

Balancing chemical equations—opening a can of worms

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February 10, 2020

Abstract

This paper is a redo of an article that first appeared in the *Arizona Journal of Natural Philosophy*, October, 1993. The controversies in chemistry that just won't go away are on the "correct" methods to balance chemical equations and also on the related topic of the meaning of "nonstoichiometric" equations. One-hundred years of debate has not brought us one centimeter closer to a reasonable consensus.

1 Introduction

This paper is a review of the main methods to solve for the coefficients of terms in an unbalanced chemical equation (also known as a *skeletal equation*). All of the papers and letters reviewed are from the *Journal of Chemical Education* over the last 70 years. The purpose of this paper is to highlight the subtle differences in definitions and methods, and to suggest a reasonable middle ground to teach students. And that's the way it is in the twenty-first century.

Of particular emphasis is the algebraic method, which has been around since at least 1878 but it has never been widely accepted or effectively suppressed. The more conventional methods of ion-reduction or oxidation accounting tend to produce unique solutions to skeletal equations that have an infinite number of algebraic solutions. A great debate opened on the meaning of these multiple solutions, under the name of "solving nonstoichiometric equations." Try to keep in mind the separate natures of solving for all formal algebraic solutions against finding among these the subset of "real" solutions; some will maintain that, in spite of multiple "solutions" found by the algebraic method, there exists at most one real solution.

2 Review of ChemBalance

Before we can review these papers we need to establish some conventional terminology and some unconventional terminology first introduced in a previous

paper [1]. Consider a chemical equation with n terms total and m chemical elements. We define *solvable* as any equation that has at least one solution. Thus, if an equation is solvable and if $m \geq n - 1$ then the equation has a unique reduced form solution and we shall say that the equation is *regular*,¹ otherwise, it is *nonregular*.

The reason for these definitions is as follows. The n coefficients we need to solve for are just n algebraic unknowns which can be determined by $n - 1$ linearly independent equations in them. The reason we need only $n - 1$ simultaneous equations is because the coefficients are not solved for uniquely, but rather are determined only up to a positive rational over-all factor. For a regular equation we get an infinite set of *equivalent* solutions from which we require only one representative, which is, by our convention, the unique reduced form of the set. Solvable nonregular equations have an infinite number of nonequivalent solutions, and thus an infinite number of reduced forms.

Consider the skeletal equation



We put a variable in front of each term to be solved for, except that we put a 1 in front of the terminal (rightmost) term, thus giving us



Now, we have two unknowns, so we need two elements in the equation to solve for. We're in luck, since we have carbon, 'C', and oxygen, 'O'. Next we balance the equation one element at a time!

Element	term 1	term 2	term 3
C :	$1x$	+	$0y = 1$
O :	$1x$	+	$2y = 2$

Table 1: Table for a simple reaction.

If you know some linear algebra you can solve these types of problems easily, perhaps by using Cramer's rule (which is what ChemBalance uses), though the present problem can be easily solved by inspection. When you do you get

$$x = 1, \quad y = \frac{1}{2}.$$

Thus we have a regular equation having as one solution



But remember that this solution was the result of choosing the coefficient of the rightmost term to be unity, which is why it is not the unique solution to the skeletal equation. Multiply this solution through by any positive rational and

¹This definition will be tightened later.

you get another solution to (1). However, all solutions have the same reduced form, which we define now. The *reduced form* to a balanced equation is the solution which has integer coefficients which taken together have no common integer factor other than unity. It is obvious that every regular equation has a unique reduced form. Thus (1) has the unique reduced form



Now, the case of nonregular equations is more interesting, and more difficult. Since nonregular equations have too few elements to determine a unique reduced form they can produce multiple nonequivalent reduced forms.

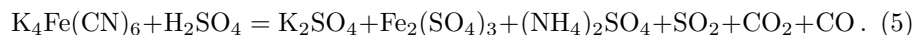
3 Review of literature from 1920s and 1930s

I've picked only two papers from this period. The first was by Bart Park [2], in which he stated that

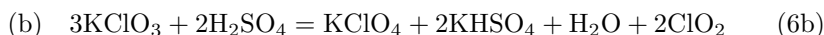
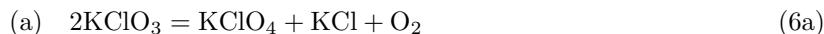
The valence assigned to any element in a compound actually makes little difference *as far as balancing the equation is concerned*. And the work involved in the process may be shortened by choosing a number to represent the valence of an element which will enable it to be eliminated as a factor of change.

