

How to determine oxidation numbers

When we assign oxidation numbers to the atoms in a molecule, we are treating every compound as though it is an ionic salt (even when we know it is not), and are determining the charge on each “ion” in the compound. Each atom gets its own oxidation number. We assign these charges based on a few simple rules.

- All atoms in their elemental state (H_2 , He, Cu, O_2 , N_2 , etc) have an oxidation number of 0.
- The oxidation state of a monatomic ion (a single atom with a charge, such as Na^+ , Fe^{3+} , F^-) is the same as the charge on the ion.
- In simple ionic compounds (NaCl , FeBr_3 , etc) the oxidation numbers are the same as the actual charges on the ions.
- The oxidation states of all the atoms in a neutral molecule add up to 0. The oxidation states of all the atoms in an ion (such as NO^{3-} or SO_4^{2-}) add up to the charge on the ion.
- Group I metals (Li^+ , Na^+ , K^+ , etc) are almost always +1 in compounds.
- Group II metals (Be^{2+} , Mg^{2+} , Ca^{2+} , Ba^{2+} , etc) are nearly always +2 in compounds.
- Hydrogen is almost always +1, except when it is:
 - 0 in elemental hydrogen (H_2 gas)
 - 1 in metal hydrides such as LiAlH_4 or NaBH_4 (these are used in organic chem).
- Oxygen is almost always -2, except when it is:
 - 0 in elemental oxygen (O_2 gas)
 - 1 in peroxides such as H_2O_2 .
 - Oxygen will be positive when paired with fluorine.
- Fluorine in a compound is always -1.
- Chlorine, bromine, and iodine in a compound are always -1 unless bonded with oxygen.

For example, in our oxidizing agent, MnO_4^- , the oxygens each have an oxidation state of -2 (for a total of -8 because there are four of them), and the overall charge on the ion is -1. This means that the manganese has to be +7 ($+7 - 8 = -1$). The manganese ion isn't really +7 (it would take an incredible amount of energy to remove another electron from an ion that was already +6) but treating the atoms as ions this way allows us to easily track the apparent movement of electrons in the compound.

After the titration, the manganese is Mn^{2+} , which has an oxidation state of +2. Since the ion has gone from +7 to +2, it has gained 5 electrons. It has been reduced.

In the oxalate ion, $\text{C}_2\text{O}_4^{2-}$, the oxygens are -2 each for a total of -8, and the overall charge is -2, so the two carbons together add up to +6. That means each carbon atom is in a +3 oxidation state.

After the titration, the carbon is in the form of CO_2 gas. Here the oxygens are again -2 each, for a total of -4, and since the molecule is neutral, the carbon atom must be +4. Each carbon atom has therefore lost one electron in the reaction, and has been oxidized.