1.1: Fundamental Properties - Oxidation State

The oxidation state of an element is defined as *the formal charge on the atom if all bonds were assumed to be fully ionic*.

In an ionic compound the oxidation state is equal to the charge on the ion, e.g., in NaCl the charge on the sodium is +1 and the oxidation state is also +1. In contrast, the charge on an atom in a covalent compound never approaches the charge implied from the oxidation number, e.g., in CCl4, the oxidation state of carbon is +4 but the charge on the carbon atom is signicantly less.

Thus, while oxidation state is a simple formulism it is very useful in a number of ways:

1. Classication of compounds of elements, especially those of the transition metals.
2. Enables the balance of reduction-oxidation (redox) reactions.

To determine the oxidation state of an element within a particular compound the following steps act as a guideline:

1. The oxidation state of any atom of any element in its elemental form is zero.
2. The oxidation state of a monatomic ion is equal to its charge.
3. Any homoleptic X-X bonds (e.g., the C-C bond in H3C-CH3) are assumed to be non-ionic and do not contribute to the oxidation state of X.
4. Fluorine always has oxidation state of 1
5. Elements of Group 1 (IA) (except hydrogen) have an oxidation state of +1 in compounds.
6. Elements of Group 2 (IIA) have an oxidation state of +2 in compounds.
7. Elements of Group 17 (VIIA) have an oxidation state of -1 when they combine with elements below or to the left of their position in the periodic table
8. Oxygen is usually assigned the oxidation state of 2, except in compounds with uorine, oxygen has a positive oxidation number.
9. Hydrogen is assigned the oxidation state of +1 with non-metals and 1 with metals.
10. In any compound the sum of the oxidation states (oxidation numbers) is equal to the overall charge.

Exercises

Exercise 1.1.1

What is the oxidation state of sulfur in Na_2SO_4?

Solution

The two sodium atoms each have an oxidation state of +1, while the oxygen atoms have an oxidation state of 2, and the overall charge is 0.

1. overall charge = sum of oxidation states
2. 0 = (2 x oxidation state of Na) + (oxidation state of S) + (4 x oxidation state of O)
3. 0 = (2 x +1) + (oxidation state of S) + (4 x -2)
4. oxidation state of S = 0 (2 x +1) - (4 x 2)
5. oxidation state of S = +6

Exercise 1.1.2

What is the oxidation state of sulfur in Na_2SO_3?

Solution

The two sodium atoms each have an oxidation state of +1, while the oxygen atoms have an oxidation state of 2, and the overall charge is 0.

1. overall charge = sum of oxidation states
2. 0 = (2 x oxidation state of Na) + (oxidation state of S) + (3 x oxidation state of O)
3. 0 = (2 x +1) + (oxidation state of S) + (3 x -2)
4. oxidation state of S = 0 (2 x +1) - (3 x 2)
5. oxidation state of S = +4

Exercise 1.1.3

What is the oxidation state of sulfur in H_2S?

Solution

The two hydrogen atoms each have an oxidation state of +1 and the overall charge is 0.

- overall charge = sum of oxidation states
- 0 = (2 x oxidation state of H) + (oxidation state of S)
- 0 = (2 x +1) + (oxidation state of S)
- oxidation state of S = 0 (2 x +1)
- oxidation state of S = -2

In writing the oxidation state of an element within a compound it is common to use a Roman numeral, rather than the charge, i.e., Al(III) rather than Al^{3+}.
