Balancing Redox Equations Using Oxidation Numbers

See pages 144 to 148 of Harwood & Petrucci

The oxidation number method of balancing equations is best explained through an example.

Example 1

(1) $Fe^{2+} + MnO_4^- + H^+ \longrightarrow Fe^{3+} + Mn^{2+} + H_2O$

Step 1: Write in the oxidation numbers where needed

$$\overset{}{Fe^{2+}} + \overset{+7\,-2}{MnO_4^-} + H^+ \longrightarrow Fe^{3+} + Mn^{2+} + \overset{+1\,-2}{H_2O}$$

Step 2: Identify the changes (in oxidation number) as being either Oxidation (increase in O.N.) or Reduction (decrease in O.N.).

Oxidation: $Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$ (X5) **

Reduction: $Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$ (X1) **

Step 3: Balance electron loss and gain by multiplying (**).

$$5Fe^{2+} + MnO_4^- + H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + H_2O$$

Step 4: Balance oxygen (by adding H_2O if necessary)

$$5Fe^{2+} + MnO_4^- + H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Step 5: Balance hydrogen by adding H^+

$$5\,Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Step 6: Check that atoms and **charge** are balanced left and right: + 17 Left + 17 Right

Example 2

$$Cu + NO_3^- + H^+ \longrightarrow Cu^{2+} + NO_2 + H_2O$$

Write in all the oxidation numbers and note changes:

$$\overset{0}{Cu} + \overset{+5\,-2}{NO_3^-} + H^+ \longrightarrow Cu^{2+} + \overset{+4\,-2}{NO_2} + \overset{+1\,-2}{H_2O}$$

$-2e^-$ $+ 1e^-$

(oxid) (red)x2 (to balance electron loss and gain)

$$Cu + 2NO_3^- + H^+ \longrightarrow Cu^{2+} + 2NO_2 + H_2O$$

Next balance oxygen by adding water:

$$Cu + 2NO_3^- + H^+ \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$$

Add H^+ to the left-hand-side)

$$Cu + 2NO_3^- + 4H^+ \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$$

Finally, check charge total left and right.
In this case, the charge is 2+ on both sides.

Balance the following redox reactions by following the steps:

★ Assign oxidation numbers to all atoms in the equation
★ Determine which elements are undergoing oxidation/reduction and balance each with temporary coefficients
★ Determine the total change in oxidation state for the oxidizing agent and the reducing agent
★ Balance the two changes in oxidation state by multiplying each by the appropriate factor.
★ Balance the rest of the equation by inspection

Examples

1. The first synthesis of chlorine gas was achieved in 1774 by oxidizing hydrochloric acid (produced by reacting salt with sulphuric acid) with manganese (IV) oxide, as follows:

$$NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnCl_2 + H_2O + Cl_2$$

2. Silver is sometimes found in nature as large nuggets, more often it is found mixed with other metals and their ores. An aqueous solution containing cyanide ion is often used to extract the silver using the following reaction:

$$CN^- + Ag + O_2 + H_2O \longrightarrow Ag(CN)_2^- + OH^-$$

3. Potassium dichromate ($K_2Cr_2O_7$) is a bright orange compound that can be reduced to a blue-violet solution of Cr^{3+} ions. Under certain conditions, $K_2Cr_2O_7$ reacts with ethyl alcohol (C_2H_5OH) as follows:

$$H^+ + Cr_2O_7^{2-} + C_2H_5OH + \longrightarrow Cr^{3+} + CO_2 + H_2O$$

4. Iron ores can be analyzed for their iron content by dissolving the ore in an acidic solution, reducing all the iron to Fe^{2+} ions, and then titrating with a standard solution of potassium permanganate (Note: this is an example of a titration that doesn't involve an acid reacting with a base!):

$$H^+ + MnO_4^- + Fe^{2+} \longrightarrow Fe^{3+} + Mn^{2+} + H_2O$$

<u>The advantages and disadvantages of the oxidation number concept:</u>

Oxidation numbers can help us to decide whether or not redox is involved in a particular process. Oxidation numbers show that neutralisation and precipitation are not redox reactions, even though they involve ions. Oxidation numbers is an important electron book-keeping device that allows us to recognise redox processes; further they allow us to see exactly which part of a molecule or a complex ion is reduced or oxidised.

The main disadvantage of the oxidation number concept is that it can lead to misunderstanding about the structure of molecular substances. The oxidation number of carbon in CO_2 is +4, but it must not be supposed that there is a charge of +4 on the carbon atom.

In some cases ambiguities can arise with oxidation numbers. For example, the rules for assigning oxidation numbers suggest that each sulphur atom in the thiosulphate ion, $S_2O_3^{-2}$, has an oxidation number of +2. However the structure of the $S_2O_3^{-2}$ ions show that the two sulphur atoms in it are quite different. One S-atom is at the centre of a tetrahedron bonded to the other four atoms (one S and three O atoms) similar to the S-atom in SO_4^{-2} ion.

Two further problems with oxidation numbers concerns their use with organic compounds. The carbon atoms in compounds in compounds such as CH_4, C_2H_6, and C_3H_8 all have four covalent bonds. In spite of this similarity, they have different oxidation numbers, i.e. -4. -3 and -2 2/3 respectively. The other problem is that in some compounds, as in C_3H_8, atoms have oxidation numbers that are not whole numbers.

In spite of these disadvantages the concept of oxidation numbers is still very useful.

Assignment: Balancing Equations Using Oxidation Numbers

1. $Co + MnO_4^- + H^+ \longrightarrow Co^{2+} + Mn^{2+} + H_2O$

2. $I^- + IO^- + H^+$ ——— $I_2 + H_2O$

3. $Cr_2O_7^{2-} + SO_3^{2-} + H^+ \longrightarrow Cr^{3+} + SO_4^{2-} + H_2O$

4. $Cr_2O_7^{2-} + S^{2-} + H^+ \longrightarrow Cr^{3+} + S + H^2O$

5. $I_2 + Cl_2 + H_2O \longrightarrow IO_3^- + Cl^- + H^+$

6. $Fe_3O_4 + Al \longrightarrow Fe + Al_2O_3$

7. $ClO^- + Cl^- + H_2O \longrightarrow Cl_2 + OH^-$

8. $S^{2-} + NO_3^- + H^+ \longrightarrow SO_2 + NO_2 + H_2O$

9. $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

10. $KMnO_4 + HCl \longrightarrow KCl + MnCl_2 + H_2O + Cl_2$

11. $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

12. $KMnO_4 + HClO_2 + H_2O$ ——— $MnO_2 + HClO_4 + KOH$

13. $PbO_2 + HI \longrightarrow PbI_2 + I_2 + H_2O$

14. $H^{+1} + Cr_2O_7^{-2} + H_2S \longrightarrow Cr^{+3} + S + H_2O$

15. $S_2O_3^{-2} + I_2 \longrightarrow S_4O_6^{-2} + I^{-1}$

16. $Cl_2 + OH^{-1} \longrightarrow Cl^{-1} + ClO^{-1} + H_2O$

17. $KIO_3 + KI + HCl \longrightarrow KCl + ICl + 3H_2O$

18. $Cu^{+2} + I^{-1} \longrightarrow CuI + I_2$