How to Balance Equations for Oxidation-Reduction Reactions

Oxidation-reduction (redox) reactions are reactions in which oxidation numbers change. *Oxidation numbers* are either real charges or formal charges which help chemists keep track of electron transfer. In practice, oxidation numbers are best viewed as a bookkeeping device.

Oxidation cannot occur without reduction. In a redox reaction the substance which is *oxidized* contains atoms which *increase* in oxidation number. Oxidation is associated with *electron loss* (helpful mnemonic: *LEO = Loss of Electrons, Oxidation*). Conversely, the substance which is *reduced* contains atoms which *decrease* in oxidation number during the reaction. Reduction is associated with *electron gain* (helpful mnemonic: *GER = Gain of Electrons, Reduction*).

Chemists often talk about oxidizing and reducing agents. Be careful with these terms! An *oxidizing agent* is a substance which *oxidizes something else*: it itself is reduced! Also, a *reducing agent* is a substance that *reduces another reactant*: it itself is oxidized. A *disproportionation reaction* is a reaction in which the *same element* is *both* oxidized and reduced.

How to Assign Oxidation Numbers: The Fundamental Rules

Rules for assigning oxidation numbers are as follows:

- The oxidation number of any *pure element* is *zero*. Thus the oxidation number of H in H_2 is zero.
- The oxidation number of a *monatomic ion* is equal to its *charge*. Thus the oxidation number of Cl in the Cl^- ion is -1, that for Mg in the Mg^{+2} ion is +2, and that for oxygen in O^{2-} ion is -2.
- The *sum* of the oxidation numbers in a compound is *zero if neutral*, or *equal to the charge if an ion*.
- The oxidation number of alkali metals in compounds is +1, and that of alkaline earths in compounds is +2. The oxidation number of F is -1 in all its compounds.
- The oxidation number of *H is +1 in most compounds*. Exceptions are H_2 (where H = 0) and the ionic hydrides, such as NaH (where H = -1).
- The oxidation number of *oxygen (O) is -2 in most compounds*. Exceptions are O_2 (where O = 0) and peroxides, such as H_2O_2 or Na_2O_2, where O = -1.
- For other elements, you can usually use rule (3) to solve for the unknown oxidation number.

Examples:

NO(g) has O = -2, so N = +2.
NO_2(g) has O = -2, so N = +4.
SO_4^{2-} has O = -2. Thus S + 4(-2) = -2. Solving the equation gives S = -2 + 8 = +6.
$K_2Cr_2O_7$ has K = +1 and O = -2. Thus 2(+1) + 2 Cr + 7(-2) = 0; 2 Cr = 12; Cr = +6.

How to Balance Redox Reactions Using the Method of Half-Reactions

Oxidation-reduction reactions are often tricky to balance without using a systematic method. We shall use the method of half-reactions which is outlined in detail below.

Method in Acidic (or Neutral) Solution

Suppose you are asked to balance the equation below:

$$NO_2^- + MnO_4^- \rightarrow NO_3^- + Mn^{+2} \text{ (in acid solution)}$$

Begin by writing the *unbalanced* oxidation and reduction *half-reactions* (you do not need to know which is which):

$$NO_2^- \rightarrow NO_3^-$$

$$MnO_4^- \rightarrow Mn^{+2}$$

Next, ***balance for atoms***. First do this for atoms *other than* O and H. (Both equations above are already balanced for N and Mn, so no change is needed in this example.) Then balance for O atoms by adding H_2O to the reaction side deficient in O:

$$\mathit{H_2O} + NO_2^- \rightarrow NO_3^-$$
$$MnO_4^- \rightarrow Mn^{+2} + \mathit{4\ H_2O}$$

This leaves H atoms unbalanced. In *acidic (or neutral) solution*, balance for H atoms by adding H^+ to the side deficient in H:

$$H_2O + NO_2^- \rightarrow NO_3^- + \mathit{2\ H^+}$$
$$\mathit{8\ H^+} + MnO_4^- \rightarrow Mn^{+2} + 4\ H_2O$$

The next step is to ***balance for charge***. To do this, add electrons (e^-) to the more positive side:

$$H_2O + NO_2^- \rightarrow NO_3^- + 2\ H^+ + \mathit{2\ e^-}$$
$$\mathit{5\ e^-} + 8\ H^+ + MnO_4^- \rightarrow Mn^{+2} + 4\ H_2O$$

Now you need to ***multiply the equations by appropriate factors*** so that the number of electrons lost in the oxidation half-reaction (LEO) is equal to the number of electrons gained in the reduction half-reaction (GER):

$$\mathit{5\ x}\ [\quad H_2O + NO_2^- \rightarrow NO_3^- + 2\ H^+ + 2\ e^-\ ]$$
$$\mathit{2\ x}\ [\ 5\ e^- + 8\ H^+ + MnO_4^- \rightarrow Mn^{+2} + 4\ H_2O\quad]$$

Then, sum the above equations to obtain

$$5H_2O + 5NO_2^- + 10\ e^- + 16H^+ + 2MnO_4^- \rightarrow 5NO_3^- + 10H^+ + 10\ e^- + 2Mn^{+2} + 8H_2O$$

Finally, ***simplify*** by subtracting out species that are identical on both sides. Our final balanced redox equation is

$$5\ NO_2^- + 6\ H^+ + 2\ MnO_4^- \rightarrow 5\ NO_3^- + 2\ Mn^{+2} + 3\ H_2O$$

Check this equation to confirm that it is *balanced for atoms* and *balanced for charg*e.

