7.5: Oxidation-Reduction Reactions

In contrast to acid–base reactions, oxidation–reduction (or redox) reactions obey a different pattern. In the simplest kinds of redox reactions, polar products are generated from non-polar reactants. You may have run into such reactions already (even if you did not know what they were called!) When iron is left in contact with oxygen (in air) and water, it rusts. The iron is transformed from a hard, non-polar metallic substance, Fe (solid), into a powdery substance, $\mathrm{Fe_2O_3.nH_2O}(s)$. Rusting is mechanistically similar to the reactions that occur when copper turns green, when silver tarnishes and turns black, or (in perhaps the favorite reaction of chemists everywhere[19]) when sodium metal explodes in water.[20]

All of these reactions start with a metal in its elemental form. Pure metals have no charge or permanent unequal distribution of charge (which makes them different from salts like NaCl). In fact we can use the synthesis of sodium chloride (NaCl) from its elements sodium (Na) and chlorine ($\mathrm{Cl_2}$) to analyze what happens during a redox reaction. The reaction can be written as:

$$2\mathrm{Na}(s) + \mathrm{Cl_2}(g) \rightleftarrows 2\mathrm{NaCl}(s) \tag{7.5.1}$$

We have already looked at the structure of ionic compounds in Chapter 4 and know that the best way to think about them is to consider NaCl as a three-dimensional lattice of alternating positive ($\mathrm{Na^+}$) and negative ($\mathrm{Cl^-}$) ions. That is as the reaction proceeds the metal atoms becomes cations, and the chlorine molecules become anions. We could write this as two separate reactions: The Na loses an electron – a process that we define as oxidation.

$$\mathrm{Na} \rightleftarrows \mathrm{Na^+} + \mathrm{e^-} (\text{an oxidation reaction}) \tag{7.5.2}$$

The electrons must go somewhere (they cannot just disappear) and since chlorine is an electronegative element, it makes sense that the electrons should be attracted to the chlorine. We define the gain of electrons as a reduction.

$$\mathrm{Cl} + \mathrm{e^-} \rightleftarrows \mathrm{Cl^-} (\text{a reduction reaction}) \tag{7.5.3}$$

It turns out that all reactions in which elements react with each other to form compounds are redox reactions. For example, the reaction of molecular hydrogen and molecular oxygen is also a redox reaction:

$$2\mathrm{H_2}(g) + \mathrm{O_2}(g) \rightleftarrows 2\mathrm{H_2O}(l) \tag{7.5.4}$$

The problem here is that there is no obvious transfer of electrons. Neither is there an obvious reason why these two elements should react in the first place, as neither of them has any charge polarity that might lead to an initial interaction. That being said, there is no doubt that $\mathrm{H_2}$ and $\mathrm{O_2}$ react. In fact, like sodium and water, they react explosively.[21] When we look a little more closely at the reaction, we can see that there is a shift in electron density on individual atoms as they move from being reactants to being products. The reactants contain only pure covalent ($\mathrm{H—H}$ and $\mathrm{O—O}$) bonds, but in the product ($\mathrm{H_2O}$) the bonds are polarized: $\mathrm{H}\delta+$ and $\mathrm{O}\delta-$ (recall that oxygen is a highly electronegative atom because of its highly effective nuclear charge.) There is a shift in overall electron density towards the oxygen. This is a bit subtler than the NaCl case. The oxygen has gained some extra electron density, and so been reduced, but only partially – it does not gain the whole negative charge. The hydrogen has also been oxidized by losing some electron density. We are really talking about where the electron spends most of its time. In order to keep this straight, chemists have developed a system of oxidation numbers to keep track of the losses and gains in electron density.

