Unbalanced Chemical Equations

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In their interesting article on the development of the G. Frederick Smith Company, McBride and Adams give an unbalanced chemical equation summarizing the experimentally observed facts for the production of perchloric acid (1):

$$aNH_4ClO_4 + bHNO_3 + cHCl + dH_2O \rightarrow$$

$$eHClO_4 \cdot 2H_2O + fN_2O + gNO + hNO_2 + iCl_2 \quad [1]$$

They further comment that the resulting "equation has been left unbalanced because no solution that has ever been proposed satisfies the observed results. It is quite an exercise to balance it at all." This "exercise" provides an excellent example of the usefulness of the technique of "material balance" for balancing chemical equations, as it is not only the most fundamental and rigorous approach to the problem, but also provides an indication as to whether the equation in question is truly a legitimate chemical equation in the first place (2, 3).

Four independent equations of balance are available involving the nine undetermined coefficients in the reaction equation:

Nitrogen: $a + b = 2f + g + h$ [2]

Hydrogen: $4a + b + c + 2d = 5e$ [3]

Chlorine: $a + c = e + 2i$ [4]

Oxygen: $4a + 3b + d = 6e + f + g + 2h$ [5]

A quick calculation of the degrees of freedom (f) for nine variables (v) and four equations (e) gives:

$$f = (v - e) = (9 - 4) = 5 \quad [6]$$

and indicates that no single unique lowest whole number solution is possible. This is in contrast to normal 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 unique chemical reaction, but rather that of the sum of several simultaneous competing reactions - in this case probably involving the production of $HClO_4 \cdot 2H_2O$, on the one hand, and various side reactions leading to the formation of the different nitrogen oxides, on the other (3).

References and Notes

1. L. C. McBride, K. L. Adams, *J. Chem. Educ.*, **1984**, *61*, 625.
2. A. Porges, *J. Chem. Educ.*, **1945**, *22*, 266.
3. G. W. Bennett, *J. Chem. Educ.*, **1954**, *31*, 324.

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