

An Analysis of the Algebraic Method for Balancing Chemical Reactions

John A. Olson

Department of Chemistry, Baylor University, Waco, TX 76798

The algebraic method was originally introduced by Bottemly (1) and combined with the inspection method by Deming (2), using as the condition a material or atom balance. This treatment can be used to balance reactions where the number of elements is at least one less than the number of reactant and product substances (the remaining coefficient can be obtained by requiring the smallest set of integers). This method was extended by Bennett (3) to include charge conservation. This condition introduces one more equation, thereby giving enough equations to balance most redox reactions (3). Kolb used both Bottemly's method (4, 5) and Deming's method (6) to balance redox reactions. Carrano (7) used an algebraic method for redox reactions where multiple changes in the oxidation state of an element occur to obtain the nonunique solutions as multiples of the various half-reactions. The algebraic method for reactions with nonunique solutions has also been discussed by Kolb (5), Jensen (8), and Filgueiras (9). Kennedy (10), Blakeley (11), Porter (12), and Alberty (13, 14) have reformulated this procedure in terms of matrices, a method that is especially suitable for computer solutions (15, 16).

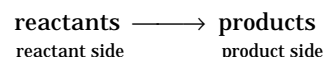
The treatments cited above are based on using the material and charge balance conditions. For most reactions, these conditions provide enough equations to obtain a solution. However, there are reactions where these two conditions do not generate enough equations and a third condition that would generate additional equations would help in extending this procedure. In most cases, these three conditions generate more equations than are needed. This is considered an advantage in that it facilitates finding a solution with only a knowledge of linear algebra. Although matrices are mathematically appealing, they are not as widely known (especially to beginning students) as sets of linear algebraic equations.

The purpose of this paper is to introduce a third general condition that involves a balance between the total amount of oxidation and reduction. In order to generate mathematical expressions, this treatment requires the specification of oxidation states for all elements throughout the reaction. Although the assignment of oxidation states is somewhat arbitrary (17), sets of reliable rules for inorganic substances that are simple to implement can be found in introductory texts (18). They can also be defined for organic compounds using a variation of the Lewis structure (19). In Section I the three general conditions that a balanced chemical reaction must satisfy are given. These conditions are expressed in a mathematical form in Section II. Section III contains some examples and a simple modification of the third condition is presented in Section IV that can be used to balance half reactions. The paper ends with conclusions in Section V.

I. The General Conditions

In this section the general conditions that all balanced reactions must satisfy are presented. The use of mathematics is postponed until Section II in order to emphasize the physical content and consequences of the conditions.

Throughout the expressions will refer to a reaction of the form



Condition 1: Atom Balance (AB)

The atom balance or material balance was introduced by Bottemly (1). Its general form is that for each element present in the chemical reaction,

$$\begin{array}{ccc} \text{total number of atoms} & = & \text{total number of atoms} \\ \text{reactant side} & & \text{product side} \end{array}$$

where both sides of this equation refer to the same element. It is also easy to see that the total number of equations generated by this condition is equal to the number of elements present in the reaction.

Condition 2: Charge Balance (CB)

The charge balance was introduced by Bennett (3) and has the general form given by

$$\begin{array}{ccc} \text{total charge} & = & \text{total charge} \\ \text{reactant side} & & \text{product side} \end{array}$$

which is a statement that the total charge in a chemical reaction is conserved.

Condition 3: Oxidation–Reduction Balance (ORB)

Oxidation–reduction reactions can usually be thought of as reactions that involve a transfer of electrons. The number of transferred electrons is conserved and can be defined in terms of changes in oxidation states. It is also possible, by using a set of rules, to assign an oxidation state to each atom on both sides of the reaction. If in going from reactants to products the oxidation state of an atom increases (decreases), the atom is said to undergo oxidation (reduction). The absolute value of the difference of the oxidation states of the atom on the two sides of the reaction is referred to as the change in the oxidation state. From the changes in the oxidation states, it is possible to define the oxidation–reduction balance condition as

$$\begin{array}{ccc} \text{the total amount of} & = & \text{the total amount of} \\ \text{oxidation} & & \text{reduction} \end{array}$$

where the total amount of oxidation (reduction) is the sum of the changes of all atoms that are oxidized (reduced). Schematically, what this condition means is that for any chemical reaction one has

