

17.3: Defining Oxidation States

We introduce oxidation states to organize our thinking about oxidation–reduction reactions and electrochemical cells. When we define oxidation states, we create a set of rules for allocating the electrons in a molecule or ion to the individual atoms that make it up. The definition of oxidation states is therefore an accounting exercise. The definition of oxidation states predates our ability to estimate electron densities through quantum mechanical calculations. As it turns out, however, the ideas that led to the oxidation state formalism are directionally correct; atoms that have high positive oxidation states according to the formalism also have relatively high positive charges by quantum mechanical calculation. In general, the absolute values of oxidation states are substantially larger than the absolute values of the partial charges found by quantum-mechanical calculation; however, there is no simple quantitative relationship between oxidation states and the actual distribution of electrons in real chemical moieties. It is a serious mistake to think that our accounting system provides a quantitative description of actual electron densities.

It is a serious mistake to think that the Oxidation State system provides a quantitative description of actual electron densities.

The rules for assigning oxidation states grow out of the primitive (and quantitatively incorrect) idea that oxygen atoms usually acquire two electrons and hydrogen atoms usually lose one electron in forming chemical compounds and ionic moieties. The rest of the rules derive from a need to recognize some exceptional cases and from applying the basic ideas to additional elements. The rules of the oxidation state formalism are these:

- For any element in any of its allotropic forms, the oxidation state of its atoms is zero.
- In any of its compounds, the oxidation state of an oxygen atom is 2–, **except** in compounds that contain an oxygen–oxygen bond, where the oxidation state of oxygen is 1–. The excepted compounds are named peroxides. Examples include sodium peroxide, Na_2O_2 , and hydrogen peroxide, H_2O_2 .
- In any of its compounds, the oxidation state of a hydrogen atom is 1+, **except** in compounds that contain a metal–hydrogen bond, where the oxidation state of hydrogen is 1–. The excepted compounds are named hydrides. Examples include sodium hydride, NaH , and calcium hydride, CaH_2 .
- In any of their compounds, the oxidation states of alkali metal atoms (lithium, sodium, potassium, rubidium, cesium, and francium) are 1+.
- In any of their compounds, the oxidation states of halogen atoms (fluorine, chlorine, bromine, iodine, and astatine) are 1–, **except** in compounds that contain a halogen–oxygen bond.
- The oxidation states of any other atoms in a compound are chosen so as to make the sum of the oxidation states in the chemical moiety equal to its charge. So, for a neutral molecule, the oxidation states sum to zero. For a monovalent anion, they sum to 1–, *etc.*

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