molecule is neutral, so the oxidation number of P, in this case, is +3.

CO_3^{2-}

The oxygen is more electronegative and receives an oxidation number of -2. The overall molecule has a net charge of 2- (an overall oxidation number of -2), therefore, the C must have an oxidation state of +4, i.e. (3*-2) + 'C' = -2.

Examples of Sulfur

H_2S

Sulfur (2.5) is more electronegative than hydrogen (2.1), thus it has an oxidation number of -2. The hydrogen will have an oxidation number of +1.

S_8

This is an elemental form of sulfur, and thus would have an oxidation number of 0.

SCl_2

Chlorine (3.0) is more electronegative than sulfur (2.5), thus it has an oxidation number of -1. The sulfur thus has an oxidation number of +2.

Na_2SO_3

Sodium (alkali metal) always has an oxidation number of +1. The oxygen (3.5) is more electronegative than sulfur (2.5), thus the oxygen would have an oxidation number of -2. The sulfur would therefore have an oxidation number of +4.

SO_4^{2-}

The oxygen is more electronegative and thus has an oxidation number of -2. The sulfur thus has an oxidation number of +6.

- Sulfur exhibits a variety of oxidation numbers (-2 to +6)
- In general the *most negative oxidation number* corresponds to the number of electrons which must be *added to give an octet* of valence electrons
- The *most positive oxidation number* corresponds to *a loss of all valence electrons*

Oxidation Numbers and Nomenclature

Compounds of the alkali (oxidation number +1) and alkaline earth metals (oxidation number +2) are typically ionic in nature.

Compounds of metals with higher oxidation numbers (e.g. tin +4) tend to form molecular compounds

- In ionic and covalent molecular compounds usually the ***less electronegative element is given first***.
- In ionic compounds the names are given which refer to ***the oxidation (ionic) state***
- In molecular compounds the names are given which refer ***to the number of molecules present in the compound***