Balancing Redox Equations

We appreciated the “Balancing Redox Equations” article by W. B. Jensen (1). For additional insights, we direct readers to an excellent Web site about chemical reaction stoichiometry (2). W. R. Smith, I. Sikaneta, and R. W. Missen established this Web site in 1998. Earlier, Smith and Missen published three articles in this Journal related to chemical stoichiometry (3–5) and more recently made reference to their Web site (6). The Web site contains a wealth of information about chemical stoichiometry. This includes the theory behind the matrix-reduction method, its application to several interesting chemical examples, and a java applet called JSTOICH.

Chemical equations are a chemical description of the conservation of chemical elements. A crucial issue is the number of such equations required for a complete description. In simple cases, a single equation suffices, but this is not always the case. An exercise that appeared in a recent edition of a general chemistry text asked the student to balance the following chemical equation (7) in basic aqueous solution:

\[
\text{H}_2\text{O}_2(\text{aq}) + \text{ClO}_2(\text{aq}) = \text{ClO}_2^-(\text{aq}) + \text{O}_2(\text{aq})
\]

The difficulty with this representation is that the student is implicitly asked to assume that only one chemical equation gives the correct answer. In fact, JSTOICH shows that two independent equations are required. A representative set of equations is

\[
2\text{ClO}_2(\text{aq}) + 2\text{OH}^-(\text{aq}) = \text{H}_2\text{O}_2(\text{aq}) + 2\text{ClO}_2^-
\]

\[
2\text{H}_2\text{O}_2(\text{aq}) = 2\text{H}_2\text{O}(\text{aq}) + \text{O}_2(\text{g})
\]

Of course, adding together an arbitrary multiple of each of the above equations produces a single equation, but this can be performed in an infinite number of ways. A key point in chemical stoichiometry problems is the number of independent chemical equations, which is two in this case. We note in passing that a chemical reaction may be restricted in its stoichiometry (4).

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Roger L. DeKock* and Benjamin M. Brandsen
Department of Chemistry and Biochemistry Calvin College Grand Rapids, Michigan 49546-4403
norbert-pienta@uiowa.edu

Response to Letter from DeKock and Brandsen about Balancing Redox Equations

As stated in my column, any mathematical technique for the solution of simultaneous equations, including those based on matrices and determinants, may be employed in conjunction with the material-balance approach to the balancing of chemical equations. Yet an additional advantage of this approach, not mentioned in the column, but to which I drew attention more than 20 years ago, is the fact that it also allows one to evaluate whether the proposed equation truly represents a unique chemical reaction (1).

If one makes all of the observed reactants and products explicit in the example given by DeKock and Brandsen, rather than implicit in the phrase “basic aqueous solution”, and assigns variables to the resulting six undetermined coefficients,

\[
a\text{OH}^- (\text{aq}) + b\text{H}_2\text{O}_2(\text{aq}) + c\text{ClO}_2(\text{aq}) = d\text{ClO}_2^-(\text{aq}) + e\text{O}_2(\text{aq}) + f\text{H}_2\text{O}(\text{l})
\]

then four independent equations of balance can be written:

hydrogen: \(a + 2b = 2f\)

oxygen: \(a + 2b + 2c = 2d + 2e + f\)

chlorine: \(c = d\)

ionic charge: \(a = d\)

A quick calculation of the mathematical degrees of freedom \((f)\) for six variables \((v)\) and four equations \((e)\),

\[f = v - e\]

gives \(f = 2\), and reveals that no unique lowest whole number solution is possible for this system as written. This is in contrast to proper chemical equations for which \(f = 1\) (i.e., setting one coefficient at the lowest possible whole number uniquely determines the values of the others). The usual interpretation of the result \(f > 1\) is that the equation in question is not that of a single.

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unique chemical reaction, but rather the sum of several simultaneous competing reactions, such as the two given by DeKock and Brandsen. The result \( f < 1 \), on the other hand, usually indicates that one or more reactants or products are missing from the proposed equation.

These simple pen-and-paper results do not require an elaborate computer program and are much more amendable to the conventional test environment of a typical chemistry course. I would further note a potential source of confusion in the use of the term “independent equations,” which usually refers to the number of independent equations of balance rather than to the number of independent competing chemical reactions.

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William B. Jensen*
Department of Chemistry University of Cincinnati
Cincinnati, OH 45221-0175
norbertpienta@ucmail.uc.edu

**Literature Cited**

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**Addition to Letter from DeKock and Brandsen about Balancing Redox Equations**

As a historical note, our algorithm for implementing the matrix-reduction method first appeared in Chemical Engineering Education (1) (interestingly, after a submission along similar lines had earlier been rejected by this Journal!). Chemical reaction stoichiometry applies to any situation in which the conservation of chemical elements arises, although the topic is often discussed in undergraduate textbooks in the context of chemical thermodynamics. Our 2003 article cited in the DeKock and Brandsen’s letter shows that the same method can also be used in the context of chemical kinetics to determine the maximum number and a realization of a set of independent mass-conservation equations implied by a given chemical reaction mechanism.

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W. R. Smith*
University of Ontario Institute of Technology, Oshawa, ON L1H 7K4, Canada
jensenwb@ucmail.uc.edu

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**Editor’s Response to Letter from DeKock and Brandsen about Balancing Redox Equations**

In 1997, the editor of this Journal, John Moore, declared a moratorium on submissions concerning the balancing of equations, encouraging authors to consider other means to discuss stoichiometry and related issues (1). At that time, it was pointed out that software could be used to accomplish these tasks. DeKock and Brandsen’s letter points out the availability of appropriate software and serves as an opportunity to continue the ban on this subject.

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Norbert J. Pienta*
Department of Chemistry University of Iowa, Iowa City, IA 52242
William.Smith@uoit.ca

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