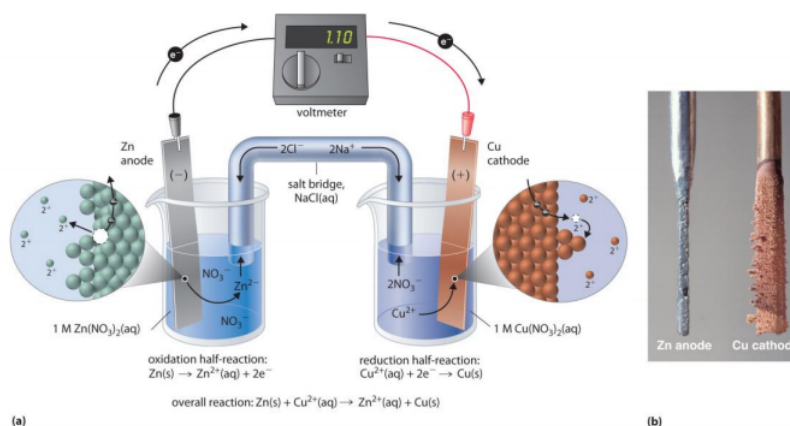
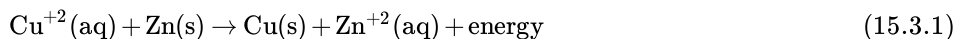


## 15.3: Oxidation and Reduction in the Context of Metabolism

Think back again to the redox chemistry that you learned in your general chemistry course. A common experiment in a general chemistry lab is to set up a galvanic cell consisting of a copper electrode immersed in an aqueous copper nitrate solution, connected by a wire to a zinc electrode immersed in an aqueous zinc nitrate solution.



When the cell is completed with a salt bridge, an electrical current begins to flow - what we have is a simple battery (figure a above). Over time, the copper electrode gets heavier as metallic copper is deposited on the copper cathode, while the zinc anode slowly dissolves into solution (figure b above). The redox reaction occurring here is:



Electrons flow from zinc metal to copper cations, creating zinc cations and copper metal: in other words, zinc metal is being oxidized to zinc cation and copper cation is being reduced to copper metal, as expressed by the two relevant half-cell reactions:

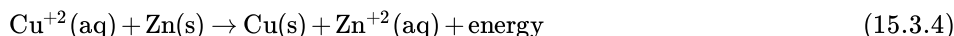


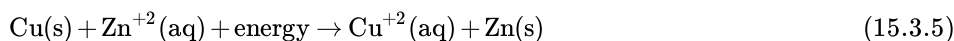
We can predict before we set up the cell that the spontaneous flow of electrons will go in the zinc to copper direction, just by looking at a table of standard reduction potentials (such a table was no doubt in your general chemistry text).

Table 15.3.1 : Standard reduction potentials at 25°

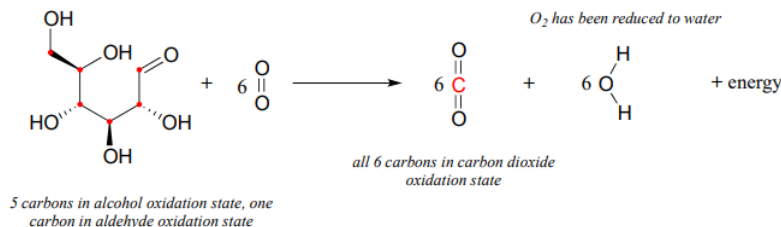
Reduction half-reaction	Reduction potential (volts)
$\text{Ag}^{+1}(\text{aq}) + \text{e}^{-} \rightarrow \text{Ag}^0(\text{s})$	0.800
$\text{Cu}^{+2}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}^0(\text{s})$	0.337
$\text{H}^{+1}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{H}_2(\text{g})$	0 (Standard)
$\text{Pb}^{+2}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Pb}^0(\text{s})$	-0.126
$\text{Fe}^{+2}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Fe}^0(\text{s})$	-0.441
$\text{Zn}^{+2}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Zn}^0(\text{s})$	-0.763

Copper ion ( $\text{Cu}^{+2}$ ) has a higher standard reduction potential than zinc ion ( $\text{Zn}^{+2}$ ), meaning that, under identical conditions, more energy is released by reducing one mole of  $\text{Cu}^{+2}$  ion to  $\text{Cu}^0$  metal than is released by reducing one mole of  $\text{Zn}^{+2}$  ion to  $\text{Zn}^0$  metal.. Another way to think about this is to imagine that the copper ion 'wants' to gain electrons more than the zinc ion does. Conversely, zinc metal 'wants' to lose electrons more than the copper metal does. Therefore, transfer of two electrons from zinc metal to  $\text{Cu}^{2+}$  is a thermodynamically downhill process, whereas the reverse process - transfer of two electrons from copper metal to  $\text{Zn}^{2+}$  - is thermodynamically uphill.



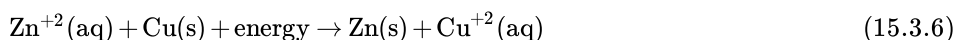


Let's now extend the idea of redox reactions to the context of metabolism in living things. When we 'burn' glucose for energy, we transfer (by a series of enzyme-catalyzed reactions) electrons from glucose to molecular oxygen ( $\text{O}_2$ ), oxidizing the six carbon molecules in glucose to carbon dioxide and at the same time reducing the oxygen atoms in  $\text{O}_2$  to water. The overall chemical equation is:



The transfer of electrons from glucose to  $\text{O}_2$  is a thermodynamically downhill, energy-releasing process, just like the transfer of electrons from zinc metal to copper ion. And while you could have used the energy released by the zinc/copper redox reaction to light a small light bulb, your cells use the energy released by the glucose/oxygen redox process to carry out a wide variety of energy-requiring activities, such as walking to your organic chemistry lecture.

