REDOX REACTIONS

The Oxidation-Number Method for Balancing Redox Equations:

There are three steps in the oxidation-number method for balancing redox reactions. We will use the following equation as an example:

Example A: $HNO_3 + H_2S \rightarrow NO + S + H_2O$

Step 1: The oxidation numbers of the atoms in the equation are determined in order to identify atoms undergoing oxidation or reduction. Thus,

$$HNO_3 + H_2S \rightarrow NO + S + H_2O$$

Nitrogen is reduced (from 5+ to 2+, a decrease of 3), and sulfur is oxidized (from 2- to 0, an increase of 2).

Step 2: Coefficients are added so that the total decrease and the total increase in oxidation number will be equal. We have a decrease of 3 and an increase of 2 indicated in the unbalanced expression.

The lowest common multiple of 3 and 2 is 6. We therefore indicate $2HNO_3$ and 2NO (for a total decrease of 6) and $3H_2S$ and 3S (for a total increase of 6):

$$\mathbf{2}HNO_3 + \mathbf{3}H_2S \rightarrow \mathbf{2}NO + \mathbf{3}S + H_2O$$

Step 3: Balancing is completed by inspection. This method takes care of only those substances that are directly involved in oxidation-number change.

In this example, the method does not assign a coefficient to H_2O. We note, however, that there are now eight H atoms on the left of the equation. We can indicate the same number of H atoms on the right by showing $4H_2O$.

$$2HNO_3 + 3H_2S \rightarrow 2NO + 3S + \mathbf{4}H_2O$$

The final, balanced equation should be checked to ensure that there are as many atoms of each element on the right as there are on the left.

Example B: The oxidation-number method can also be used to balance net ionic equations, in which only those ions and molecules that take part in the reaction are shown.

Consider the reaction between $KClO_3$ and I_2 :

$$H_2O + I_2 + ClO_3^- \rightarrow IO_3^- + Cl^- + H^+$$

(The K^+ ion does not take part in the reaction and is not shown in the equation.)

Step 1. $H_2O + I_2 + ClO_3^- \rightarrow IO_3^- + Cl^- + H^+$

Step 2. Each iodine atom undergoes an increase of 5 (from 0 to 5+), but there are two iodine atoms in I_2. The increase in oxidation number is therefore 10. Chlorine undergoes a decrease of 6 (from 5+ to 1-). The lowest common multiple of 6 and 10 is 30. Therefore, $3I_2$ molecules must be indicated (a total increase of 30) and $5ClO_3^-$ ions are needed (a total decrease of 30). The coefficients of the products, IO_3^- and Cl^-, follow from this assignment.

$$H_2O + \mathbf{3}I_2 + \mathbf{5}ClO_3^- \rightarrow \mathbf{6}IO_3^- + \mathbf{5}Cl^- + H^+$$

Step 3. If H_2O is ignored, there are now 15 oxygen atoms on the left and 18 oxygen atoms on the right. To make up 3 oxygen atoms on the left, we must indicate $3H_2O$ molecules. It then follows that the coefficient of H^+ must be 6 to balance the hydrogens of the H_2O molecules:

$$\mathbf{3}H_2O + 3I_2 + 5ClO_3^- \rightarrow 6IO_3^- + 5Cl^- + \mathbf{6}H^+$$

The Ion-Electron Method of Balancing Redox Equations:

1. Divide the equation into two skeleton partial equations. Balance the atoms that change their oxidation numbers in each partial equation.

2. Balance O and H atoms in each partial equation.
   a.) For reactions occurring in acid solution:
      i.) For each O atom that is needed, add one H_2O to the side of the partial equation that is deficient in oxygen.
      ii.) Add H^+ where needed to bring the hydrogen into balance.
   b.) For reactions in alkaline solution:
      i.) For each O atom that is needed, add one H_2O to the side of the partial equation that is deficient in oxygen.
      ii.) For each H atom that is needed, add one H_2O to the side of the partial equation that is deficient in H, and add one OH^- to the opposite side.

3. To each partial equation, add electrons in such a way that the net charge on the left side of the equation equals the net charge on the right side.

4. If necessary, multiply one or both partial equations by numbers that will make the number of electrons lost in one partial equation equal the number of electrons gained in the other partial equation.

