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 $x+3\times(-2)=-2 \quad x=S==+4$

$KMnO_4$ – 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
BLB Method (OOHe)

Discussed in the lecture text by Brown and Lemay, this method, which I call the OOHe method (pronounced ooooweeeee!) 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**:** $Cr_2O_7^{-2}$ + $H_2C_2O_4$ $\rightarrow$ Cr^{+3} + CO_2

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

Ox # +6 +3
$Cr_2O_7^{-2} \rightarrow Cr^{+3}$ (reduction half reaction)

Ox # +3 +4
$H_2C_2O_4 \rightarrow CO_2$ (oxidation half reaction)

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

$Cr_2O_7^{-2} \rightarrow \mathbf{2}\ Cr^{+3}$

$H_2C_2O_4 \rightarrow \mathbf{2}\ CO_2$

Step 3: Balance oxygen atoms using water (<u>O</u> = Oxygens)

$Cr_2O_7^{-2} \rightarrow 2\ Cr^{+3} + \mathbf{7\ H_2O}$

$H_2C_2O_4 \rightarrow 2\ CO_2$ **Note: Oxygen atoms are already balanced here.**

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

$\mathbf{14\ H^+} + Cr_2O_7^{-2} \rightarrow 2\ Cr^{+3} + 7\ H_2O$

$H_2C_2O_4 \rightarrow 2\ CO_2 + \mathbf{2\ H^+}$

Step 5: Balance the charges electrons using water (<u>e</u> = Electrons)

$\mathbf{6\ e^-} + 14\ H^+ + Cr_2O_7^{-2} \rightarrow 2\ Cr^{+3} + 7\ H_2O$

$H_2C_2O_4 \rightarrow 2\ CO_2 + 2\ H^+ + \mathbf{2\ e^-}$

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

Multiply oxalate ($H_2C_2O_4$) equation by 3. Combining yields

$14\ H^+ \ + \ Cr_2O_7^{-2} \ + \ \mathbf{3}\ H_2C_2O_4 \ \rightarrow \ \mathbf{6}\ CO_2 \ + \ \mathbf{6}\ H^+ \ + \ 2\ Cr^{+3} \ + \ 7\ H_2O$

or canceling excess hydrogen ions and waters…

$$\mathbf{8\ H^+ \ + \ Cr_2O_7^{-2} \ + \ 3\ H_2C_2O_4 \ \rightarrow \ 6\ CO_2 \ + \ 2\ Cr^{+3} \ + \ 7\ H_2O}$$

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..

$$\mathbf{14\ H_2O} \ + \ \mathbf{Cr_2O_7^{-2}} \ + \ 3\ C_2O_4^{-2} \ \rightarrow \ 6\ CO_2 \ + \ 2\ Cr^{+3} \ + \ 7\ H_2O \ + \ \mathbf{14\ OH^-}$$

Canceling the extra waters give the final result…

$$\mathbf{7\ H_2O \ + \ Cr_2O_7^{-2} \ + \ 3\ C_2O_4^{-2} \ \rightarrow \ 6\ CO_2 \ + \ 2\ Cr^{+3} \ + \ 14\ OH^-}$$

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…

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