$$(\text{OX})_{\text{R}} = (\text{RED})_{\text{R}} \quad (1\text{a})$$

$$(\text{OX})_{\text{P}} = (\text{RED})_{\text{P}} \quad (1\text{b})$$

$$(\text{OX})_{\text{R}} = (\text{RED})_{\text{P}} \quad (1\text{c})$$

and

$$(\text{OX})_{\text{P}} = (\text{RED})_{\text{R}} \quad (1\text{d})$$

Also by combining eq 1a with eq 1c and eq 1b with eq 1d one also has

$$(\text{RED})_{\text{R}} = (\text{RED})_{\text{P}} \quad (1\text{e})$$

and

$$(\text{OX})_{\text{R}} = (\text{OX})_{\text{P}} \quad (1\text{f})$$

In these expressions, (OX) and (RED) are the total amount of oxidation and reduction, respectively, and the subscript R or P indicates the reactant or product side of the reaction. The quantities corresponding to the product side are obtained by viewing the reaction in the opposite direction, that is, products \rightarrow reactants. One sees that this condition can generate, at most, six equations.

II. The Mathematical Treatment

In this section, a simple method of obtaining mathematical expressions for the three conditions is presented. This method is based on writing the reaction in terms of unknown integers, a, b, c, d, \dots , and using the conditions to generate as many algebraic equations as possible. The equations are solved to give the lowest set of integers, which are called the stoichiometric coefficients.

To begin with, consider some substance present in the reaction of the form X_xY_y^c , where X and Y are elements, x and y are their relative or absolute numbers, and c is the charge (negative, positive, or zero). Let n be the unknown integer so that, in the reaction, this term would be written as $n\text{X}_x\text{Y}_y^c$. For condition 1, this term would contribute nx and ny to the atom balance (AB) equations for elements X and Y, respectively. The contributions can be written as

$$(\text{AB})_{\text{X,sub}} = nx \quad (2\text{a})$$

and

$$(\text{AB})_{\text{Y,sub}} = ny \quad (2\text{b})$$

For condition 2, this term would contribute nc to the charge balance (CB) equation, which can be positive, negative, or zero depending on the value of c . This contribution can be written as

$$(\text{CB})_{\text{sub}} = nc \quad (3)$$

If the oxidation state of X *uniquely* changes by k , its contribution to the equations for condition 3 would be nxk . This result simply says that the total change for X in this compound is just the number of atoms of X (nx) times the change per atom of X (k). If the oxidation state of X increased (oxidation), this can be written as

$$(\text{OX})_{\text{X,sub}} = nxk \quad (4\text{a})$$

or if it decreased (reduction), as

$$(\text{RED})_{\text{X,sub}} = nxk \quad (4\text{b})$$

It should be noted that the uniqueness criterion must be satisfied in order to construct eq 4a or 4b. The uniqueness criterion means that *all* of the X atoms (nx) must either be oxidized or reduced by k . For example, if the X atoms on the reactant side were in a single oxidation state but on the product they were in two oxidation states, it would not be possible to write eq 4a or eq 4b for X on the reactant side. This criterion will be further clarified in the examples.

With the above analysis for each substance in the reaction, it is now straightforward to construct equations for

the conditions given in Section I. For condition 1 or atom balance (AB), one has, for each element X,

$$\sum_{(\text{sub,reactants})} (\text{AB})_{\text{X,sub}} = \sum_{(\text{sub,products})} (\text{AB})_{\text{X,sub}} \quad (5)$$

where (sub,reactants) indicates that the sum (Σ) is over substances that are reactants and similarly for (sub,products), and $(\text{AB})_{\text{X,sub}}$ is defined in eq 2a. For condition 2 or the charge balance, one has that

$$\sum_{(\text{sub,reactants})} (\text{CB})_{\text{sub}} = \sum_{(\text{sub,products})} (\text{CB})_{\text{sub}} \quad (6)$$

where $(\text{CB})_{\text{sub}}$ is defined in eq 3. Finally, for condition 3 or the oxidation reduction balance, one has that the quantities needed in eqs 1a through 1f are given by

$$(\text{OX})_{\text{R(P)}} = \sum_{(\text{sub,reactants(products)})} \sum_{(\text{X})} (\text{OX})_{\text{X,sub}} \quad (7\text{a})$$

