

Assignment of Oxidation Numbers Preliminary Guidelines

There are a number of rules guiding the assignment of oxidation numbers to elements, however, 95+% of the assignments may be made using the following basic rules.

1.) Elements in their standard states are assigned an oxidation number of 0

Examples: H_2 O_2 Pb S_8 all have oxidation numbers of 0.

2.) Monatomic ions are assigned an oxidation number equal to the charge on the ion.

Examples: Na^+ Oxidation No. = +1, S^{2-} Oxidation No. = -2 etc.

3.) Elements in Group I, Group II are usually assigned oxidation numbers equal to their common charge.

Examples: NaClO_3 - Na is assigned an oxidation number of +1
 KMnO_4 - K is assigned an oxidation number of +1
 Mg(OH)_2 - Mg is assigned an oxidation number of +2
 CaC_2O_4 - Calcium is assigned an oxidation number of +2

4.) Oxygen in **usually** assigned an oxidation number of -2 in a polyatomic molecule.

The exceptions are O_2 , molecules of oxygen alone, such as ozone, O_3^{-1} and peroxides such as hydrogen peroxide, H_2O_2 .

Examples: In SO_2 , KMnO_4 HNO_3 , **each** of the oxygens are assigned an oxidation number of -2.

This last one ties everything together in order to allow the assignment of more difficult elements.

5.) The sum of all the oxidation numbers of the elements in a molecule must be equal to the charge on the molecule.

Examples: NaF - From Rule 3.), Na is assigned an oxidation number of +1. The molecule is neutral, therefore, F must be assigned an oxidation number of -1.

SO_3^{-2} - From 4.) oxygen is assigned an oxidation number of -2. Since there are 3 oxygens, each with -2 and the charge on the molecule is -1, Sulfur must have an oxidation number of $x + 3 \times (-2) = -1$ $x = S = +5$

KMnO_4 - From 3.), K is assigned an oxidation number of +1 and from From 4.) oxygen is assigned an oxidation number of -2. Since there are 4 oxygens, each with -2 and the charge on the molecule is 0, Mn must have an oxidation number of $(+1) + x + (4 \times (-2)) = 0$ or $x = Mn = +7$

Redox Balancing Method BLB Method (OOHe)

Discussed in the lecture text by Brown and Lemay, this method, which I call the OOHe method (pronounced oooooweeeee!) stands for the order in which the items in the reaction are balanced. In order, the letters mean:

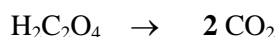
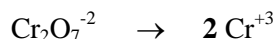
O = Other atoms
O = Oxygen
H = Hydrogen
e = electrons

Consider the reaction: $\text{Cr}_2\text{O}_7^{-2} + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Cr}^{+3} + \text{CO}_2$

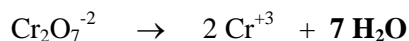
Step 1: Assign oxidation numbers and break up the reaction into an oxidation half reaction and a reduction half reaction.



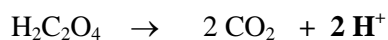
Step 2: Balance all the other atoms except for oxygen and hydrogen. (O = Other atoms)



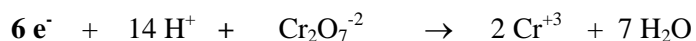
Step 3: Balance oxygen atoms using water (O = Oxygens)



Step 4: Balance the hydrogen atoms using H^+ ions. (H = Hydrogens)

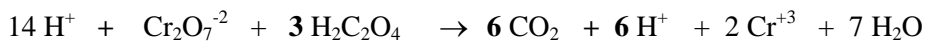


Step 5: Balance the charges electrons using water (e = Electrons)



Step 6: Recombine equations, multiplying as needed to eliminate the appearance of electrons on either side of the reaction.

Multiply oxalate ($\text{H}_2\text{C}_2\text{O}_4$) equation by 3. Combining yields



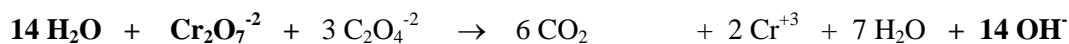
or canceling excess hydrogen ions and waters...



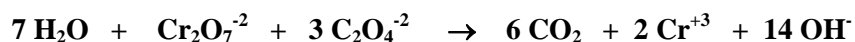
Step 7 – If necessary for basic solutions.

For basic solutions, add OH^- 's on both sides to neutralize **all** the acidic hydrogen ions, turning them into water. In this instance, I need to add 8 for the H^+ ions **and** 6 for the oxalic acid for a TOTAL of 14 OH^- 's.

Executing, I get..



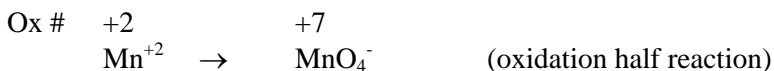
Canceling the extra waters give the final result...



Redox Balancing Method

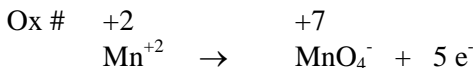
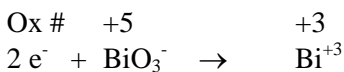
Consider the reaction: $\text{BiO}_3^- + \text{Mn}^{+2} \rightarrow \text{MnO}_4^- + \text{Bi}^{+3}$

Step 1: Assign oxidation numbers and break up the reaction into a oxidation half reaction and a reduction half reaction.

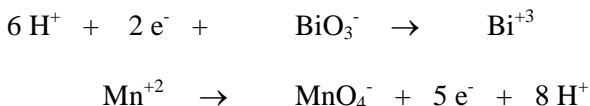


Step 2: Balance the atoms undergoing a change in oxidation number
Balanced in this case

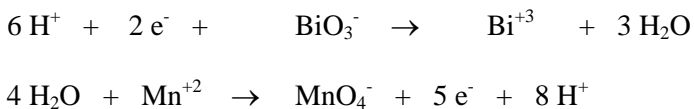
Step 3: Balance oxidation numbers using electrons



Step 4: Balance ACTUAL CHARGES using H^+ ions in acid solution or OH^- ions in basic solution.



Step 5: Balance hydrogens using water

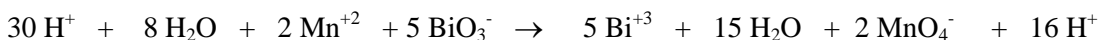


Step 6: Check oxygen balance. If everything has been done correctly to this point, the oxygens will automatically balance!

Balanced !

Step 7: Recombine equations, multiplying as needed to eliminate the appearance of electrons on either side of the reaction.

Multiply bismuth equation by 5 and manganese equation by 2. Combining yields



or canceling excess hydrogen ions and waters...

