Expanded Definition of the Oxidation State

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The oxidation state is defined by IUPAC as (1)

The oxidation state is... a measure of the degree of oxidation of an atom in a substance. It is defined as the charge an atom might be imagined to have when electrons are counted according to an agreed-upon set of rules: (1) the oxidation state of a free element (uncombined element) is zero; (2) for a simple (monatomic) ion, the oxidation state is equal to the net charge on the ion; (3) hydrogen has an oxidation state of 1 and oxygen has an oxidation state of −2 when they are present in most compounds. (Exceptions to this are that hydrogen has an oxidation state of −1 in hydrides of active metals, e.g., LiH, and oxygen has an oxidation state of −1 in peroxides, e.g., H2O2); (4) the algebraic sum of oxidation states of all atoms in a neutral molecule must be zero, while in ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion. For example, the oxidation states of sulfur in H2S, S8 (elementary sulfur), SO2, SO3, and H2SO4 are, respectively: −2, 0, +4, +6, and +6. The higher the oxidation state of a given atom, the greater is its degree of oxidation; the lower the oxidation state, the greater is its degree of reduction.

With some variations, the IUPAC guidelines are reproduced in most North American textbooks. IUPAC’s definition of the oxidation state is based on an identical definition published in the “Glossary of Atmospheric Chemistry Terms” that was compiled by Calvert in 1990 (2). Calvert did not distinguish between oxidation state and oxidation number, whereas IUPAC defines the oxidation number as (1)

Of a central atom in a coordination entity, the charge it would bear if all the ligands were removed along with the electron pairs that were shared with the central atom. It is represented by a Roman numeral.

That is, the oxidation number refers only to a single atom in a coordination compound, whereas the oxidation state can, in principle, be given for all atoms including ligand atoms.

In this article, we propose a simpler definition for the oxidation state that encompasses more compounds, has no exceptions, and is closer to being “a measure of oxidation of an atom in a substance”:

The oxidation state of an atom in a compound is given by the hypothetical charge of the corresponding atomic ion that is obtained by heterolytically cleaving its bonds such that the atom with the higher electronegativity in a bond is allocated all electrons in this bond. Bonds between like atoms (having the same formal charge) are cleaved homolytically. This is not a new definition, but it predates the IUPAC rules by several decades. For example, Linus Pauling provided a similar definition of the oxidation state in his 1947 edition of General Chemistry (3). An excellent historic overview and a strong argument for the expanded, older definition was made by Steinborn in 2004 in this Journal (4). It is obvious that the compounds for which the IUPAC rules apply are readily encompassed by the older definition. For example, all atoms in the simple sulfur-containing molecules that were mentioned in the IUPAC definition can readily be assigned the correct oxidation states. H atoms (O atoms) automatically arrive at oxidation states of +1 (−II), since they have a lower (higher) electronegativity compared to the sulfur (and H) atom and form one (two) covalent bonds. Similarly, the oxidation state of the sulfur atom is determined by the number of bonds to the less electronegative H atom and the more electronegative O atom. The definition also applies to molecular ions, such as nitrate, NO3− (Figure 1). Here, in a given resonance structure, each of the O atoms either forms a single bond and carries a negative charge or forms a double bond. By heterolytically cleaving all bonds, both “types of O atoms” arrive at an oxidation state of −II, whereas the oxidation state of nitrogen is +V. In all figures, the arrowheads of the bonds point toward the atom with the higher electronegativity.

Compounds such as LiH and H2O2, which were treated as exceptions by IUPAC, are expected to have unusual oxidation states considering the low electronegativity of Li and the O−O single bond in H2O2. Of course, the oxidation states of monatomic ions such as Na+ are identical to their charge. The definition also extends to other simple compounds such as thiocyanate SCN− (Figure 1), ClO3−, FCl, and others to which the IUPAC definition is not readily applied.