and

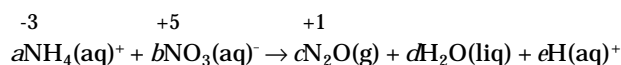
$$(\text{RED})_{\text{R(P)}} = \sum_{(\text{sub,reactants(products)})} \sum_{(\text{X})} (\text{RED})_{\text{X,sub}} \quad (7\text{b})$$

where the sum over X includes only the elements that are oxidized in eq 7a or those that are reduced in eq 7b. It should again be emphasized that for eq 7a or 7b to exist, the uniqueness criterion discussed for eqs 4a and 4b must be satisfied for all elements in the second summation. This is why it was stated that at most six equations are generated.

III. Redox Reactions

In this section, several examples involving balancing oxidation-reduction (redox) reactions are presented. Unbalanced redox reactions are usually written without including the solvent, which normally is water, and either hydronium ions ($\text{H}[\text{aq}]^+$) or hydroxide ions ($\text{OH}[\text{aq}]^-$). To be consistent, these will always be included as the last terms on the product side of the reaction. If the mathematics generates negative integers for these terms, it simply means that they should be placed on the reactant side. Thus it is arbitrary which side of the reaction these are placed on as long as the results are interpreted correctly.

To begin with, consider the redox reaction that takes place in an acidic solution (the last two terms on the product side),



where the oxidation states of the atoms that change in the reaction are included above the corresponding atom. There are three elements, so that AB gives

$$\begin{array}{ll} \text{N:} & a + b = 2c \\ \text{H:} & 4a = 2d + e \\ \text{O:} & 3b = c + d \end{array}$$

The CB gives

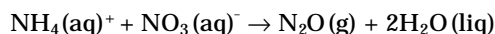
$$a(+1) + b(-1) = e(+1)$$

For the ORB, one sees that, on the reactant side, all a N's are oxidized from -3 to +1, which is a change of 4, and all b N's are reduced from 5 to 1, which is again a change of 4. Then eq 1a becomes

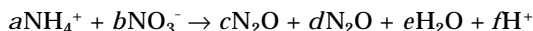
$$a(4) = b(4) \quad (1\text{a}')$$

On the product side, no unique change for all c N's exists, so that eq 1b cannot be defined in terms of eqs 4a and 4b. Obviously, the rest of eqs 1c through 1f are not defined either.

Choosing $a = 1$ gives $b = 1$, $c = 1$, $d = 2$, and $e = 0$, so that the balanced reaction is



In this example five equations were generated, which is one more than necessary. However, the simple equation from ORB made the solution of the set of equations trivial. As an example of the flexibility in this procedure, consider the reaction written as



where on the product side the N_2O has been written as two terms that undergo unique changes in oxidation states. For AB, one has

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

$$\text{H: } 4a = 2e + f$$

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

For CB one has

$$a - b = f$$

For ORB, letting the $2c$ N's be oxidized by 4 and the $2d$ N's be reduced by 4 leads to

$$a(4) = b(4) \quad (1a')$$

$$2c(4) = 2d(4) \quad (1b')$$

$$a(4) = 2d(4) \quad (1c')$$

$$2c(4) = b(4) \quad (1d')$$

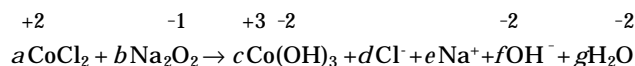
$$b(4) = 2d(4) \quad (1e')$$

and

$$a(4) = 2c(4) \quad (1f')$$

Setting $a = 2$ gives $b = 2$, $c = 1$, $d = 1$, $e = 4$, and $f = 0$, and after simplification leads to the same balanced reaction.

