

The Origin of the Oxidation-State Concept

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Question

What is the origin of the oxidation state concept?

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Answer

The concept of oxidation states ultimately derives from the oxygen-based dualistic system of chemistry introduced by the French chemist, Antoine Lavoisier, in the last quarter of the 18th century (1). It is here that the terms oxidation and reduction first appear in the literal sense of the reaction of an element with oxygen and its converse. The dualistic system further recognized that a given element could exhibit several degrees of oxidation - a fact which was incorporated into Lavoisier's reform of chemical nomenclature via the introduction of such distinctions as sulfuric versus sulfurous acid (2).

In both Lavoisier's original system, and in its later electrochemical elaboration by Berzelius, the oxides of nonmetals were thought to function as acids and those of metals as bases. These, on reacting with one another, formed salts, which were, in effect, higher order or ternary oxides. If a particular element gave rise to several oxides, each could generate its own series of salts and these salts were interconvertible through the selective oxidation or reduction of one or both of their component oxides. Thus, using a modernized version of Berzelius' dualistic formulas, we see that the difference between calcium sulfite [$\text{CaO}\cdot\text{SO}_2 = \text{CaSO}_3$] and calcium sulfate [$\text{CaO}\cdot\text{SO}_3 = \text{CaSO}_4$] was viewed as being literally due to the increased oxidation of the sulfur atom in the acidic oxide component, whereas the difference between ferrous sulfate [$\text{FeO}\cdot\text{SO}_3 = \text{FeSO}_4$] and ferric sulfate [$\text{Fe}_2\text{O}_3\cdot 3\text{SO}_3 = \text{Fe}_2(\text{SO}_4)_3$] was instead due to the further oxidation of the iron atom in the basic oxide component.

Starting with the discovery of Davy and others that the hydracids and halide salts of the halogens contained no oxygen, Lavoisier's original contention that



Figure 1. Harry Shipley Fry (1878-1949).

oxygen formed the common "bond of union" in all salts came under increasing attack in the first half of the 19th century. Yet, despite these discoveries, no attempt was made to discontinue the underlying practice of applying the terms oxidation and reduction to the reactions of salts and other compounds which were now known to contain no oxygen. Thus by 1884, the British chemist, M. M. Pattison Muir, had to confess that the original literal meaning of oxidation had now been considerably widened (3):

... until at present it is applied to all chemical changes which result in an addition of a negative radicle, simple or compound, to elements or compounds, or to a decrease in the relative quantity of the positive radicle of a compound, whether this is or is not accomplished by substitution of negative radicles.

Writing over 20 years later, the British chemists, Caven and Lander, were still giving essentially the same definition, though they now also attempted to rationalize this extended usage through the concept of “equivalent” processes (4):

Oxidation may therefore be described as the conversion of a compound representing a lower into one representing a higher stage of combination with oxygen, by the addition of either oxygen or an equivalent electronegative atom or radicle, or by the removal of hydrogen or an electropositive atom or radicle. Reduction may be defined as the result of the converse operations.

Meanwhile, in the field of electrochemistry, proponents of the new ionic theory of dissociation began to forge a connection between oxidation and reduction and changes in net ionic charges. Thus, writing in 1893, Wilhelm Ostwald observed that (5):

... fundamentally, oxidation and reduction processes in electrolytes consist in the acquisition or release of ionic charges; oxidants are those substances which acquire negative charges or release positive ones, reductants are those for which the opposite takes place.

- an extension which Talbot and Blanchard tacked on to the more conventional definition in their 1907 student booklet on the ionic theory of dissociation (6):

The oxidation of any body may, then, consist in the addition of the atoms of a negative element to its molecules, atoms, or ions, or the withdrawal of the atoms of a positive element; or it may consist in the addition of positive charges of electricity, or the withdrawal of negative charges. Reduction is the reverse of this...