The main advantage of the expanded definition lies in its application to organic compounds. For example, the oxidation states of the carbon atoms in ethanol are −III for the methyl carbon and −I for the hydroxyl-substituted carbon (Figure 2). This indicates, correctly, that the functionalized carbon atom is more oxidized. Further oxidation to acetaldehyde and acetic acid changes the oxidation state of this carbon atom to +I and +III. Here, the definition provides for an accurate “measure of oxidation of an atom in a substance”, whereas with the IUPAC

Figure 1. Oxidation states in the nitrate and thiocyanate ions.

Figure 2. Oxidation states in the series ethanol, acetaldehyde, and acetic acid.
definition one has no means of distinguishing the oxidation states of the two carbon atoms.

In substituted aromatic compounds, the phenyl carbon atoms may have different oxidation states as is intuitively apparent. Examples of m-nitrotoluene and 1-chloronaphthalene are given in Figure 3. As expected, one finds that the potential to undergo further oxidation is different for the different carbon atoms. The expanded definition also sheds light on the oxidation states in oxidative addition reactions and reductive elimination reactions and correctly predicts the oxidation states of the metal atoms and their ligands. In metal–ligand complexes, the oxidation state, according to the expanded definition, is identical to IUPAC’s oxidation number, if the metal atom has a lower electronegativity than any of the atoms to which it forms a bond. The expanded definition also applies to fragments of larger molecules, that is, oxidation states can be assigned even if only parts of a molecule are given, for example, for polypeptide fragments of a protein.

In teaching high school or first-year college chemistry classes, the instructor may find it helpful to contrast the expanded definition of the oxidation state with that of a “formal charge”. Whereas the former requires that each bond is cleaved heterolytically and according to the electronegativity difference, the latter requires homolytic cleavage of the covalent bonds.

Limits of the definition are given by molecules or fragments for which Lewis structures are not easily available or when electronegativity differences are negligibly small. For example, the electronegativity difference between S and C is small enough that the oxidation state of S in SCN$^-$ may well be assigned to be zero in the top Lewis structure of Figure 1. However, using this approximation, the lower Lewis structure leads to S(−1). The ambiguity may be resolved by realizing that in the lower “charged” Lewis structure the shared covalent bond should be heterolytically cleaved and assigned to the more (electro-)positive atom in the bond. Steinborn also discusses the oxidation states of the sulfur atoms in the thiosulfate ion, which are equally ambiguous since different Lewis structures may lead to different oxidation states (4). Again, we propose to cleave the bond homolytically only when the atoms in the Lewis structure are identical and carry the same formal charge (Figure 4).

This expanded definition of oxidation states builds on the knowledge of electronegativity, whereas the IUPAC definition builds on a set of rules. In my experience, students accept a definition built on chemical concepts more readily. The definition of the oxidation state that is used here is commonplace in Germany and other European countries, but apparently has not widely been accepted in North America. General chemistry textbooks such as Atkins and Jones (5) exemplify the conundrum of the chemistry instructor. The textbook points out that the oxidation state (or oxidation number) arises from the concept of electronegativity differences, but then provides only the IUPAC rules as a tool to assign oxidation states. This Journal has also presented many different notions about the assignment and physical meaning of oxidation states. Some authors have even suggested to abolish the concept of oxidation states altogether, as assigning them appears to be a matter of definition and not related to physical observables (6).

The 1990 publication of the “Glossary of Atmospheric Chemistry Terms” by Calvert (2) and its three rules led to the IUPAC definition of the oxidation state, but Calzaferri pointed out that the IUPAC rules, and the expanded definition based on electronegativity differences, led to unreasonably low oxidation states of carbon in many organic compounds (7). He proposed neglecting the electronegativity differences in the C−H, B−H, Sn−H, and Ge−H bonds. At about the same time, Packer and Woodgate (8, 9) provided a different set of seven rules to help assign oxidation states. More recently, Woolf (10, 11), Menzek (12), and Steinborn (4) have proposed a return to the older, expanded definition; a view that is endorsed with this article.

Conclusion

We submit the expanded definition as a useful alternative to the IUPAC definition because it fully encompasses all of the previously covered atoms and compounds, includes compounds that could previously only be regarded as exceptions, and extends to compounds that were difficult or even impossible to address previously.

Literature Cited