■ Oxidation numbers

In the Lewis model of bonding, when nonidentical atoms are bonded together, an important consideration is how the bonding electrons are apportioned between the atoms. There are two different ways of doing this, the formal charge method and the oxidation number method. The two ways give different results and has different uses.

We introduced formal charge as an electron counting device for deciding between different possible Lewis structures and also identifying electrophilic and nucleophilic atoms in molecules. Formal charge is defined by assuming that electrons in a bond are *shared equally*, so that half are assigned to each atom of the bond. Formal charge tell us about the tendency of electrons to shift among different atoms in a molecule.

Oxidation number is an alternative electron counting device. While formal charge tells us about the tendency of electrons to shift when a bond is formed, oxidation number tells us about actual shifts of electrons in that a change in oxidation number of an atom corresponds to the transfer of that number of electrons to the atom (if the number decreases) or from the atom (if the number increases)

We assign formal charge by apportioning bonding electrons equally. We assign oxidation numbers by a "winner take all" scheme, that is, by assigning all of the electrons in a bond to one or the other atom. The atom that gets the electrons is the one that is more electronegative. The resulting oxidation numbers can be quickly determined using the following rules. The rules are to be applied in order.

1. Oxidation number is 0 for atoms in an element.

2. The sum of all oxidation numbers in a molecule or ion must add up to the total charge.

3. In compounds, alkalis have oxidation number +1; alkaline earths have oxidation number +2.

4. In compounds, fluorine always has oxidation number −1; other halogens have oxidation number −1, except when bonded to elements that are more electronegative, such fluorine and oxygen, where they can have positive oxidation numbers.

5. In compounds, hydrogen has oxidation number +1, except when bonded to metals (see above), where its oxidation number is −1.

6. In compounds, oxygen has oxidation number −2, except when bonded to fluorine, where fluorine's rule takes precedence (for example, in OF_2, oxygen has oxidation number +2), and if there are O–O (peroxide) bonds (for example, in H_2O_2 and Na_2O_2, oxygen has oxidation number −1), where earlier rules take precedence.

We get the oxidation numbers of all other atoms in compounds and ions by application of these rules.

To see how these rule work, let's apply them to $Na_2S_2O_3$. First, we know that Na is +1 and O is −2. We can determine the oxidation number of S by requiring that the sum of the oxidation numbers is the total charge, 0:

$$0 = 2 \times (+1) + 2\,S + 3 \times (-2) = 2 + 2\,S - 6 = 2\,S - 4$$

and so S is +2. Note that we have assumed that the oxidation number of every atom of a given element in the compound is the same.

Another example is $(NH_4)_2HPO_4$. A short cut is to recall the cation NH_4^+, so that we know that the anion is HPO_4^{2-} and so that it has charge −2. Then we can work with the anion and cation separately. For NH_4^+, the H's are +1, so that N must be −3, since that the sum of the oxidation numbers is the total charge on the cation.

$$+1 = -3 + 4 \times (+1)$$

For HPO_4^{2-}, the sum of the oxidation numbers must be its charge, -2; the H is $+1$ and the O's are -2, so that

$$-2 = +1 + P + 4 \times (-2) = P - 7$$

and so P is $+5$. You can use the same technique whenever common ions appear in compounds. For example, in $Ca(NO_3)_2$, recall the anion NO_3^-.

Finally, when applying these rules, sometimes oxidation numbers will come out to be non-integers. An example is Fe_3O_4. Since O is -2, the Fe must have oxidation number $8/3 = 2 \times (2/3)$. A way to think about fractional oxidation numbers is to remember that electrons are delocalized in atoms and so fractional amounts of electrons can be transferred from one atom to another.

> Determine the oxidation number each of the C's in ethanol, CH_3CH_2OH. Hint: Use the Lewis structure to assign bonding electrons to the more negative of two different atoms and to equally partition bonding electrons shared by identical atoms. Answer: -3 for the CH_3 – carbon and -1 for the $–CH_2$ – carbon.

Heuristic determination of oxidation state

When molecular oxygen reacts with a substance, oxygen bonds to other elements are formed. Since oxygen is more electronegative than most other elements, this bond formation means that electrons are withdrawn from elements bonded to the oxygen. In this way we see that *forming bonds between an element and oxygen increases the oxidation state (number) of the element*. In this sense, oxygenation—incorporating oxygen atoms—is equivalent to oxidation.

Since hydrogen is less electronegative than elements other than alkalis and alkaline earths and metals, binding to hydrogen donates electrons to the partner in the bond. In this way we see that *the more hydrogens bonded to an element, the lower the oxidation state (number) of the element*. In this sense, hydrogenation—incorporating hydrogen atoms—is equivalent to reduction.