Thus, according to Park, oxidation numbers are no more than an arbitrary heuristic device, which need not represent any real chemistry at all.

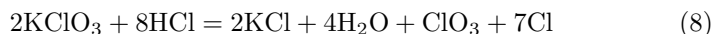
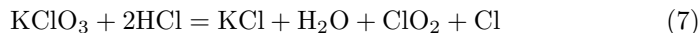
He then solved the **regular 8-termer**:



My next review is of J. H. Melville's recollections [3] on his earliest exposure to the algebraic method, which he claimed was in the 1880s and 1890s. He presented these reactions:

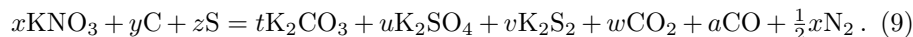


He stated that (b) is unique but that (c) isn't and he gave the other solutions



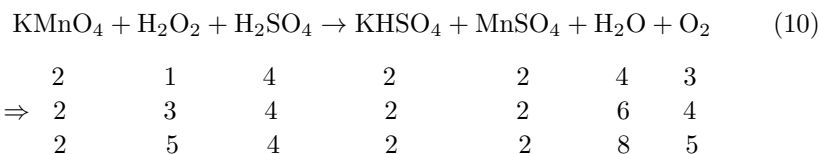
Melville is not very clear about why (b) is unique (up to constant multiple), or why (c) isn't. In our current vocabulary we can say that (b) is unique because it's regular, and that (c) isn't unique because it's nonregular.

He left us with this **nonregular 9-termer**:



4 Review of some literature from the 1940s

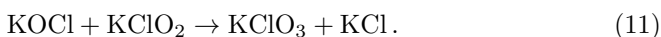
Here we review a few articles/letters that appeared on the topic of balancing chemical equations. First came Otto Steinbach's article "Non-stoichiometric Equations" [4] (Feb. 1944). He started off his article saying, "While chemical equations may balance algebraically, they are not necessarily stoichiometrically exact." What he meant by "they" are the skeletal equations themselves, not their formal solutions. This is the first of a long series of confusing statements made by authors. By "exact" he means has a unique reduced solution. Steinbach suggests that the only way to guarantee that a formal solution to a nonregular equation has any "stoichiometric meaning" is to balance the equation either by the valence-change or the ion-reduction method. As an example he gave the **7-termer**:



The arrow tells us the only "stoichiometrically meaningful" reaction.

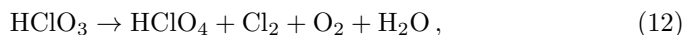
To understand this next presenter, we must first give a definition. The combination of n chemical elements are said to form an n -plex if 1) whenever they occur together in any term they always appear in the same ratios, each to each other, and 2) whenever any one of them appears in any term then all the rest appear as well. Thus an n -plex forms an algebraic unit, or *algebraic element*, regardless of how many chemical elements are in it. Remember that a regular equation was defined as any solvable equation having at least $n - 1$ chemical elements. We can now give this more accurate definition: a *regular* equation is any n -term equation having at least $n - 1$ algebraic elements from a consistent set of algebraic elements.

Steinbach presented a number of similar reactions to (10). An interesting one was the following **nonregular** equation



Notice that this equation has only two algebraic elements 'O' and 'KCl', the latter being a 2-plex.

Even more interesting is this next **nonregular** equation:



with the only valid solution for coefficients (3, 1, 1, 2, 1). (Notice that 'HCl' does not form a 2-plex because of either the Cl_2 term or the H_2O term.) Steinbach says:

The variability [in coefficients] is probably due to the fact that in this particular equation, two or more chemical reactions are taking place and such an equation has no particular significance.

A number of questions come to mind. Why is this equation treated differently from the others he presented? In other words, why aren't the others given the same questionable status? Why must he speak in terms of "probability" rather than with certainty?

