

# Chapter 12, Electrochemistry: Harnessed spontaneity

## ■ 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 when bonded to elements of higher electronegativity (most elements, including carbon), an oxidation number  $-1$  bonded to metals (see above), which have lower electronegativity.
6. In compounds, oxygen has oxidation number  $-2$ , except when bonded to fluorine, where fluorine's rule takes precedence (for example, in  $\text{OF}_2$ , oxygen has oxidation number +2), and if there are O–O (peroxide) bonds (for example, in  $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{O}_2$ , 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  $\text{Na}_2\text{S}_2\text{O}_3$ . 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:

$$0 = 2 \times (+1) + 2 \text{ S} + 3 \times (-2) = 2 + 2 \text{ S} - 6 = 2 \text{ S} - 4$$

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  $(\text{NH}_4)_2\text{HPO}_4$ . A short cut is to recall the cation  $\text{NH}_4^+$ , so that we know that the anion is  $\text{HPO}_4^{2-}$  and so that it has charge  $-2$ . Then we can work with the anion and cation separately. For  $\text{NH}_4^+$ , 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  $\text{HPO}_4^{2-}$ , the sum of the oxidation numbers must be its charge,  $-2$ ; the H is +1 and the O's are  $-2$ , so that

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

and so P is +5. You can use the same technique whenever common ions appear in compounds. For example, in  $\text{Ca}(\text{NO}_3)_2$ , recall the anion  $\text{NO}_3^-$ .

Determine the oxidation number each of the C's in ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ . 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  $\text{CH}_3$  – carbon and  $-1$  for the  $-\text{CH}_2-$  carbon.

In the same way as the previous question, show for ethanol that O has oxidation number  $-2$ , and all of the H's have oxidation number 0, except the  $-\text{OH}$  hydrogen which has oxidation number +1.

Finally, when applying these rules, sometimes oxidation numbers will come out to be non-integers. An example is  $\text{Fe}_3\text{O}_4$ . 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.

### 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.