

Ask the Historian

Balancing Redox Equations

by William B. Jensen

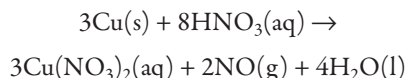
Question

What is the origin of our current techniques for balancing redox equations?

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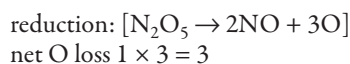
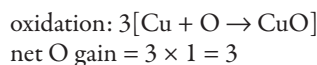
Answer

Most students of chemistry are currently taught to balance simple chemical equations by “inspection”, which is a polite way of saying that each student develops his or her own personal, albeit often subconscious, method based on practice (1). This haphazard approach also works with simple oxidation–reduction or redox equations, but usually proves insufficient when it comes to relatively complex redox reactions, such as the oxidation of copper with nitric acid:



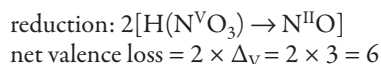
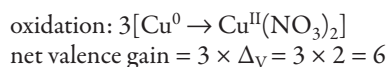
The most common approach in these cases is to explicitly identify which species is being oxidized and which is being reduced. By applying the general rule that the change in oxidation must be equal to the change in reduction, one then obtains the coefficients for these two species, after which those of the remaining reactants and products are easily determined by inspection. What has evolved over time is, of course, the definition of what changes during oxidation and reduction. Not unexpectedly, the historical evolution of the various techniques for balancing redox equations is a direct reflection of this changing definition as outlined in a previous column (2).

In keeping with the original literal meaning of oxidation and reduction as the addition and removal of oxygen respectively, the earliest conserved quantity for redox reactions was nascent or atomic oxygen (O). Rewriting the oxidant ($2\text{HNO}_3 = \text{H}_2\text{O} \cdot \text{N}_2\text{O}_5$) and reductant ($\text{Cu(NO}_3)_2 = \text{CuO} \cdot \text{N}_2\text{O}_5$) in dualist notation (modernized) and focusing on only those portions actually undergoing oxidation and reduction, one obtains the result that the coefficients for $\text{Cu(NO}_3)_2$ and NO must be 3 and 2, respectively, after which the remaining coefficients are easily determined (3):



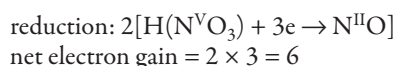
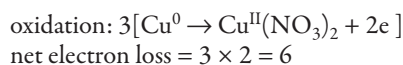
With the advent of the concept of polar valence in the 1870s and the generalization of oxidation to subsume valence

increase in general and reduction to subsume valence decrease in general, the conserved quantity now became the change in valence Δ_V :



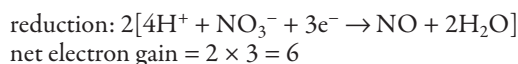
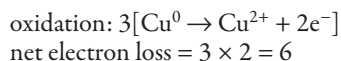
from which it once again follows that the coefficients for $\text{Cu(NO}_3)_2$ and NO must be 3 and 2, respectively. This approach was first explicitly articulated by the American chemist, O. C. Johnson, in 1880, though he unfortunately equated valence with the number of bonds an atom could form and was thus forced to awkwardly talk of balancing changes in positive and negative bonds (4). Reformulated in terms of changes in valence number, it was still being used by some authors as late as the 1920s (5).

With the explicit identification of oxidation and reduction with electron loss and gain, respectively, in the first decade of the 20th century, the polar valence method was modified to reflect conservation of electrons:



In this form it was made the subject of a small monograph by Keach in 1926 (6) and is still taught in our textbooks under the guise of the oxidation number or oxidation state method.

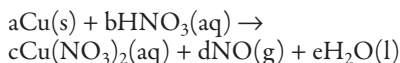
The advent of the electron loss and gain approach was also closely allied to the ionic theory of dissociation and the electrochemical theory of electrolysis and voltaic cells, and in 1927 Eric Jette and Victor K. La Mer published an article in this *Journal* arguing that, since all aqueous redox reactions could in principle be made the basis of various voltaic cells, they should be written as the sum of the resulting balanced cathode and anode cell reactions using net ionic rather than molecular equations (7):



Furthermore, they argued that both electron loss and gain and the subsequent weighting of the two half-cell equations should be based on the balancing of net ionic charges rather than on hypothetical polar valence or oxidation numbers. Dubbed the ion–electron method, the approach was made the basis of a small book published by Jette the same year and was also the subject of a subsequent debate in this *Journal* (1, 8). Like the valence or oxidation number approach, it is still widely used in modern textbooks.

Ask the Historian

Finally, mention should be made of a far more general method of balancing all chemical equations, whether redox or nonredox, molecular or net ionic. Introduced by the British chemist, James Bottomley, in 1878, it is variously known as the algebraic method or the method of material balance and is based on the fundamental principle of the conservation of chemical elements in chemical reactions first explicitly articulated by Lavoisier in 1789 (9, 10). In this approach one represents the various coefficients in the unbalanced equation as variables:



and writes down explicit equations of balance for each element (and for ionic charge in the case of net ionic equations):

$$\text{Cu} \quad a = c$$

$$\text{H} \quad b = 2e$$

$$\text{N} \quad b = 2c + d$$

$$\text{O} \quad 3b = 6c + d + e$$

These are then solved using any of the various methods available for the solution of simultaneous equations. Since such algebraic prowess is beyond the abilities of most introductory students, this approach is seldom taught in chemistry departments, though it is widely employed by chemical engineers. As a result, the chemical education literature continues to be plagued with arguments over the best approximate method for balancing equations—so much so that some years ago the editor of this *Journal* felt compelled to call a moratorium on papers dealing with this subject (11).

Literature Cited

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