Oxidation number change and types of inorganic reactions

Chemical reactions that we work with are classified broadly as precipitation reactions, acid-base reactions or oxidation-reduction reactions.

> *Precipitation reactions* generally involve small energy changes and no changes in the electron clouds around each atom, and so no changes in either formal charge or oxidation number.

> *Acid-base reactions* can involve intermediate amounts of energy and there is always a change in sharing of electrons and so a change in formal charge.

> *Oxidation-reduction reactions* can involve large changes in energy and always transfer electrons from one species to another and so a change in oxidation number.

■ Balancing redox equations

The simplest approach to balance chemical equations is by "inspection". This method works well for simple chemical equations. Redox equations, however, can be quite difficult to balance by inspection. Fortunately, systematic procedures are available that allow these equations to be balanced easily. The key idea of the procedures is that the number of electrons released by the species being oxidized (the *reducing agent*) is equal to the number of electrons consumed by the species being reduced (the *oxidizing agent*).

The procedure that we will use, the half-reaction method, works with the so-called half-reactions that describe separately the oxidation and reduction parts of the process. Most of the time this method does not require knowledge of oxidation numbers. However, in some cases oxidation numbers are helpful in using the half-reaction method (see below).

There are three "big pieces" to the half-reaction method. Let's illustrate everything with the reaction

$$MnO_4^- + H_2C_2O_4 \rightarrow Mn^{2+} + CO_2$$
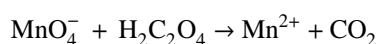
Aqueous solution is assumed but the hydration indication, (*aq*), is not shown.

Big piece one: Get the balanced half-reactions for acidic solution

Step 0: Write down the skeleton of the oxidation and the reduction parts of the process. At this stage we usually do not need to know what is being oxidized and what is being reduced; we will find this out automatically as we proceed. The two skeletons are

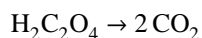$$MnO_4^- \rightarrow Mn^{2+}$$

$$H_2C_2O_4 \rightarrow CO_2$$
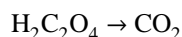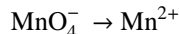
The subsequent steps transform these skeletons into fully balanced half-reactions.

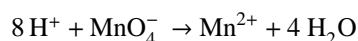**Step 1: Balance, by inspection, all of the elements except O and H.** The skeletons become

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

$$H_2C_2O_4 \rightarrow 2\,CO_2$$
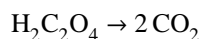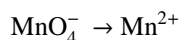
There is no change in the first half-reaction in this case.

Step 2: Balance O by adding H_2O.

$$MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O$$

$$H_2C_2O_4 \rightarrow 2\,CO_2$$

There is no change in the second half-reaction in this case.

Step 3: Balance H by adding H^+.

$$8\,H^+ + MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O$$

$$H_2C_2O_4 \rightarrow 2\,CO_2 + 2\,H^+$$
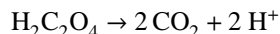
Step 4: Balance charge by adding electrons, e^-, to the side of the half-reactions that is most positive. Here is how to do this. First, determine the total charge on each side of the reaction. For the reaction
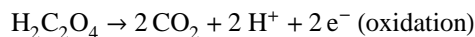
$$8\,H^+ + MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O$$
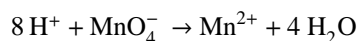
the charge on the left is $8 \times (+1) + (-1) = +7$, and the charge on the right is $+2$, and so the magnitude of the charge difference is $|7 - 2| = 5$. For the reaction

$$H_2C_2O_4 \rightarrow 2\,CO_2 + 2\,H^+$$
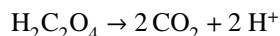
the charge on the left is 0, and the charge on the right is $2 \times (+1) = +2$, and so the magnitude of the charge difference is $|0 - 2| = 2$. To balance the charge difference on the two sides of each equation, we add the number of electrons equal to the charge difference to the side of the corresponding equation that is most positive.

Next, compute the magnitude of the charge difference. This is 8 - 2 = 6 for the first reaction and 2 - 0 = 2 for the second reaction. Finally, add this number of electrons to the side that is most positive.
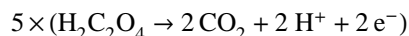
$$5\,e^- + 8\,H^+ + MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O \text{ (reduction)}$$

$$H_2C_2O_4 \rightarrow 2\,CO_2 + 2\,H^+ + 2\,e^- \text{ (oxidation)}$$

Step 5: Check your work. For each equation, make sure the there are the same number of atoms of each elements on each side of each equation. Then, make sure that the total charge is the same on each side of the equation; it does not have to be zero, it just has to be the same.
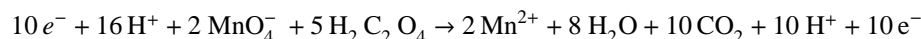
This completes big piece one. The result is the fully balanced half-reactions for the oxidation and the reduction. The oxidation reaction is the one with electrons as product. The reduction reaction is the one with electrons as reactant.