In April 1944, William T. Hall had his letter published which debunked the nonstoichiometric equations of Steinbach. Hall is much better at polemics than at shoring up the weaknesses of his own presentation. Still, he probably brought some useful insights into the "discussion."

His letter was titled "Non-stoichiometric equations." He began with the statement

Under this title, Otto F. Steinbach points out that an equation may balance algebraically and yet not represent the truth. This fact is one that probably has bothered every student of chemistry at one time or another, and every teacher frequently has students ask why a certain equation is marked wrong in spite of the fact that it balances.

Certainly, Hall has laid the proper foundation for the importance of studying this issue for the sake of the proper teaching of it. But his use of the term "truth" is going to lead to ambiguity, as we shall see. It's immediate impression on the reader is that there really is a foundation of certitude involved in balancing chemical equations. His next statement is that

Chemical equations are commonly written for two purposes: 1) to show the probable reaction products, and 2) to show the quantities of materials that enter into reaction. If an equation does not fulfill the latter requirement it can be termed "nonstoichiometric."

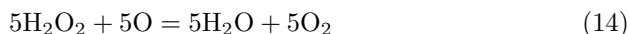
So Hall is not against the term "non-stoichiometric"; in fact, he used it to describe the typical "equations" of organic chemistry, but he does seem to be unaware of the subjective nature of his espoused purposes for writing chemical equations.

Hall totally rejected Steinbach's presentation. In particular, he rejected Steinbach's supposed example of a non-stoichiometric equation (10). He claimed that (10) is actually "stoichiometric" and that its solution is



Hall's entire case rests on the examination of this reaction by the chemist F. Schönbein, who died in 1868! Are there no multiple reaction paths for this?

Next Hall analyzes the hydrogen peroxide reactions to explain why Schönbein is right and Steinbach is wrong. He presented



as what "may be" the correct equation. He complained that Steinbach had not taken into account the "empirical" value of H_2O_2 as a reducing agent.

Remember that both Hall and Steinbach agree that there is only one correct solution to balance (10), but they disagree on two aspects of its discovery:

1) Steinbach recommended the ion-reduction or valence-change methods to find the solution to (10), but Hall recommend laboratory experiments.

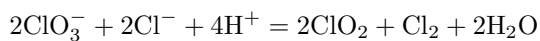
2) Steinbach defines a skeletal equation as being non-stoichiometric if it has more than one reduced-form solution, in other words, if the equation is solvable-nonregular, but Hall defines an equation as non-stoichiometric only if one cannot find the unique empirical solution.

Or is that correct? Later he analyzes Steinbach's **7-termer**



with coefficients (1, 5, 5, 2, 1, 9, 4) as incorrect because it “makes 6 equivalents of $\text{K}_2\text{Cr}_2\text{O}_7$ equal to $5\text{H}_2\text{O}_2$,” but that's a theoretical, not strictly empirical, evaluation. A bit later, Hall refers to an example of Steinbach involving chlorine, in which he says, “I know of no way of tagging the chlorine atoms and finding out just where all the Cl_2 formed originated.” Perhaps we've hit on another criterion for stoichiometry—you must be able to account for the movement of each atom on the reactant side to the product side.

Hall offered the reaction



as “perhaps the simplest reaction.” Again, more *perhaps's* in the search for “truth.”

Another letter published on the same topic just after Hall's is Alexander Lehrman's [6], also contradicting Steinbach's paper. He says:

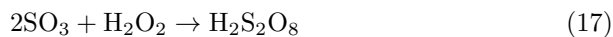
Though he seems not to realize it the author brings up the old, old error involved in adding equations for concurrent reactions...The rule that should be followed is: equations for consecutive reactions may be added; equations for concurrent reactions may not be added.

Lehrman goes on to say that adding two or more concurrent reactions together can give an infinite number of balanced equations, none of which is stoichiometric. However, he doesn't clearly explain why they are not stoichiometric.