<u>Method in Basic Solution</u>

Suppose you are asked to balance the equation below:

$$I^- + MnO_4^- \rightarrow I_2 + MnO_2 \quad \text{(in basic solution)}$$

Begin by writing the *unbalanced* oxidation and reduction *half-reactions* (you do not need to know which is which):

$$I^- \rightarrow I_2$$
$$MnO_4^- \rightarrow MnO_2$$

Next, ***balance for atoms***. First do this for atoms *other than* O and H:

$$\mathit{2}\ I^- \rightarrow I_2$$
$$MnO_4^- \rightarrow MnO_2$$

Then balance for O atoms by adding H_2O to the reaction side deficient in O:

$$2\ I^- \rightarrow I_2$$
$$MnO_4^- \rightarrow MnO_2 + \mathit{2\ H_2O}$$

This leaves H atoms unbalanced. In *basic solution* (just as in acidic or neutral solution) first balance for H atoms by adding H^+ to the side deficient in H:

$$\mathit{4\ H^+} + MnO_4^- \rightarrow MnO_2 + 2\ H_2O$$

In basic solution, follow this step by neutralizing the H^+; do this by adding an equivalent amount of OH^- to both sides of the equation.

$$\mathit{4\ OH^-} + 4\ H^+ + MnO_4^- \rightarrow MnO_2 + 2\ H_2O + \mathit{4\ OH^-}$$

Then form water on the side which has both H^+ and OH^- (recall that $H^+ + OH^- \rightarrow H_2O$): in this case we form 4 H_2O on the left:

$$\mathit{4\ H_2O} + MnO_4^- \rightarrow MnO_2 + 2\ H_2O + 4\ OH^-$$

Next simplify the water by subtracting 2 H_20 from both sides. The half-reactions are now:

$$2\ I^- \rightarrow I_2$$
$$\mathit{2\ H_2O} + MnO_4^- \rightarrow MnO_2 + 4\ OH^-$$

At this point the equations should be balanced for atoms. The next step is to ***balance for charge***. To do this, add electrons (e^-) to the more positive side:

$$2\ I^- \rightarrow I_2 + \mathit{2\ e^-}$$
$$\mathit{3\ e^-} + 2\ H_2O + MnO_4^- \rightarrow MnO_2 + 4\ OH^-$$

Now you need to ***multiply the equations by appropriate factors*** so that the number of electrons lost in the oxidation half-reaction (LEO) is equal to the number of electrons gained in the reduction half-reaction (GER):

$$\mathit{3\ x}\ [\ 2\ I^- \rightarrow I_2 + 2\ e^-\ ]$$
$$\mathit{2\ x}\ [\ 3\ e^- + 2\ H_2O + MnO_4^- \rightarrow MnO_2 + 4\ OH^-\ ]$$

Sum the equations to obtain

$$6\ I^- + 6\ e^- + 4\ H_2O + 2\ MnO_4^- \rightarrow 3\ I_2 + 6\ e^- + 2\ MnO_2 + 8\ OH^-$$

Finally, ***simplify*** by subtracting out species that are identical on both sides:

$$6\ I^- + 4\ H_2O + 2\ MnO_4^- \rightarrow 3\ I_2 + 2\ MnO_2 + 8\ OH^-$$

Check our final equation above to confirm that it is *balanced for atoms* and *balanced for charg*e.

Exercises*:*

Balance the following redox reactions. In each case

- (a) give the balanced half-reactions; identify the oxidation half-reaction and the reduction half-reaction.
- (b) give the balanced net reaction.
- (c) identify the oxidizing agent and the reducing agent.

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1. $Cl_2(g) + S_2O_3^{2-}(aq) \rightarrow Cl^-(aq) + SO_4^{2-}(aq)$ *in acid solution*.

Answers:

(a) $S_2O_3^{2-}(aq) + 5\ H_20 \rightarrow 2\ SO_4^{2-}(aq) + 10\ H^+(aq) + 8\ e^-$ *(oxidation half-reaction – LEO);*

$Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq)$ *(reduction half-reaction – GER).*

(b) $S_2O_3^{2-}(aq) + 5\ H_20 + 4\ Cl_2(g) \rightarrow 2\ SO_4^{2-}(aq) + 10\ H^+(aq) + 8\ Cl^-(aq)$

(c) $S_2O_3^{2-}(aq)$ *is the reducing agent;* $Cl_2(g)$ *is the oxidizing agent.*

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2. $O_3(g) + Br^-(aq) \rightarrow O_2(g) + BrO^-(aq)$ *in basic solution*.

Answers:

(a) $Br^-(aq) + H_20 + 2\ OH^-(aq) \rightarrow BrO^-(aq) + 2H_2O + 2\ e^-$ or, after simplifying,

$Br^-(aq) + 2\ OH^-(aq) \rightarrow BrO^-(aq) + H_2O + 2\ e^-$ *(oxidation half-reaction – LEO)*;

$O_3(g) + 2\ H_2O + 2\ e- \rightarrow O_2(g) + H_2O + 2\ OH^-(aq)$ or, after simplifying,

$O_3(g) + H_2O + 2\ e- \rightarrow O_2(g) + 2\ OH^-(aq)$ *(reduction half-reaction – GER)*.

(b) $Br^-(aq) + O_3(g) \rightarrow BrO^-(aq) + O_2(g)$

(c) $Br^-(aq)$ *is the reducing agent;* $O_3(g)$ *is the oxidizing agent.*

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3. Balance the reaction, $Br_2(l) \rightarrow Br^-(aq) + BrO_3^-(aq)$ in basic solution. *Hint*: this is a *disproportionation reaction*!

Answer: $6\ Br_2(l) + 12\ OH^-(aq) \rightarrow 10\ Br^-(aq) + 2\ BrO_3^-(aq) + 6\ H_2O$