Oxidation States and Numbers

Now, we may seem to be deploying more arcane terms designed to confuse the non-chemist, but in fact, oxidation numbers (or oxidation states) can be relatively easy to grasp as long as you remember a few basic principles:[22]

- For an ion, the charge is the oxidation number. The oxidation number of $\mathrm{Na^+}$ is +1, the oxidation number of the oxide ion ($\mathrm{O_2}^-$) is –2.
- For elements that are covalently bonded to a different element, we imagine that all the electrons in the bond are moved to the most electronegative atom to make it charged. As an example, the oxygen in water is the more electronegative atom. Therefore, we imagine that the bonding electrons are on oxygen and that the hydrogen atoms have no electrons (rather, they have a +1 charge). The oxidation number of H (in water) is +1, whereas in oxygen it is -2, because of the -2 charge of the two imagined extra electrons that came from the bond.
- Elements always have an oxidation number of zero (because all of the atoms in a pure element are the same, so none of the bonds are polar).

Remember this is just a way to keep track of the electrons. Oxidation numbers are not real; they are simply a helpful device. It is also important to remember that the oxidation number (or state) of an atom is dependent upon its molecular context. The trick to spotting a redox reaction is to see if the oxidation number of an atom changes from reactants to products. In the reaction:

$$2H_2(g) + O_2(g) \rightleftarrows 2H_2O(l) \tag{7.5.5}$$

H changes from zero in the reactants (H_2) to +1 in the products (H_2O), and the oxygen goes from zero (O_2) to –2 (H_2O). When oxidation numbers change during a reaction, the reaction is a redox reaction.

Now lets look at the reaction sodium and water, which is a bit more complicated to see if we can spot what is oxidized and what is reduced.

$$2Na(s) + 2H_2O(l) \rightleftarrows 2Na + (aq) + 2^-OH(aq) + H_2(g) \tag{7.5.6}$$

It is relatively easy to see that the sodium gets oxidized, because it loses an electron, going from Na to Na^+. But which species gets reduced? Is it the oxygen or the hydrogen? Or could it be both? If we check for changes in oxidation state, the oxygen in water starts at –2 and in hydroxide (^-OH) it is still –2 (it has not been reduced or oxidized). If we check the hydrogens, we see two distinct fates. One of the hydrogen atoms stays bonded to the oxygen atom (in hydroxide); it starts at +1 and stays there. However, the other type ends up bonded to another hydrogen atom; it starts at +1 and ends at zero. It is these latter two hydrogen atoms that have been reduced!

Historically, the term oxidation has denoted a reaction with oxygen. For example, in simple combustion reactions:

$$CH_4(g) + O_2(g) \rightleftarrows CO_2(g) + H_2O(g) \tag{7.5.7}$$

Oxidation reactions like this provide major sources of energy, in the burning of fuel (natural gas, gasoline, coal, etc.) and also in biological systems. In the latter, carbons containing molecules such as sugars and lipids react with molecular oxygen to form compounds with very stable bonds (CO_2 and H_2O), releasing energy that can be used to break bonds and rearrange molecules. In a similar vein the original meaning of reduction was reaction with hydrogen, for example acetic acid can be reduced to ethanol by reacting with hydrogen:

$$CH_3CO_2H + H_2(g) \rightleftarrows CH_3CH_2OH \tag{7.5.8}$$

What is important to note is that, there cannot be an oxidation without a reduction – and vice-versa. Just like there can be no acid without a base.

Questions

Questions to Answer

- For the reaction $CH_4(g) + O_2(g) \rightleftarrows CO_2(g) + H_2O(g)$, which atoms are oxidized and which are
- reduced?
- For the reaction $CH_3CO_2H + H_2(g) \rightleftarrows CH_3CH_2OH$ which atoms are oxidized and which are reduced?
- Write an explanation to a friend who has no chemistry background to explain the difference between these two reactions that give the same product:

$$2H_2(g) + O_2(g) \rightleftarrows 2H_2O(l) \text{ and } H^+(aq) + -OH(aq) \rightleftarrows H_2O(l) \tag{7.5.9}$$

Questions for Later

- Is it possible to separate out the oxidation reaction (where electrons are lost) and the reduction reaction (where electrons are gained)? What would happen?
- What if you separate the two reactions but join them by an electrical connection? What do you think would happen?