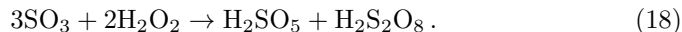
Although it's clear that adding together two reactions which have different reactants is not impressive, it is also clear that when the same reactants can combine in different ways, the result of adding them together is meaningful, even if it is complicated. Complications do not destroy meaning. He claimed that adding



and

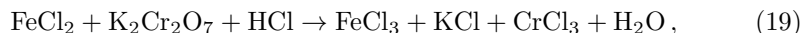


only gives the “meaningless equation”

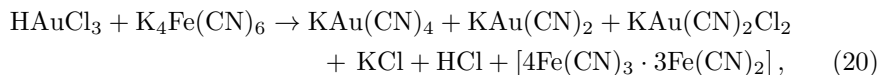


However, if (16) and (17) are “meaningful” then so is any linear combination of them. It must be observed that the term “meaningful” is manifestly subjective.

Next came “A Question of Balancing,” by Arthur Porges [7]. He demonstrated the algebraic method on a few equations, including the **7-termer**



which is **regular**, and so he solved it with straightforward algebra. He also presented the **8-termer**



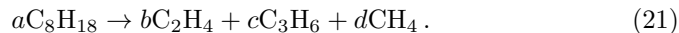
which is **nonregular**. (Standen [8] p. 481 calls this “about the most complicated chemical equation ever written.”) So he presented a few constraints on the system of possible solutions to help narrow things down. Ultimately, however, his hope was in finding a sort of *least-action principle* similar to that in mechanics which would select physically real solutions.

My next review is William C. McGavock’s paper [9] “Nonstoichiometric Equations,” published the same time as Porges’s. McGavock takes an opposing view to Steinbach’s interpretation of the meaning of “stoichiometric.” Remember that Steinbach believed that out of every set of multiple nonequivalent solutions to a skeletal equation only one would be stoichiometric and the rest nonstoichiometric—the stoichiometric solution being found (or at least verified) by the method of ion-electron accounting or oxidation–reduction. But McGavock believed that was all wrong. He proposed his own definition:

Definition: A nonstoichiometric reaction may be defined as one in which a given set of reactants yields end products whose molecular proportions are variable in a continuous sense.

Whether you agree with this definition or not, at least it’s an attempt to give a formal definition of “nonstoichiometric,” which I haven’t found anywhere else in the literature.

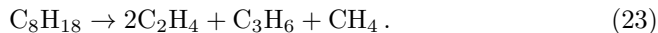
To demonstrate, he solves by the algebraic method (sloppily applied) the following equation



Although this equation cannot have its coefficients solved for uniquely, we can still set any one of them however we like. McGavock chose $a = 1$. From that he found the relation

$$2b + 3c = 7 \quad (22)$$

whose only “integral” solution is $b = 2$ and $c = 1$, yielding the solution



But McGavock claims that we cannot eliminate the possibility that b and c can take on suitable rational (his meaning for “continuous”) values. What does this mean? Well, two things.

The first thing it means is that (21) is a composite of two or more independent reactions which “add” together in some ratio dependent on temperature and pressure, etc. But this interpretation seems to have another duplicitous interpretation. Remember that (22) and (23) are both dependent on the arbitrary $a = 1$ condition. Now we can reset a to any integer value we please by multiplying (22) through by any integer we like. Thus, the various solutions to (22) for the “continuous” values of b and c become an infinite set of nonequivalent solutions with integral coefficients.

Going beyond the controversy on nonstoichiometric equations, McGavock credits Bottomley [10] with having the first published promotion of the algebraic method. He then used the method to arrive at an algebraic solution set to the **7-termer**:



Since this equation is **nonregular** it has an infinite set of nonequivalent solutions. McGavock is not at all impressed that Steinbach found a few of them.

In 1945, Anthony Standen [8] used the algebraic method to explain Steinbach’s “bizarre” nonstoichiometric equations. He concluded that they are just simultaneous reactions occurring in arbitrary ratios.

It’s easy to get inductive rules wrong if you don’t have a lot of examples at your disposal. Standen proved this by this statement:

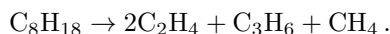
Whenever it occurs that an equation can be balanced in different ways that are not related as multiples, this is a sign that the equation as originally written is not one equation but two equations, or possibly more.

The problem with this statement is that it seems to be predicated on examples in which there are at least two reactants. When just a single “reactant” decomposes to many-product terms, it may be that there are multiple nonequivalent solutions to this decomposition, in which case it is a matter of convention whether we should regard these as separate reactions or as a single reaction taking place with fraction coefficients on the products and unity as the coefficient of the decomposing reactant. Again, convention is subjective, not objective.