The fourth and final stage came with the development of the electronic theory of bonding and structure in the first quarter of the 20th century. Already in the last quarter of the previous century chemists had recognized the necessity of having to distinguish between positive and negative valence (7), and in 1907 Caven and Lander had noted in passing that “oxidation usually denotes an increase in the active valency of the central atom” - a view made even more explicit by Hildebrand in 1918 when he wrote that (4, 8):

The term oxidation is applied whenever valence takes on a more positive (or less negative) value. The opposite process ... the decrease in valence, is called by the more obvious general name of reduction.

More radical still was the impact of the ionic bonding model, as it revealed that, not only changes in polar valence, but also the loss and gain of both positive and negative atoms and of positive and negative net charges, were ultimately all reducible to one and the same process - the loss and gain of electrons - thus allowing Fry (figure 1) to conclude in 1915 (albeit parenthetically) that (9):

The development of a positive valency by an atom (schematically through the loss of an electron) corresponds to oxidation. When an atom develops a negative valence (schematically through the gain of an electron) it is reduced.

As early as 1907 Talbot and Blanchard made reference to the various “oxidation states” of an element, but used the word valence to describe their numerical characterization, whereas Hildebrand preferred the term “valence number.” In 1913 Branch and Bray suggested that the term “polar number” would be less misleading (10), and in 1938 Latimer officially introduced the terms “oxidation number” or “oxidation state,” along with the parallel term “oxidation potential” (11). Though there was little controversy over the final identification of oxidation and reduction with electron loss and gain, the 20th-century chemical education literature would be characterized by considerable debate over the two related questions of how one goes about assigning oxidation numbers and how these numbers are to be used in balancing redox equations. Lack of space precludes further elaboration, but the history of both of these questions, as well as the history of the oxidation potential concept, would make interesting columns of their own.

Literature Cited

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2. L. Guyton de Morveau, A. Lavoisier, C. Berthollet, A. Fourcroy, *Méthode de nomenclature chimique*, Cuchet: Paris, 1787, pp. 40-41.
3. M. M. Pattison Muir, “Oxidation,” in H. Forster Morley, M. M. Pattison Muir, Eds., *Watts' Dictionary of Chemistry*, Vol. 3, Longmans, Green & Son: London, 1888, pp. 657-658.
4. R. M. Caven, G. D. Lander, *Systematic Inorganic Chemistry From the Standpoint of the Periodic Law*, Blackie and Son: London, 1907, p. 75.
5. W. Ostwald, *Lehrbuch der allgemeinen Chemie*, Vol. 2(1), Engelmann: Leipzig, 1893, p. 891.

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6. H. P. Talbot, A. A. Blanchard, *The Electrolytic Dissociation Theory with Some of Its Applications*, Macmillan: New York, NY, 1907, p. 54.

7. W. B. Jensen, "Electronegativity from Avogadro to Pauling. II. Late 19th- and Early 20th-Century Developments," *J. Chem. Educ.*, **2003**, *80*, 279-287.

8. J. H. Hildebrand, *Principles of Chemistry*, Macmillan: New York, NY, 1918, p. 94 and Chapter 15.

9. H. S. Fry, "The Electronic Conception of Positive and Negative Valences," *J. Am. Chem. Soc.* **1915**, *37*, 2368-2373. Definition on page 2371.

10. W. C. Bray, G. Branch, "Valence and Tautomerism," *J. Am. Chem. Soc.*, **1913**, *35*, 1440-1447.

11. W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solution*, Prentice-Hall: New York, NY, 1938, p. vii.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemis-

try, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

2009 Update

Most historians attribute the first explicit identification of oxidation and reduction with electron loss and gain to Harry Shipley Fry, as was done in the original column. However, since writing the column, I have discovered an even earlier source:

G. Buchner, *Angewandte Ionenlehre*, Lehmann: München, 1912.

where, on page 70, the author writes:

In a wider sense one can now understand the oxidation of metals as any loss of electrons whereby the positive charge increases. Reduction is then the uptake of electrons and/or loss of positive charge.