

## 11.1: Oxidation Numbers

### Learning Outcomes

- Assign oxidation numbers to free elements or elements in a compound or ion.

### Oxidation Numbers

An **oxidation number** is a positive or negative number that is assigned to an atom to indicate its degree of oxidation or reduction. The term oxidation state is often used interchangeably with oxidation number. A partial electron transfer is a shift in the electron density near an atom as a result of a change in the other atoms to which it is covalently bonded. That charge shift is based on the relative electronegativities of the atoms involved in the bond.

Overall, the oxidation number of an atom in a molecule is the charge that the atom would have if all polar covalent and ionic bonds resulted in a complete transfer of electrons from the less electronegative atom to the more electronegative one. Oxidation numbers can be assigned using the set of rules outlined below.

- The oxidation number of an atom in a neutral free element is zero. A free element is considered to be any element in an uncombined state, whether monatomic or polyatomic. For example, the oxidation number of each atom in Fe, Li, N<sub>2</sub>, Ar, and P<sub>4</sub> is zero.
- The oxidation number of a monatomic (composed of one atom) ion is the same as the charge of the ion. For example, the oxidation numbers of K<sup>+</sup>, Se<sup>2-</sup>, and Au<sup>3+</sup> are +1, -2, and +3, respectively.
- The oxidation number of oxygen in most compounds is -2.
- The oxidation number of hydrogen in most compounds is +1.
- The oxidation number of fluorine in all compounds is -1. Other halogens usually have an oxidation number of -1 in binary compounds, but can have variable oxidation numbers depending on the bonding environment.
- In a neutral molecule, the sum of the oxidation numbers of all atoms is zero. For example, in H<sub>2</sub>O, the oxidation numbers of H and O are +1 and -2, respectively. Because there are two hydrogen atoms in the formula, the sum of all the oxidation numbers in H<sub>2</sub>O is 2(+1) + 1(-2) = 0.
- In a polyatomic ion, the sum of the oxidation numbers of all atoms is equal to the overall charge on the ion. For example, in SO<sub>4</sub><sup>2-</sup>, the oxidation numbers of S and O are +6 and -2, respectively. The sum of all oxidation numbers in the sulfate ion would be 1(+6) + 4(-2) = -2, which is the charge of the ion.

An examination of the rules for assigning oxidation numbers reveals that there are many elements for which there are no specific rules, such as nitrogen, sulfur, and chlorine. These elements, as well as some others, can have variable oxidation numbers depending on the other atoms to which they are covalently bonded in a molecular compound. It is useful to analyze a few molecules in order to see the strategy to follow in assigning oxidation numbers to other atoms.

Oxidation numbers for the atoms in a binary ionic compound are easy to assign because they are equal to the charge of the ion (rule 2). In FeCl<sub>3</sub>, the oxidation number of iron is +3, while the oxidation number of chlorine is -1. In Ca<sub>3</sub>P<sub>2</sub>, the calcium is +2, while the phosphorus is -3. This is because an ionic compound is in the form of a crystal lattice that is actually composed of these ions.

Assigning oxidation numbers for molecular compounds is trickier. The key is to remember rule 6: that the sum of all the oxidation numbers for any neutral species must be zero. Make sure to account for any subscripts which appear in the formula. As an example, consider the compound nitric acid, HNO<sub>3</sub>. According to rule 4, the oxidation number of hydrogen is +1. According to rule 3, the oxidation number of oxygen is -2. There is no rule regarding nitrogen, but its oxidation number can be calculated as follows.

$$1(+1) + x + 3(-2) = 0, \text{ where } x \text{ is the oxidation number of nitrogen} \quad (11.1.1)$$

$$\text{Solving: } x = 0 - 1 - (-6) = +5 \quad (11.1.2)$$

The oxidation number of the nitrogen atom in HNO<sub>3</sub> is +5. Often when assigning oxidation numbers, it is convenient to write it above the symbol within the formula.



You may wonder if there are any limits on the value of oxidation numbers. The key point to consider is the octet rule. Since nitrogen has 5 valence electrons, the most that it can "lose" while forming bonds in a molecule is 5, so its highest possible oxidation number is +5. Alternatively, it could gain up to 3 electrons, and so its lowest (most negative) possible oxidation number is -3. Similarly, chlorine can have oxidation numbers ranging from -1 to +7.

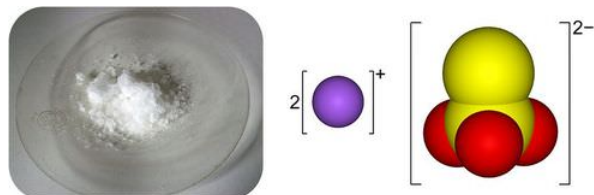


Figure 11.1.1: Sodium thiosulfate is a white crystalline compound (left) composed of two sodium ions ( $\text{Na}^+$ ) for every one thiosulfate ion ( $\text{S}_2\text{O}_3^{2-}$ ) (right).

Now consider the ionic compound sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$  (Figure 11.1.1). It contains the thiosulfate polyatomic ion,  $\text{S}_2\text{O}_3^{2-}$ . The sodium is not part of the covalently bonded polyatomic ion, and so its oxidation number is the same as it would be in a binary ionic compound, +1. The sulfur is the atom whose oxidation number is not covered by one of the rules. The oxidation number of sulfur is assigned the variable  $x$  in the following calculation. Remember the sum of the oxidation numbers of all the elements must equal zero because  $\text{Na}_2\text{S}_2\text{O}_3$  is a neutral compound.

$$2(+1) + 2(x) + 3(-2) = 0 \quad (11.1.4)$$

$$2 + 2x - 6 = 0 \quad (11.1.5)$$

$$-4 + 2x = 0 \quad (11.1.6)$$

$$2x = +4 \quad (11.1.7)$$

$$x = +2 \quad (11.1.8)$$

Sulfur has an oxidation number of +2 in  $\text{Na}_2\text{S}_2\text{O}_3$ . Notice how the subscript of 2 for the S atom had to be accounted for by dividing the result of the subtraction by 2. When assigning oxidation numbers, you do so for each individual atom. In the above example, the oxidation number of sulfur could also have been determined by looking at just the thiosulfate ion,  $\text{S}_2\text{O}_3^{2-}$ .

$$2(x) + 3(-2) = -2 \quad (11.1.9)$$

$$2x - 6 = -2 \quad (11.1.10)$$

$$2x = +4 \quad (11.1.11)$$

$$x = +2 \quad (11.1.12)$$

## Contributors and Attributions

- 
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)

This page titled [11.1: Oxidation Numbers](#) is shared under a [CK-12](#) license and was authored, remixed, and/or curated by [CK-12 Foundation](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.