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: $\mathbf{H_2}$ $\mathbf{O_2}$ **Pb** $\mathbf{S_8}$ 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 **<u>usually</u>** 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 $x + 3 \times (-2) = -1 \quad x = M = +5$

$KMnO_4$ – 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 $(+1) + x + (4 \times (-2)) = 0 \quad or \quad x = Mn = +7$

Redox Balancing Method

Consider the reaction**:** BiO_3^- + Mn^{+2} $\rightarrow$ MnO_4^- + Bi^{+3}

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

Ox # +5 +3
BiO_3^- $\rightarrow$ Bi^{+3} (reduction half reaction)

Ox # +2 +7
Mn^{+2} $\rightarrow$ MnO_4^- (oxidation half reaction)

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

Balanced in this case

Step 3: Balance oxidation numbers using electrons

Ox # +5 +3
$2\ e^-$ + BiO_3^- $\rightarrow$ Bi^{+3}

Ox # +2 +7
Mn^{+2} $\rightarrow$ MnO_4^- + $5\ e^-$

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

$6\ H^+$ + $2\ e^-$ + BiO_3^- $\rightarrow$ Bi^{+3}

Mn^{+2} $\rightarrow$ MnO_4^- + $5\ e^-$ + $8\ H^+$

Step 5: Balance hydrogens using water

$6\ H^+$ + $2\ e^-$ + BiO_3^- $\rightarrow$ Bi^{+3} + $3\ H_2O$

$4\ H_2O$ + Mn^{+2} $\rightarrow$ MnO_4^- + $5\ e^-$ + $8\ H^+$

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

$30\ H^+$ + $8\ H_2O$ + $2\ Mn^{+2}$ + $5\ BiO_3^-$ $\rightarrow$ $5\ Bi^{+3}$ + $15\ H_2O$ + $2\ MnO_4^-$ + $16\ H^+$

or canceling excess hydrogen ions and waters…

$14\ H^+$ + $2\ Mn^{+2}$ + $5\ BiO_3^-$ $\rightarrow$ $5\ Bi^{+3}$ + $2\ MnO_4^-$ + $7\ H_2O$