

Additional Notes (Class 7)

Oxidation-reduction for the Non-chemical Skeptic (Chapter 2)

Amongst many other things, oxidation-reduction chemistry underlies battery-cell technology; that is, if the device is properly constructed, we can drive electrons through external circuits (the reverse of formal current flow). So, if you believe that electronic devices can be powered with batteries (!) you basically have to accept that oxidation-reduction chemistry takes place. Similarly, while it might not be so immediately obvious, ecosystems are powered by oxidation-reduction chemistry, but living systems are mainly configured to convert the “free energy” derived from the reactions into other chemical forms rather than produce (or draw) electric currents.

Oxidation-reduction chemistry involves transfer of electrons: if an atom, or part of some molecule (or ion) gains one or more electrons, the process is called a reduction; whereas loss of one or more electrons is termed oxidation (*N.B.* there need be no oxygen involved). The two processes have to happen simultaneously, the reductant (or “donor”) passing electrons to the oxidant (or “acceptor”) – hence the common use of the alternate contracted acronym “redox” chemistry. Notice also that the reductant must itself become oxidized during the reaction while, the oxidant becomes reduced. This same central idea of electrons being shuttled from reductant to oxidant also holds in the case of battery-powered electronics; the oxidation and reduction processes must still be essentially simultaneous, but are spatially separated, allowing the transferring electrons to be, in effect, transiently “borrowed” while passing through the external circuit.

Oxidation Numbers

Identifying electrons moving among the individual atoms and bonds between (and perhaps within) molecules is often too difficult to be of much practical value and so, we adopt a formalism to help us keep track of these things. The formalism involves determining the change in the oxidation number of a key moiety (one or more atoms) within a molecule. Note that some elements have a greater affinity for electrons than others; for example, oxygen tends to exist as the O^{2-} species in its ionic compounds. Other elements prefer to ionize by loss of electrons; for instance, hydrogen tends to behave as H^+ in all cases of concern to us here. Consequently, we may propose that, in molecules, hydrogen will have an “oxidation number of +1” and oxygen will have an “oxidation number of -2.” Using examples of simple organic compounds containing only C, H, and O, in order to determine the oxidation numbers of the key C atom(s) one proceeds as follows:

- 1) Identify the C atom(s) in a structure that undergo(es) change during the redox reaction and assign an initial value of zero.
- 2) To the initial value add 2 for every O bound, and subtract 1 for every H bound; bound C has no impact.

3) The sum of the oxidation numbers of all the atoms in the ion or molecule will add up to the charge on the ion, or zero in the case of a molecule.

4) In the case of more complicated molecules, additional rules apply, but this simplified subset (1-3 above) will illustrate the points we need to consider here.

Examples

The oxidation number of C in carbon dioxide (CO₂) is (rules 1 & 2):

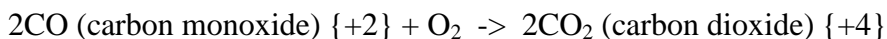
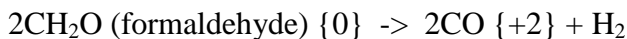
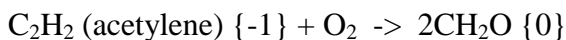
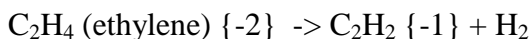
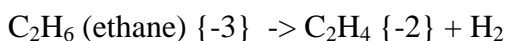
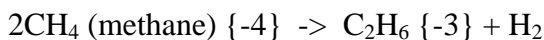
$$0 + (2 \times 2) = +4 \quad [\text{Check (rule 3): } +4 + 2(-2) = 0]$$

The oxidation number of C in methane (CH₄) is (rules 1 & 2):

$$0 - (4 \times 1) = -4 \quad [\text{Check (rule 3): } -4 + 4(-1) = 0].$$

So, from this we can deduce that converting carbon dioxide into methane is a reduction reaction (oxidation number becomes more negative) requiring 8 electrons. Conversely, converting methane to carbon dioxide is an oxidation reaction (increasing oxidation number) abstracting 8 electrons.

A sequence of oxidation reactions is presented below, showing a series of possible intermediates between methane and carbon dioxide. Of course, if you read the sequence backwards with the arrows reversed in your mind, it becomes a series of reductions. The oxidation numbers of carbon in the intermediates are given. Note that removal of dihydrogen is an oxidation and addition of dihydrogen corresponds to a reduction. Also note that the oxidation number of C in formaldehyde (CH₂O) is the same as it is in sugars ({CH₂O}_n) *i.e.* $0 - 2 \times 1 + 2 = 0$; therefore, conversion of sugar to carbon dioxide is an oxidation involving the abstraction of 4 electrons per carbon. Importantly, if you make both methane and carbon dioxide in equal quantities from sugar (a process known as “fermentative” methanogenesis) there is no net redox chemistry.



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