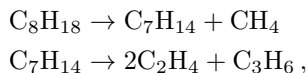
Then Standen implicitly gives his own definition of nonstoichiometric equations. A reaction is said to be *nonstoichiometric* if it is

- 1) nonregular, and
- 2) not the sum of two or more concurrent reactions.

He gave an example. Consider the **nonregular** reaction



This can be considered stoichiometric if it can be written as two stoichiometric concurrent reactions, such as



if the last two are indeed stoichiometric.

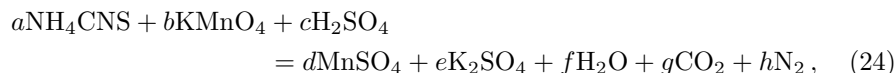
As you can see, the great confusion in this subject results from

- 1) the lack of a consensus on how to keep the subject fresh and presentable to students, and
- 2) the multiple definitions of “nonstoichiometric” and implicitly of “stoichiometric.”

5 Review of literature from the 1950s

George Bennett’s paper [11] “Material Balances and Redox Equations,” challenged the conventional balancing approaches as convenient reactions for the oxidation concept and “imaginary reactions without basis of fact” for the half-reactions. What he wanted to present to students was a truthful method. And he was sure the algebraic method was the answer to that.

He demonstrated how a chemical engineer would solve the following **regular 8-termer**



obtaining the solution (5, 14, 16, 14, 7, 26, 5, 5).

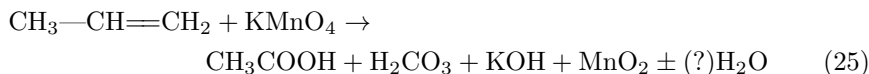
Bennett’s objective all along has been to offer the student a method having verity despite its being sometimes tedious. His interest is more theoretical in presenting the algebraic method. He points out that conventional methods are often better, though sometimes they’re worse. He concludes with this:

The teacher, moreover, needs to make no apology when he admits forthrightly that the conventional methods are used simply because they are both convenient and expeditious.

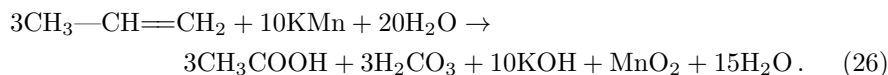
I will not spend much time on this next paper by Harold P. C. Burrell [12] (Feb. 1959) entitled “Balancing Organic Redox Equations.” His approach is to

investigate the bond structure itself to determine possible reactions. However, he admits that his method is heuristic, requiring a “hypothetical assumption,” but that his method is no less secure than conventional ones.

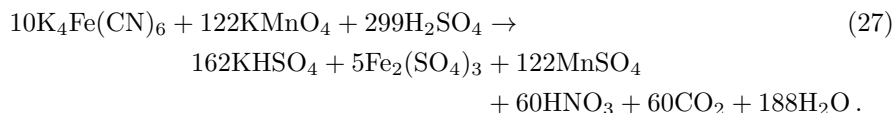
He demonstrated his technique on the **7-termer** oxidation of propylene



He claims that by his approach one gets the unique solution

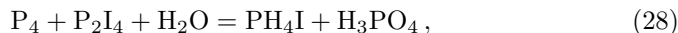


Just for fun he gave the **regular 9-termer**

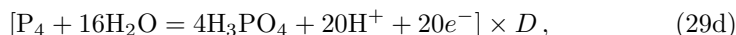
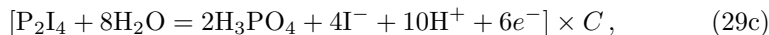
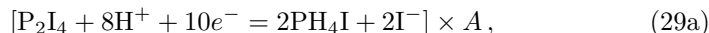


6 Review of literature from the 1970s

After this, the subject seemed to have taken a long rest until the late 1970s. The first paper I found to start stirring up controversy again was S. A. Carrano’s [13] opening salvo in which he presented the following skeletal equation



an equation offered as a test case during the Fourth Biennial Conference on Chemical Education. Before we look at his solution, let’s first notice that this is a regular equation (assuming it has any solution) and so it has a unique solution in reduced form. He then offered a set of possible half reactions to solve the system:



yielding a system of equations for the indeterminates A, B, C, D which do not have a unique solution. This strongly cast doubt on the claim that half-reaction analysis will produce true reactions for nonregular equation when they produce spurious solutions to regular ones. Or perhaps these indeterminates must be empirically determined.