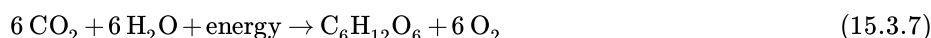
In your general chemistry copper/zinc experiment, was it possible to reverse the reaction so that it runs in the uphill direction - in other words, to oxidize copper and reduce zinc?



Just ask yourself the question: is it possible to get water to flow uphill? Of course it is - but only if you supply a pump and some energy!

The same idea applies to 'pumping' electrons uphill in your copper-zinc electrochemical cell: all you need to do is to provide some energy in the form of an external electrical current in order to pump the electron flow in the uphill direction. You are recharging your battery.

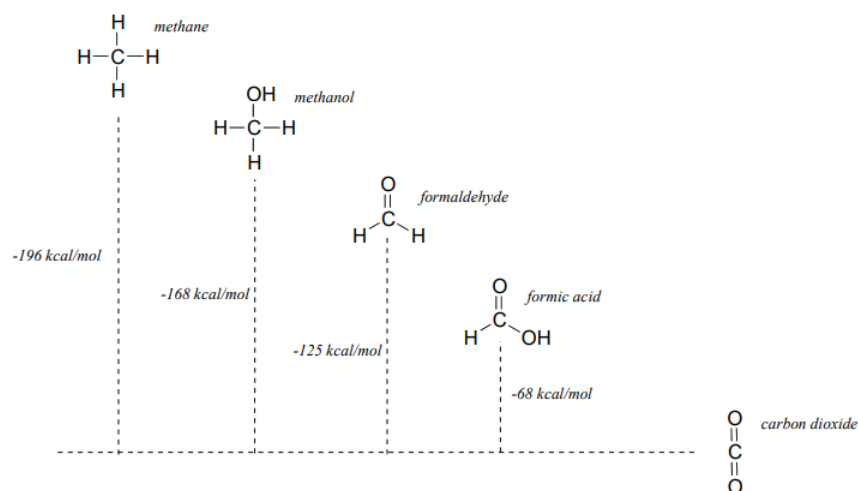
Thinking again in a biochemical context: plants are able, by a process called photosynthesis, to reduce carbon dioxide and oxidize water to form glucose and molecular oxygen: essentially recharging the ecosystem's biochemical battery using energy from the sun.



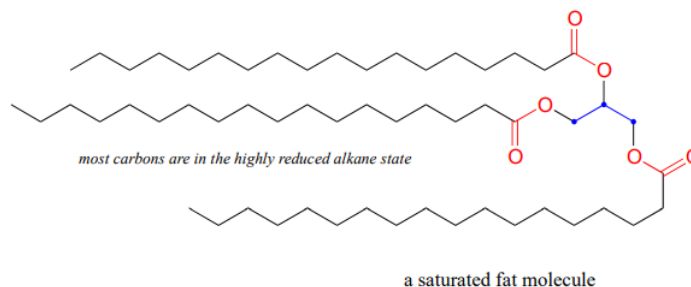
On a global scale, oxidation of the carbons in glucose to  $\text{CO}_2$  by non-photosynthetic organisms (like people) and the subsequent reductive synthesis of glucose from  $\text{CO}_2$  by plants is what ecologists refer to as the 'carbon cycle'.

In general the more reduced an organic molecule is, the more energy is released when it is oxidized to  $\text{CO}_2$ . Going back to our single-carbon examples, we see that methane, the most reduced compound, releases the most energy when oxidized to carbon dioxide, while formic acid releases the least:

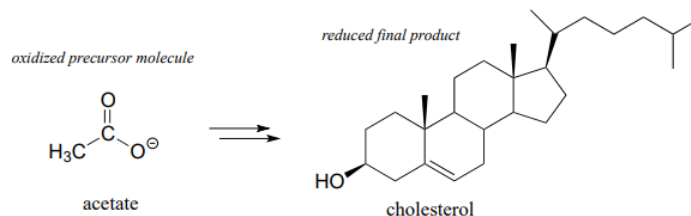
energy of oxidation to CO<sub>2</sub>:



A lipid (fat) molecule, where most of the carbons are in the highly reduced alkane state, contains more energy per gram than glucose, where five of the six carbons are in the more oxidized alcohol state (look again at the glucose structure we saw just a couple of pages back).



After we break down and oxidize sugar and fat molecules to obtain energy, we use that energy to build large, complex molecules (like cholesterol, or DNA) out of small, simple precursors. Many biosynthetic pathways are reductive: the carbons in the large biomolecule products are in a reduced state compared to the small precursors. Look at the structure of cholesterol compared to that of acetate, the precursor molecule from which all of its carbon atoms are derived - you can see that cholesterol is overall a more reduced molecule.



While we are focusing here on the mechanistic details of the individual organic redox reactions involved in metabolism, if you take a course in biochemistry you will learn much more about the bigger picture of how all of these reactions fit together in living systems.

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