Big piece two: Combine the half-reactions into the full equation, so that the electrons produced and consumed cancel

Step 1: Multiply each half-reaction so that the number of electrons is the same.

$$2 \times (5\,e^- + 8\,H^+ + MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O)$$

$$5 \times (H_2C_2O_4 \rightarrow 2\,CO_2 + 2\,H^+ + 2\,e^-)$$

Step 2: Combine the half-reactions.

$$10\,e^- + 16\,H^+ + 2\,MnO_4^- + 5\,H_2C_2O_4 \rightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2 + 10\,H^+ + 10\,e^-$$

Step 3: Cancel species as possible. We have 16 H^+ on the left and 10 H^+ on the right, for a net of 6 H^+ on the left. Also, and this is the crucial part, there are equal numbers of electrons on each side, so the net is none—oxidation is balanced by reduction.The result is

$$6\,H^+ + 2\,MnO_4^- + 5\,H_2C_2O_4 \rightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2$$
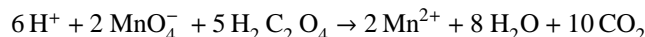
Step 4: Check your work. Once again, you should double-check to be sure your equation is balanced, for atoms and for charge.

This completes big piece two. The result is the balanced full redox equation, for acid solution.

### Big piece three: If necessary, convert the equation to basic solution

If the redox process is actually carried out in basic solution, then the redox equation needs to be converted to its form in excess OH-.

### Step 1: Add OH- to both sides of the equation, to neutralize any H+

$$6\,OH^- + 6\,H^+ + 2\,MnO_4^- + 5\,H_2C_2O_4 \rightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2 + 6OH^-$$
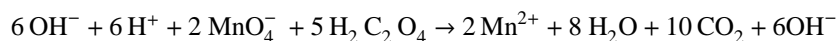
Because OH^- is added to both sides of the equation, the equation is still balanced.

Step 2: Combine OH^- and H^+ to form H_2O

$$6\,H_2O + 2\,MnO_4^- + 5\,H_2C_2O_4 \rightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2 + 6OH^-$$
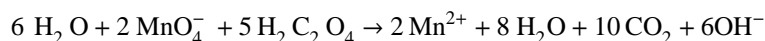
Step 3: Cancel H_2O as possible. There are 6 H_2O on the left and 8 H_2O on the right, for a net of 2 H_2O on the right.

$$2\,MnO_4^- + 5\,H_2C_2O_4 \rightarrow 2\,Mn^{2+} + 2\,H_2O + 10\,CO_2 + 6OH^-$$
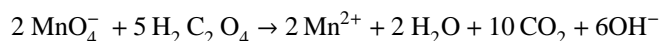
Step 4: Check your work. One last time, make sure that your equation is balanced.

Disproportionation

It is possible for one species to be simultaneously oxidized and reduced. This is called disproportionation. An example is

$$H_2O_2 \rightarrow H_2O + O_2$$
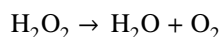
In such a case, one species appears in both the oxidation half-reaction and the reduction half-reaction.

$$H_2O_2 \rightarrow H_2O$$

$$H_2O_2 \rightarrow O_2$$
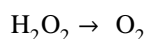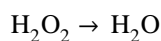
Using oxidation numbers as a guide

A feature of the half-reaction method is that oxidation numbers are not used. Sometimes, though, it is unclear exactly how to form the half-reaction skeletons. In such cases, oxidation number changes make clear what is going on.

The following problem, 4-50d from Zumdahl, *Chemical Principles*, 2e, is such a case. The unbalanced equation is

$$MnO_4^- + S_2^- \rightarrow MnS + S$$
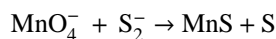
The Mn oxidation number changes from $+7$ (in MnO_4^-) to $+2$ (in MnS). The sulfur oxidation number changes from -2 (in S_2^-) to 0 (in S), but it stays the same at -2 in MnS. This means the half-reaction skeletons are

$$MnO_4^- + S_2^- \rightarrow MnS$$

$$S_2^- \rightarrow S$$
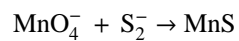
The S_2^- in the first equation is just a spectator. Using these skeletons, the balanced full equation turns out to be

$$16\ H^+ + 2\ MnO_4^- + 7\ S_2^- \rightarrow 2\ MnS + 5\ S + 8H_2O$$
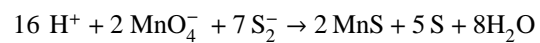
This example shows that the combination of oxidation-number changes and the half-reaction method can be very useful.