In order to arrive at the unique solution one must adopt some arbitrary assumption, such as $C = A$, finally arriving at the reduced form



Carrano concludes with this remark: “As it turns out, [the] reaction... lends itself to a simple and direct solution by the method of simultaneous equations alone, and this may well turn out to be the more appealing procedure for most readers.”

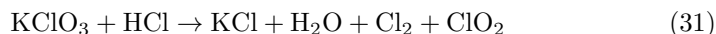
Next came Doris Kolb’s three papers on balancing chemical equations. Her first is a simple introduction to balancing for high-school students, called “The Chemical Equation: Part 1: Simple Reactions” [14] (1978). She does a good job at introducing the subject. She even almost gives a definition of “stoichiometry.” She left all the controversy for another paper.

In Part II, Kolb [15] published “Oxidation-Reduction Reactions.” In it she presented a good introduction to the three methods of balancing equations: oxidation number, ion-electron, and algebraic methods. She says of the latter (p.329):

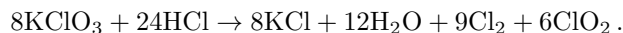
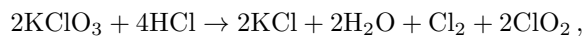
With the algebraic method it is not necessary to locate the elements being oxidized and reduced or to determine oxidation numbers, but the algebraic method does have one distinct drawback. Algebraic equations can have more than one solution, and sometimes several different sets of coefficients can be obtained for the same equation, although only one set represents the correct stoichiometric coefficients.

Unfortunately, she didn’t prove her last assertion about the uniqueness of the solution.

A year later she returned to the same topic to pick up the controversial matters of stoichiometry (“More on Balancing Redox Equations,” [16]), where she used the **nonregular equation**



with three particular solutions



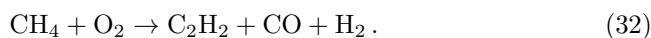
She explained the difference in these equations due to them all being linear combinations of the two **regular** equations



Apparently, she feels that all nonregular equations can be written as linear combinations of regular equations for she says (p. 182), “It is probably inaccurate

to label any reaction as non-stoichiometric, since each atom in the reactants must be accountable among the products, regardless of how many simultaneous reactions happen to be occurring.”

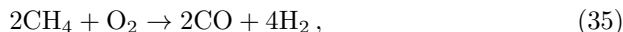
Since I’m not sure how the term “nonstoichiometric” is “really” defined, I’ll adopt a different term. If the solutions to any skeletal equation cannot be expressed as linear combinations of two or more balanced regular equations each of fewer product terms than the original, but having the same number of reactant terms, then we shall say that the original skeletal equation is *primitive*, otherwise it is *nonprimitive*. Now the question is, Are there any skeletal nonregular equations that are primitive? Yes. Consider the following:



It has only two possible “components”



But although the second of these balances to give

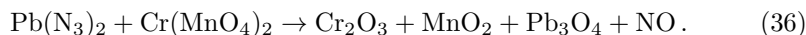


the first does not balance. Now since the original cannot be expressed in terms of the second alone, it is therefore primitive.

Kolb (p. 184) says, “The oxidation number concept has been criticized because it is an artificial device, and surely it is true that much of our assignment of oxidation numbers is quite arbitrary.” She goes on to say that “as for the ion-electron method, some of the half-reactions we write are really fictitious and written only because they are convenient.”

