The chemist's toolkit 9 Oxidation numbers

The **oxidation number**, N_{ox}, of an element is a formal measure of the extent to which an atom can be considered to have lost electrons when it becomes part of a compound. An increase in oxidation number for an atom in a reaction signifies that it is has been oxidized; a decrease signifies it has been reduced. The element is said to be in an **oxidation state** with the specified oxidation number, but many use the terms 'oxidation number' and 'oxidation state' interchangeably.

Oxidation numbers are assigned as follows. The rules are based on exaggerating the ionic nature of the bonding, assigning ownership of shared electrons to the more electronegative element in a bond, and ensuring that the sum of the oxidation numbers is equal to the overall charge of the species. Thus:

1. The oxidation number of an uncombined form of the element is 0.
2. For monatomic ions, the oxidation number is the charge number of the ion. Thus, the oxidation number of Fe^{2+} is +2 and that of Cl^- is −1.
3. The oxidation number of oxygen is assigned as follows:

Species	Oxidation number of O
Element, O_2	0
Superoxide ion, O_2^-	$-\frac{1}{2}$
Peroxide ion, O_2^{2-}	−1
Oxide ion, O^{2-}	−2

4. The oxidation numbers of elements other than oxygen are assigned, as indicated above, by ensuring that the sum of all the oxidation numbers in the compound or ion is equal to the overall charge of the species. Thus, hydrogen in H_2O_2 is ascribed the oxidation number +1 so that the net oxidation number of the molecule is 0. Thus, the oxidation number of nitrogen in some biochemically significant species is as follows:

Species	Oxidation number of N
Element, N_2	0
Ammonia, NH_3; ammonium, NH_4^+; amines; amides; cyanide (CN^-)	−3
Nitrogen oxide, NO	+2
Nitrite, NO_2^-	+3
Nitrate, NO_3^-	+5

Many biochemically significant molecules are so complex that external information is used as a guide. Thus, NADH, with molecular formula $C_{21}H_{27}N_7O_{14}P_2$, is treated by noting that it is a hydride ion donor in some of its reactions, so it is treated as NAD^+H^-, with the hydridic hydrogen atom ascribed the oxidation number −1 and noting only the net oxidation number of the rest of the molecule (as for NAD^+ itself) as +1.