5. Add partial equations. In the addition, cancel terms common to both aides of the final equation.

Examples:
1.) $MnO_4^- + As_4O_6 \rightarrow Mn^{2+} + H_3AsO_4$ (acidic condition)

Step1. Divide the equation into two skeleton partial equations.

Reduction: $MnO_4^- \rightarrow Mn^{2+}$
Oxidation: $As_4O_6 \rightarrow \mathbf{4}H_3AsO_4$ (*As* atoms are balanced using coefficient 4)

Step 2. The reduction equation can be brought into material balance by the addition of $4H_2O$ to the right side and $8H^+$ to the left side. In the oxidation equation $10H_2O$ must be added to the left side to make up the needed 10 oxygen atoms.

Reduction: $\mathbf{8}H^+ + MnO_4^- \rightarrow Mn^{2+} + \mathbf{4}H_2O$
Oxidation: $\mathbf{10}H_2O + As_4O_6 \rightarrow 4H_3AsO_4 + \mathbf{8}H^+$

Step 3. To balance the net charges, electrons are added:

Reduction: $\mathbf{5e^-} + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
Oxidation: $10H_2O + As_4O_6 \rightarrow 4H_3AsO_4 + 8H^+ + \mathbf{8e^-}$

Step 4. The reduction equation must be multiplied through by 8 and the oxidation equation by 5 so that the number of electrons gained equals the number of electrons lost.

Reduction: $\mathbf{40}e^- + \mathbf{64}H^+ + \mathbf{8}MnO_4^- \rightarrow \mathbf{8}Mn^{2+} + \mathbf{32}H_2O$
Oxidation: $\mathbf{50}H_2O + \mathbf{5}As_4O6 \rightarrow \mathbf{20}H_3AsO_4 + \mathbf{40}H^+ + \mathbf{40}e^-$

Step 5. When these two partial equations are added, water molecules and hydrogen ions must be cancelled as well as electrons. Therefore,

$24H^+ + 18H_2O + 5As_4O_6 + 8MnO_4^- \rightarrow 20H_3AsO_4 + Mn^{2+}$

2.) $MnO_4^- + N_2H_4 \rightarrow MnO_2 + N_2$ (Basic solution)

Step 1. Divide the equation into two skeleton partial equations.

Reduction: $MnO_4^- \rightarrow MnO_2$
Oxidation: $N_2H_4 \rightarrow N_2$

Step 2. For reactions occurring in basic solutions, OH^- And H_2O are used to balance oxygen and hydrogen. For each oxygen atom that is needed, one H_2O molecule is added to the side of the partial equation that is deficient. The hydrogen is balanced next. For each hydrogen that is needed, one H_2O molecule is added to the side that is deficient and one OH^- is added to the opposite side.

Reduction: $MnO_4^- \rightarrow MnO_2 + 2H_2O$
$4H_2O + MnO_4^- \rightarrow MnO_2 + 2H_2O + 4OH^-$
(Eliminate $2H_2O$ from both sides of the eqn.)
$2H_2O + MnO_4^- \rightarrow MnO_2 + 4OH^-$

Oxidation: $4OH^- + N_2H_4 \rightarrow N_2 + 4H_2O$

Step 3. Electrons are added to effect charge balances:

Reduction: $3e^- + 2H_2O + MnO_4^- \rightarrow MnO_2 + OH^-$

Oxidation: $4OH^- + N_2H_4 \rightarrow N_2 + 4H_2O + 4e^-$

Step 4. The lowest common multiple of 3 and 4 is 12. Therefore, reduction equation is multiplied by 4 and the oxidation equation is multiplied by 3.

Reduction: $12e^- + 8H_2O + 4MnO_4^- \rightarrow 4MnO_2 + 16OH^-$

Oxidation: $12OH^- + 3N_2H_4 \rightarrow 3N_2 + 12H_2O + 12e^-$

Step 5. Addition of these partial equations, with cancellation of OH^- ions and H_2O molecules as well as electrons, gives the final equation:

$$4MnO_4^- + 3N_2H_4 \rightarrow 4MnO_2 + 3N_2 + 4H_2O + 4OH^-$$