As another illustration, consider the reaction in a basic solution



where for simplicity, the (aq), (s), etc. have been omitted. For AB, one has

$$\text{Co: } a = c$$

$$\text{Cl: } 2a = d$$

$$\text{Na: } 2b = e$$

$$\text{O: } 2b = 3c + f + g$$

$$\text{H: } 0 = 3c + f + 2g$$

For CB, one has

$$0 = d(-1) + e(+1) + f(-1)$$

For ORB on the reactant side, all a Co's are oxidized by one and all $2b$ O's are reduced by one, so that eq 1a becomes

$$a(1) = 2b(1) \quad (1a')$$

On the product side (viewing the reaction as products \longrightarrow reactants), all c Co's are reduced by 1 and all $(3c + f + g)$ O's are oxidized by 1 so that eq 1b becomes

$$(3c + f + g)(1) = c(1) \quad (1b')$$

Then eqs 1c through 1f are easily found to be

$$a(1) = c(1) \quad (1c')$$

$$(3c + f + g)(1) = 2b(1) \quad (1d')$$

$$2b(1) = c(1) \quad (1e')$$

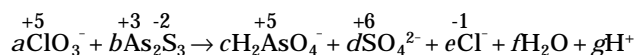
and

$$a(1) = (3c + f + g)(1) \quad (1f')$$

One notices that although six equations were generated by the ORB, two of them (eqs 1c' and 1d') were already generated by the AB. This is not a deficiency of this method, in that the objective is to generate as many equations as possible in order to help solve the problem. Setting $a = 2$ gives $b = 1$, $c = 2$, $d = 4$, $e = 2$, $f = -2$ and $g = -2$. The negative values for f and g indicate that the water and hydroxide ions were placed on the wrong side of the reaction, so that

$2\text{CoCl}_2 + \text{Na}_2\text{O}_2 + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow 2\text{Co}(\text{OH})_3 + 4\text{Cl}^- + 2\text{Na}^+$ is the balanced reaction.

As a third example, consider the reaction



which occurs in an acidic solution. The AB gives

$$\text{Cl: } a = e$$

$$\text{O: } 3a = 4c + 4d + f$$

$$\text{As: } 2b = c$$

$$\text{S: } 3b = d$$

$$\text{H: } 0 = 2c + 2f + g$$

The CB gives

$$a(-1) = c(-1) + d(-2) + e(-1) + g(+1)$$

For the ORB, on the reactant side, all $2b$ As's are oxidized by 2, all $3b$ S's are oxidized by 8, and all a Cl's are reduced by 6, so that eq 1a is

$$2b(2) + 3b(8) = a(6) \quad (1a')$$

On the product side, all c As's are reduced by 2, all d S's are reduced by 8, and all e Cl's are oxidized by 6, so that eq 1b becomes

$$e(6) = c(2) + d(8) \quad (1b')$$

The other equations are found to be

$$2b(2) + 3b(8) = c(2) + d(8) \quad (1c')$$

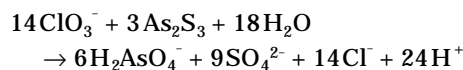
$$e(6) = a(6) \quad (1d')$$

$$a(6) = c(2) + d(8) \quad (1e')$$

and

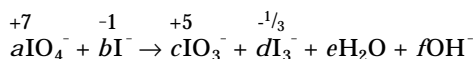
$$2b(2) + 3b(8) = e(6) \quad (1f')$$

It should be mentioned that in order to be consistent with the ORB, all equations should be written down without any simplifications. For example, eq 1a' simplifies to $14b = 3a$, but this does not mean that in eq 1c' $14b = 2c + 8d$. Setting $b = 3$ gives $a = 14$, $c = 6$, $d = 9$, $e = 14$, $f = -18$, and $g = 24$, so that



is the balanced chemical reaction.

As a final example, consider the reaction



which occurs in a basic solution. From AB one has that

$$\begin{array}{lcl} \text{I:} & a + b = c + 3d \\ \text{O:} & 4a = 3c + e + f \\ \text{H:} & 0 = 2e + f \end{array}$$

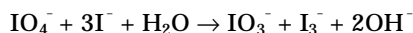
From CB one has that

$$a(-1) + b(-1) = c(-1) + d(-1) + f(-1)$$

For the ORB, the a I's on the reactant side can be reduced to either the +5 or the $-1/3$ state, or some into each. The same ambiguity exists for the b I's that are oxidized. To obtain a balanced reaction, an assumption can be made. If it is assumed that all a I's are reduced by 2 and all b I's are oxidized by $2/3$, then eqs 1a through 1f are

$$\begin{array}{lcl} b(2/3) = a(2) & (1a') \\ c(2) = 3d(2/3) & (1b') \\ b(2/3) = 3d(2/3) & (1c') \\ a(2) = c(2) & (1d') \\ a(2) = 3d(2/3) & (1e') \\ b(2/3) = c(2) & (1f') \end{array}$$

