Rules for Assigning Oxidation Numbers

1. ***The oxidation number of an element in any elementary substance is zero.***

   For example, the oxidation number of chlorine in Cl_2, phosphorus in P_4, and sulfur in S_8 is 0.

2. ***The oxidation number of an element in a monatomic ion is equal to the charge on that ion.***

Compound	Ions	Oxidation No.
NaCl	Na^+	+1
	$Cl^–$	–1
Al_2O_3	Al^{3+}	+3
	$O^{2–}$	–2

3. ***Certain elements have the same oxidation number in almost all their compounds.***

   - Group 1 *always* forms +1 ions: Li^+, Na^+, K^+, etc. — oxidation number +1
   - Group 2 *always* forms +2 ions: Mg^{2+}, Ca^{2+}, etc. — oxidation number +2
   - Fluorine *always* has an oxidation number of –1.
   - Oxygen has oxidation number of –2 except in peroxides, $O_2^{2–}$, (examples: H_2O_2, Na_2O_2) and in superoxides, $O_2^–$, (example: KO_2) where it has oxidation numbers of –1 and –½, respectively.
   - Hydrogen has oxidation number of +1 except in hydrides, $H^–$, (examples: NaH, CaH_2) where it has an oxidation number of –1.

4. ***The sum of the oxidation numbers of all the atoms in a neutral species is zero; in an ion, it is equal to the charge of that ion.***

   Li_3N: ox. no. of Li^+ is +1

   3(+1) + ox. no. of N = 0

   ox. no. of N = –3

   $ClO_2^–$: ox. no. of O is –2

   ox. no. of Cl + 2(–2) = –1

   ox. no. of Cl – 4 = –1

   ox. no. of Cl = +3

Rules for Balancing Redox Equations

We will use the example:

$$Cu(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO_2(g) \quad \text{(acidic solution)}$$

1. Split the equation into two half-equations, one for oxidation and one for reduction.

Remember: oxidation is an increase in oxidation number and reduction is a decrease in oxidation number.

Using the rules for determining oxidation numbers (ox. no.):

$$\begin{array}{llllll} & Cu & + \; NO_3^- & \rightarrow & Cu^{2+} & + \; NO_2 \\ \text{ox. no.} & Cu{=}0 & N{=}+5 & & Cu{=}+2 & N{=}+4 \\ & & O{=}-2 & & & O{=}-2 \end{array}$$

reduction half equation: $NO_3^- \rightarrow NO_2$ (ox. no. of N decreases: $+5 \rightarrow +4$)

oxidation half-equation: $Cu \rightarrow Cu^{2+}$ (ox. no. of Cu increases: $0 \rightarrow +2$)

(Notice that we have left out H^+ and H_2O for acidic solution or OH^- and H_2O for basic solution for now. We will add these in later as we need them.)

2. Balance one of the half-equations with respect to both atoms and charge.

First we balance the oxidation half-equation since it is easier.

(a) Balance the atoms of the element being oxidized.

The atoms of Cu are already balanced.

$$Cu \rightarrow Cu^{2+}$$

(b) Balance oxidation number by adding electrons.

For an oxidation half-equation, we add electrons to the right. Since the oxidation number of copper increases from 0 to +2, we add two electrons to the right.

$$\begin{array}{lcccc} & Cu & \rightarrow & Cu^{2+} & + \; 2\,e^- \\ \text{ox. no.:} & 0 & & (+2 & -2 = 0) \end{array}$$

The oxidation half-equation is now balanced since there are no other atoms to balance.

3. Balance the other half-equation with respect to both atoms and charge.

Next we balance the reduction half-equation.

(a) Balance the atoms of the element being reduced.

The N atoms are already balanced, and O atoms will be balanced later.

$$NO_3^- \rightarrow NO_2$$

(b) Balance oxidation number by adding electrons.

For an reduction half-equation, we add electrons to the left. Since the oxidation number of nitrogen decreases from +5 to +4, we add one electron to the left.

$$\begin{array}{lccccc} & NO_3^- & + \; e^- & \rightarrow & NO_2 \\ \text{ox. no.:} & (+5 & -1 = +4) & & +4 \end{array}$$

(c) Balance charge by adding H^+ ions in acidic solution.

(**Note:** If this were basic solution, we would balance charge by adding OH^- ions to the more **positive** side of the equation.)

$$\begin{array}{lccccc} & NO_3^- & + \; e^- & \rightarrow & NO_2 \\ \text{charge:} & (-1 & -1 = -2) & & 0 \end{array}$$

We balance the charge with positive H^+ ions by adding two H^+ ions to the more **negative** side of the equation – the left side.

$$\begin{array}{lcccccc} & NO_3^- & + \; 2H^+ & + \; e^- & \rightarrow & NO_2 \\ \text{charge:} & (-1 & +2 & -1 = 0) & & 0 \end{array}$$

(d) Balance hydrogen by adding H_2O molecules.