7 Review of literature from the 1980s

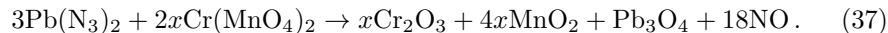
In August 1981, Charles Mickey [17] published “Balancing Complex Redox Equations by Inspection,” in which he upgrades the “trial-and-error” method with algebraic equations. He demonstrated his technique (borrowed from Jason Ling) on the **regular 6-termer**



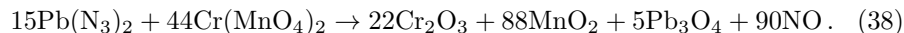
Then he states (p. 644):

In this reaction there are 4 different elements being changed in oxidation state, and several of the oxidation numbers are fractions. Balancing this equation is quite difficult whether the “ion-electron” or the “change in oxidation number” method is used. On the other hand, it can easily be balanced in less than 2 minutes by using the inspection method coupled with the simplified algebraic technique.

So he writes

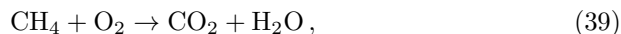


On solving for x we get $x = 22/5$ so



In the 1970s, the battle over the meaning of regular vs. nonregular and stoichiometric vs. nonstoichiometric equations had been fought largely in that Journal's section on Secondary Chemistry Education, but that would soon change. Like a sudden plot twist in mystery book, in comes G. R. Blakley, a mathematician, who published his "Balancing Chemical Equations" [18], in 1982, in which he presented a definitive examination of the algebraic method. His particular version of it stressed using matrices and the Gauss-Jordan method of row reduction to arrive at the Hermite normal form.

He gave this example (p. 731):



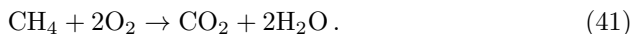
which gives the matrix

$$\Sigma = \begin{array}{c} \text{CH}_4 \quad \text{O}_2 \quad \text{CO}_2 \quad \text{H}_2\text{O} \\ \text{hydrogen} \\ \text{carbon} \\ \text{oxygen} \end{array} \begin{pmatrix} 4 & 0 & 0 & 2 \\ 1 & 0 & 1 & 0 \\ 0 & 2 & 2 & 1 \end{pmatrix}. \quad (40)$$

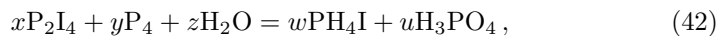
In Hermite form, this becomes

$$\Phi = \begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & -1/2 \end{pmatrix}.$$

Now all we have to do is to solve for the subspace of "vectors" λ such the $\Phi\lambda = 0$. Having done that we can take the vector with smallest integer entries to obtain the coefficients, yielding



For example, let's look again at



which gives the homogeneous matrix equation

$$\begin{array}{ccccc}
& \text{P}_2\text{I}_4 & \text{P}_4 & \text{H}_2\text{O} & -\text{PH}_4\text{I} & -\text{H}_3\text{PO}_4 \\
\text{P} & \left(\begin{array}{ccccc} 2 & 4 & 0 & -1 & -1 \\ 4 & 0 & 0 & -1 & 0 \\ 0 & 0 & 2 & -4 & -3 \\ 0 & 0 & 1 & 0 & -4 \end{array} \right) & \begin{pmatrix} x \\ y \\ z \\ w \\ u \end{pmatrix} & = & \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} . & (43)
\end{array}$$

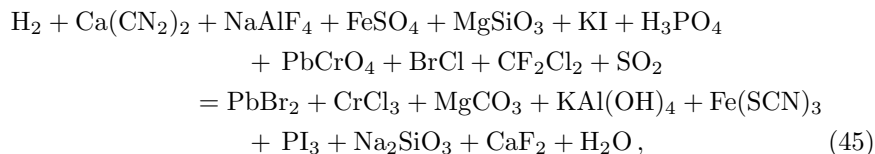
But rather than using row reduction in this case we can also use Cramer's Rule. We can choose to fix any one coefficient we like. Then, if we choose $u = 1$ in (42), we get the matrix equation

$$\begin{array}{ccccc}
& \text{P}_2\text{I}_4 & \text{P}_4 & \text{H}_2\text{O} & -\text{PH}_4\text{I} \\
\text{P} & \left(\begin{array}{ccccc} 2 & 4 & 0 & -1 \\ 4 & 0 & 0 & -1 \\ 0 & 0 & 2 & -4 \\ 0 & 0 & 1 & 0 \end{array} \right) & \begin{pmatrix} x \\ y \\ z \\ w \end{pmatrix} & = & \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} . & (44)
\end{array}$$

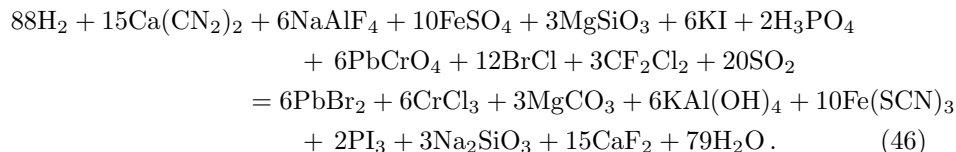
Cramer's rule isn't too bad because of all the zeros as entries. However, many computers will have programs available to solve matrix equations.