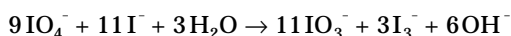
With this assumption, one obtains



as the balanced reaction. However, if the assumption is that all a I's are reduced by $22/3$ and all b I's are oxidized by 6, eqs 1a through 1f become

$$\begin{array}{lcl} b(6) = a(22/3) & (1a'') \\ 3d(22/3) = c(6) & (1b'') \\ b(6) = c(6) & (1c'') \\ 3d(22/3) = a(22/3) & (1d'') \\ a(22/3) = c(6) & (1e'') \\ b(6) = 3d(22/3) & (1f'') \end{array}$$

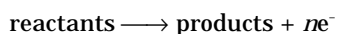
With this assumption, one has



as the balanced reaction. Linear combinations of the balanced reactions for these two assumptions will lead to more balanced reactions. This is therefore an example of a system that does not have a unique balanced reaction.

IV. Half Reactions

In many cases, redox reactions can be described in terms of two half-reactions. One of the half reactions is an oxidation reaction, which produces electrons; the other is a reduction reaction, which consumes electrons. A common method of balancing redox reactions is to balance the half reactions and add them so that the electrons cancel. Since the third condition does not apply to half reactions, a modification of this condition is needed to balance half reactions. Consider a half reaction that corresponds to oxidation of the form



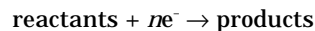
where n is the unknown integer for the electrons that appear on the product side. The oxidation states of all elements on both sides of the reaction are well defined, so that it is still possible to define the total amount of oxidation (reactants \rightarrow products) and reduction (products \rightarrow reactants). Then the third condition for half reactions, which will be referred to as electron balance (EB), is

$$(\text{OX})_{\text{R}} = n \quad (8a)$$

and

$$(\text{RED})_{\text{P}} = n \quad (8b)$$

where n is the number of electrons in the half reaction and $(\text{OX})_{\text{R}}$ and $(\text{RED})_{\text{P}}$ were defined previously. Similarly, for the reduction half-reaction of the form



the EB becomes

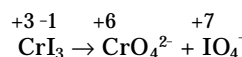
$$(\text{RED})_{\text{R}} = n \quad (8c)$$

and

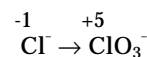
$$(\text{OX})_{\text{P}} = n \quad (8d)$$

One sees that for each half reaction, this condition generates two equations.

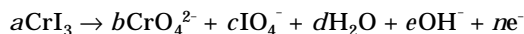
Consider as an example the unbalanced half reactions



and



The first half-reaction, which corresponds to oxidation, becomes



The AB gives

$$\begin{array}{lcl} \text{Cr:} & a = b \\ \text{I:} & 3a = c \\ \text{O:} & 0 = 4b + 4c + d + e \\ \text{H:} & 0 = 2d + e \end{array}$$

The CB gives

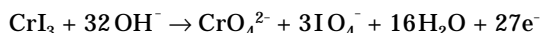
$$0 = b(-2) + c(-1) + e(-1) + n(-1)$$

Finally, the EB gives

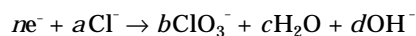
$$a(3) + 3a(8) = n \quad (8a')$$

$$b(3) + c(8) = n \quad (8b')$$

so that after solving, the balanced half-reaction is



The other half reaction, which corresponds to reduction, becomes



The AB gives

$$\begin{array}{lcl} \text{Cl:} & a = b \\ \text{O:} & 0 = 3c + d + e \\ \text{H:} & 0 = 2c + d \end{array}$$

The CB gives

$$n(-1) + a(-1) = b(-1) + d(-1)$$

Finally, the EB gives

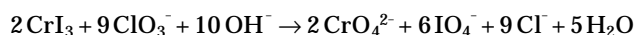
$$6a = n \quad (8c')$$

$$6b = n \quad (8d')$$

so that after solving, the balanced half-reaction is



Combining these half reactions so that the electrons cancel gives

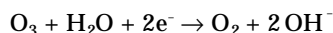


as the balanced redox reaction.

