Redox Balancing without Puzzling
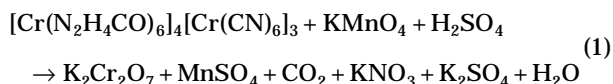
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A chemical equation shows which reactants are converted into which products. Because of the law of conservation of matter, such an equation must be balanced. Stated in chemical terms, this means that the number of atomic particles of each occurring element must remain unchanged.

Once it has been established by experiment that the given reactants can indeed be converted into the given products, chemistry has done its job. Balancing the equation of the reaction is a matter of mathematics only. One would, therefore, expect that all chemical equations are balanced in the same way. However, the number of articles on balancing chemical equations in general, and redox equations in particular, is quite large. Some of the proposed methods have even been given descriptive names. Thus, balancing may be accomplished by the "ping-pong method" (*1*), or by executing a "fair swap" (*2*).

Very recently, Stout (*3*) gave three examples of equations of actually occurring redox reactions that allegedly could not be balanced. Being a puzzle fanatic, he took up the challenge, and he succeeded in balancing these equations. He used the "standard method", which consists of constructing oxidation and reduction half-equations that are combined to yield the redox equation. The application of this method to his third example with the skeletal equation

$$[Cr(N_2H_4CO)_6]_4[Cr(CN)_6]_3 + KMnO_4 + H_2SO_4$$
$$\rightarrow K_2Cr_2O_7 + MnSO_4 + CO_2 + KNO_3 + K_2SO_4 + H_2O \quad (1)$$
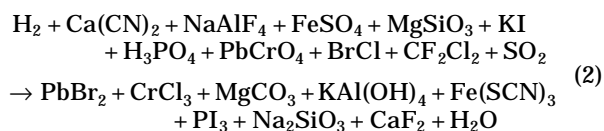
was found to be "exceedingly difficult", and it took him several hours to complete.

Equation 1 can be balanced easier and faster by the mathematical method of linear equations. This has been demonstrated by Hart (*4*), who solved these equations by hand.

Blakley's Equation

The solution of a set of linear equations can be obtained in a mathematically more sophisticated way by manipulating appropriate matrices (*5, 6*). Blakley (*5*) has suggested that only this matrix method is powerful enough to balance his horrendous equation

$$H_2 + Ca(CN)_2 + NaAlF_4 + FeSO_4 + MgSiO_3 + KI$$
$$+ H_3PO_4 + PbCrO_4 + BrCl + CF_2Cl_2 + SO_2$$
$$\rightarrow PbBr_2 + CrCl_3 + MgCO_3 + KAl(OH)_4 + Fe(SCN)_3 \quad (2)$$
$$+ PI_3 + Na_2SiO_3 + CaF_2 + H_2O$$

but at least three other authors (*1, 7, 8*) were able to solve the problem in other ways. I have satisfied myself that Blakley's balanced equation (*5*) can be reproduced by the method of linear equations, when used similarly as in Hart's treatment of Stout's third example. However, because now 19 (instead of 8) linear equations had to be considered, it took a few hours more.

Amazingly, none of the authors (*1, 7, 8*) made any comment on the feasibility of the chemical reaction suggested by the balanced version of eq 2. Blakley maintains that the

20 chemical species of eq 2 are "all, or nothing. If you want a reaction you do it the way the above balancing indicates, or not at all." In the balanced equation the products $MgCO_3$ and Na_2SiO_3 are found in equal amounts. The total heat of formation (as well as the total free energy of formation) of equal amounts of $MgCO_3$ and Na_2SiO_3 happens to be equal to that of the same amounts of $MgSiO_3$ and Na_2CO_3 (*9*). Consequently, these last substances could have been formed just as well. Without disturbing the balance, we could (on the right-hand side of eq 2) change $MgCO_3$ into $MgSiO_3$ *and* Na_2SiO_3 into Na_2CO_3. But then $MgSiO_3$ would not be needed, and a slightly simpler equation would be found.

Let us now consider the reactants and products in more detail. First, it is peculiar that a reaction involving the acidic substances H_3PO_4 and SO_2 yields the highly alkaline product $KAl(OH)_4$. Second, among the products we find both PI_3 and H_2O, although it is known that PI_3 is rapidly hydrolyzed by water (*10*). Third, despite the large amount of reducing hydrogen, Fe^{2+} is oxidized to Fe^{3+}. Finally, if we (just for fun) change the product H_2O into recently identified H_2O_3 (*11*), then the new equation can also be balanced. The coefficient of H_2O_3 is 79, that of H_2 becomes 106, and all the other coefficients are now three times as large as those found for Blakley's equation. But it is unlikely that unstable H_2O_3 would be formed. Hence, the mere fact that a chemical equation can be uniquely balanced does not mean that the reaction it represents is feasible. We must conclude that, *until a chemist has shown that the reaction can occur*, balancing eq 2 should be considered an exercise in (chemical) mathematics, rather than in (mathematical) chemistry.

The Method of Linear Equations

The equation of any unique chemical reaction can be balanced mathematically by solving a set of linear equations. This procedure requires the application of simple algebra only. Hence, the method may even be useful in high school chemistry teaching. Its power can be illustrated by balancing the skeletal equation (*12*)

$$K_4Fe(CN)_6 + H_2SO_4 + KMnO_4$$
$$\rightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + HNO_3 + CO_2 + H_2O \quad (3)$$
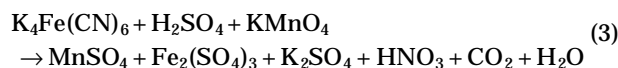
How the method can be used for cases in which the equations contain both molecules and ions, has been discussed in an excellent article by Porter (*13*).

The method is probably most useful for cases with an intermediate number of coefficients, as in eqs 1 and 3. If this number is appreciably larger, as in eq 2, its matrix version may be more useful, especially when implemented on a computer, or a modern hand-held calculator. If the number of coefficients is much smaller, the equation can usually be balanced by inspection. This merely means that the linear equations are not written down, but are solved at once mentally.

Occasionally the method of linear equations breaks down. This happens when the number of linear equations is too small to permit expressing all coefficients in terms of one chosen one. Then the equation could be balanced in an

infinite number of ways. In such a case the chemical equation does not represent a unique chemical reaction, but is a linear combination of the equations of at least two competing reactions (*13–15*). The proper coefficients now depend on the way in which the reactions are executed, and these can only be determined by experiment.

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