One advantage of Blakley's method is that it gives a means to find independent primitive solutions that can be added to get at the nonprimitive solutions to nonregular equations.

Blakley presented this **regular 20-termer** for demonstration:



which he balanced with his computer program, to get



But because Blakley boasted so emphatically that only the matrix method could solve his **20-termer**, that drew the ire of D. F. Swinehart [19] (three years later) who, being retired and having a lot of time on his hands, decided to solve the equation by the method of partial reactions. I won't attempt to reproduce his solution here, but I will give his final comment:

As final comments, the time it took originally to accomplish the above balancing was a couple hours. It probably took Blakley only a matter of seconds on a computer. However, that does not count the time required to write the program and to trouble-shoot it. The present author used a hand-held calculator to do the simple arithmetic.

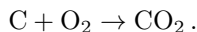
What Swinehart doesn't get is that once the program is done, it's done, and you can throw a thousand equations at it to solve them all in almost no time.

8 Sweeping it under the rug

Many of the papers presented in the previous reviews were specifically titled as regarding "redox" equations. It would have been nice if one of those authors had taken the time to rigorously define what a redox equation is. I came across a paper from September 1945 by Vanderwerf *et al*, titled "Oxidation-reduction: A Re-evaluation" [20], in which the authors express their dissatisfaction with the oxidation-reduction approach, saying (p. 450):

After years of presenting the electron-transfer idea of oxidation and reduction to their students, however, the authors have come to view their own teaching with skepticism, and to believe that, in the interest of logic and consistency, a re-investigation of the meaning and application of the terms "oxidation" and "reduction" is necessary.

As an example they offered the following case:



The issue is the interpretation of assigned valences. If the valences do not represent charges per se, what do they represent? The authors put it this way:

By universal agreement, the carbon is oxidized by four units. But the assumption that carbon has lost four electrons in its oxidation to carbon dioxide requires that the carbon exist in the compound as C^{+4} ion, a postulate which is, of course, entirely inadmissible.

The authors tell us that there may be a consensus on which reactions are redox and which aren't, but that doesn't change the fact that there is also room for disagreement. Their own attempt to frame a definition of "redox" would occasionally include some that were not considered redox, and at other times leave some out that were. One example of a non-redox equation is $\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}$.

After presenting their evidence, the authors conclude that oxidation-reduction does not represent fundamental chemistry but rather an arbitrary utilitarian device. They offer as a generalized definition of redox as: oxidation is any decrease in electron density and reduction any increase in electron density. They admit that their definition is only of use to experienced chemists and useless to inexperienced students. It certainly does not make it easy to decide which reactions are "redox" or not.

I leave this section with a question that the authors asked but only partially answered themselves (p. 454).

The question might well be raised how a concept so arbitrary as that of change of oxidation state ever came to gain such wide acceptance among chemists, whose squeamishness about dependence upon an arbitrary rule or convention is demonstrated in their persistent attempts to characterize oxidation-reduction as a fundamental phenomenon.

9 Conclusion

A lot of things trouble me about this controversy. First, since stoichiometry is the study of the relations of gram-to-mole, mole-to-mole, etc. of reactants and products of equations that are already balanced, what in the world does that have to do with the solutions to nonregular equations?

Second, why doesn't the chemistry community finally resolve and publish something to settle this seemingly important issue of nonstoichiometric solutions, whatever they are.

Let me proffer the following definition: A skeletal equation is said to be *stoichiometric* if it has a nonempty solution set for the coefficients, and each set of balancing coefficients is a physically realizable function of environment variables, such as temperature, pressure, concentrations, etc.

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