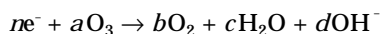
V. Conclusions

An analysis of the algebraic method has been presented. It incorporates a third condition and emphasizes the correspondence between the algebraic equations and the general conditions that must be satisfied for balanced reactions. The overall strategy is to generate as many equations as possible, which facilitates finding the solution for the unknown coefficients using only techniques requiring a knowledge of linear algebraic equations. The algebraic method has a number of advantages. As should be clear from the examples, generation of the algebraic equations is not difficult and does not increase in complexity for more complicated reactions. This method also unambiguously determines on which side, via positive or negative integers, the solvent and either the hydronium or hydroxide ions belong in redox reactions. Furthermore, this method does not change for acidic and basic solutions. Finally, although the algebraic method is easily extended to half reactions, it would be much easier to just add the half reactions together, add in the solvent and either the hydronium or hydroxide ions, and balance with the conditions used in section III.

A possible disadvantage of this method is that an unambiguous assignment of oxidation states is necessary to define the equations from the third condition. This could cause a problem in some cases, such as the reduction half-reaction for ozone. This half reaction is

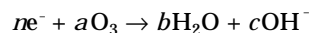


If one were to try to balance the reaction

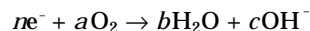


a difficulty would arise when one tries to assign an oxidation state to the O's in O_3 . A way of balancing this would be to use the formal charges from the Lewis structure, which are +1, -1, and 0. Assuming minimal changes in oxidation states—that is, the +1 O is reduced to 0 and the -1 O is re-

duced to -2—leads to the correct balanced half-reaction. Another method would be to balance the two half-reactions



and



which leads, after the appropriate addition, to the correct half reaction. Fortunately, instances like this are not too common so that the vast majority of reactions can be balanced with this method without these kinds of modifications.

In closing, I would like to address two of the major criticisms of the algebraic method. The first is that it is "mathematics, not chemistry". One of the purposes of the first section was to emphasize that the mathematics in the second section was a consequence of the three general conditions, which *is* chemistry. One also has that the total amount of oxidation or reduction gives the number of moles of electrons needed in the Nernst equation. The second criticism involves the difficulty in solving sets of linear algebraic equations. I have found that it is helpful to list the unknown coefficients (letters) in a row. Inspection of the set of equations usually gives at least one unknown present in one or more simple equations of the form $xa = yb$. Making a reasonable choice for a gives an integer for b , and these results are recorded below a and b in the list. As other integers are determined they are recorded also. The list helps to inspect more difficult equations to determine if only one unknown is present in it that has not been previously determined.

Literature Cited

1. Bottemly, J. *Chem. News* **1878**, 37, 110.
2. Deming, H. G. *J. Chem. Educ.* **1943**, 11, 125.
3. Bennett, G. W. *J. Chem. Educ.* **1954**, 31, 324.
4. Kolb, D. J. *J. Chem. Educ.* **1987**, 55, 326.
5. Kolb, D. J. *J. Chem. Educ.* **1979**, 56, 181.
6. Kolb, D. J. *J. Chem. Educ.* **1981**, 58, 642.
7. Carrano, S. A. *J. Chem. Educ.* **1978**, 55, 382.
8. Jensen, B. J. *J. Chem. Educ.* **1987**, 64, 646.
9. Filgueiras, C. A. L. *J. Chem. Educ.* **1992**, 69, 276.
10. Kennedy, J. H. *J. Chem. Educ.* **1981**, 58, 523.
11. Blakley, G. R. *J. Chem. Educ.* **1982**, 59, 728.
12. Porter, S. K. *J. Chem. Educ.* **1985**, 62, 507.
13. Alberty, R. A. *J. Chem. Educ.* **1991**, 68, 984.
14. Alberty, R. A. *J. Chem. Educ.* **1992**, 69, 493.
15. Missen, R. W.; Smith, W. R. *J. Chem. Educ.* **1989**, 66, 217.
16. Weltin, E. J. *J. Chem. Educ.* **1994**, 71, 295.
17. Swinehart, D. F. *J. Chem. Educ.* **1952**, 29, 284.
18. Petrucci, R. H.; Harwood, W. S. *General Chemistry: Principles and Modern Applications*, 6th ed.; Macmillan: New York, 1993; p 79.
19. Kauffman, J. M. *J. Chem. Educ.* **1986**, 63, 523.