Since we have two hydrogen atoms on the left and none on the right, we add one H_2O molecule to the right.

$$NO_3^- + 2\,H^+ + e^- \rightarrow NO_2 + H_2O$$

(e) Check to make sure that oxygen is balanced.

If it is, the half-equation is almost certainly balanced correctly with respect to both mass (atoms) and charge.

There are three oxygen atoms on the left and three on the right. Oxygen is balanced.

4. Combine the two half-equations in such a way as to eliminate electrons.

We generally do this by multiplying each half-equation by the number of electrons in the *other* half-equation:

$$\begin{array}{ll} 1 \times \text{oxidation eq.:} & Cu \rightarrow Cu^{2+} + \cancel{2\,e^-} \\ 2 \times \text{reduction eq.:} & 2\,NO_3^- + 4\,H^+ + \cancel{2\,e^-} \rightarrow 2\,NO_2 + 2\,H_2O \\ \hline & Cu(s) + 2\,NO_3^-(aq) + 4\,H^+(aq) \rightarrow Cu^{2+}(aq) + 2\,NO_2(g) + 2\,H_2O \end{array}$$

This equation is now balanced: one Cu atom is on both sides of the equation, two N atoms are on both sides, six O atoms are on both sides, and four H atoms are on both sides. The total charge is +2 on both sides of the equation.

****Simplifying Balanced Equations ****

- For an equation in **acidic solution**, there will sometimes be H_2O molecules and H^+ ions on *both* sides of the equation. We want to cancel out the excess amounts of these. The equation we just balanced doesn't have any excess H_2O molecules or H^+ ions, but in the equation

$$2MnO_4^-(aq) + 5HSO_3^-(aq) + 5H_2O + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 8H_2O + 15H^+(aq)$$

there are both excess H_2O molecules and H^+ ions. After canceling five H_2O molecules and fifteen H^+ ions from both sides of the equation

$$2MnO_4^-(aq) + 5HSO_3^-(aq) + \cancel{5H_2O} + \cancel{16H^+}(aq) \rightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + \cancel{8H_2O} + \cancel{15H^+}(aq)$$

we have

$$2MnO_4^-(aq) + 5HSO_3^-(aq) + H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 3H_2O$$

In **basic solution**, there will sometimes be H_2O molecules and OH^- ions on both sides of the equation. We want to cancel as many of them as possible. For example, in the equation

$$3ClO^-(aq) + 2NO(g) + 8OH^-(aq) + 3H_2O \rightarrow 3Cl^-(aq) + 2NO_3^-(aq) + 6OH^-(aq) + 4H_2O$$

we can cancel six OH^- ions and three H_2O molecules

$$3ClO^-(aq) + 2NO(g) + \cancel{8OH^-}(aq) + \cancel{3H_2O} \rightarrow 3Cl^-(aq) + 2NO_3^-(aq) + \cancel{6OH^-}(aq) + \cancel{4H_2O}$$

resulting in

$$3ClO^-(aq) + 2NO(g) + 2OH^-(aq) \rightarrow 3Cl^-(aq) + 2NO_3^-(aq) + H_2O$$

- In a few cases, we find that the final equation doesn't have the smallest whole number coefficients possible. In the equation

$$6\ Cl_2(g) + 6\ H_2O \rightarrow 10\ Cl^-(aq) + 2\ ClO_3^-(aq) + 12\ H^+(aq)$$

we divide each coefficient by two to obtain the smallest whole number coefficients:

$$3\ Cl_2(g) + 3\ H_2O \rightarrow 5\ Cl^-(aq) + ClO_3^-(aq) + 6\ H^+(aq)$$

Summary of the Half-equation Method for Balancing Redox Reactions

1. Assign oxidation numbers to each atom in the equation. Split the equation into two half equations:
   oxidation half equation – element increases in oxidation number
   reduction half-equation – element decreases in oxidation number

2. Balance one of the half-equations with respect to both atoms and charge using the following steps:

   a. Balance the atoms of the element being oxidized or reduced
   b. Balance the oxidation number by adding electrons, e^-.
   c. Balance the charge with H^+ ions in acidic solution, OH^- ions in basic solution.
   d. Balance hydrogen with H_2O molecules.
   e. Check to make sure oxygen is balanced. If it is, the half-equation is probably balanced.

3. Balance the other half-equation by steps 2a – 2e.

4. Combine the half equations so electrons cancel. Multiply each half equation by the number of electrons in the *other* half equation. Suggestion for simplifying: First take out any common factor, e.g., divide $4e^-$ and $6e^-$ by 2.

   - Cancel excess H^+ ions and H_2O molecules in acidic solution or excess OH^- ions and H_2O molecules in basic solution.

   - Make sure that the equation has the smallest whole-number coefficients. If not, divide each coefficient by the largest common factor. See page 5 for an example.