The Use of Matrix Inversion in Spreadsheet Programs To Obtain Chemical Equations

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Spreadsheet programs make it easy to carry out many calculations on chemical systems that previously needed specially coded programs (*1*). Beyond their capacity to hold and analyze columns of data, most spreadsheets contain convenient functions for advanced computations. One example is the invocation of iterative calculations, which has been discussed previously in *this Journal* (*2*). Spreadsheets can also quickly carry out certain matrix manipulations, although these tools have not, to my knowledge, been applied previously to a chemical problem.

The use of matrix methods to obtain chemical equations is well-understood, as discussed by Alberty in a recent article in *this Journal* (*3*). Reacting chemical systems can be described by a matrix formulation, and the corresponding chemical equations can be obtained through the application of linear algebra (*4*). The classic work in this area is the monograph of Smith and Missen (*5*), who develop this method in detail in the context of a general mathematical treatment of chemical equilibrium.

The essence of the method is the solution of the matrix equation.

$$\mathbf{A}v = \mathbf{0} \tag{1}$$

where $\mathbf{A}$ is a system formula matrix with N columns for the N chemical substances and M rows for the M elements; n is a stoichiometric matrix, whose columns contain the coefficient for the substances in a balanced chemical equation; and $\mathbf{0}$ is a zero matrix. This equation shows mathematically that the amounts of the elements are conserved in a chemical reaction.

The algebraic challenge consists of finding a matrix n from a starting matrix $\mathbf{A}$. This can be done, by hand or with a computer program, through the elementary matrix method (*5, 6*). For some cases a suitable alternative is the use of a personal computer and a spreadsheet program to obtain n by the inversion of a matrix obtained simply from the formula matrix. The mathematical justification for this method is described in the appendix.

The Water–Gas Reaction A Simple Example

As an example of the matrix inversion method to obtain chemical equations, consider the reaction of coal and steam to make carbon monoxide and hydrogen. The formula matrix for this system is

$$\begin{array}{lc}
\text{Substance} & \begin{array}{cccc} H_2O & C & CO & H_2(g) \end{array} \\
\begin{array}{cc} & H \\ \text{Element} & O \\ & C \end{array} & \left[\begin{array}{cccc} 2 & 0 & 0 & 2 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 1 & 0 \end{array}\right] = \mathbf{A}
\end{array} \tag{2}$$

We make this a square matrix by appending a unit vector as an additional row to give the matrix $\mathbf{A}'$.

$$\begin{array}{c}
\begin{array}{cccc} H_2O & C & CO & H_2 \end{array} \\
\left[\begin{array}{cccc} 2 & 0 & 0 & 2 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{array}\right] = \mathbf{A}'
\end{array} \tag{3}$$

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The inverse of $\mathbf{A}'$ may be obtained in a variety of spreadsheet products (*7*) in a few keystrokes.

$$\begin{bmatrix} 1/2 & 0 & 0 & -1 \\ 1/2 & -1 & 1 & -1 \\ -1/2 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 \end{bmatrix} = (\mathbf{A}')^{-1} \quad (4)$$

The last column of this matrix is the stoichiometric matrix n for $\mathbf{A}$ and corresponds to the chemical equations presented below.

$$0 = -1H_2O - 1C + 1CO + 1H_2 \quad (5)$$

$$H_2O + C = CO + H_2 \quad (6)$$

Redox Reactions of Ions in Aqueous Solution

There is no reason to restrict the method to the conservation of chemical elements within a chemical reaction (*5*). One can include any characteristic of the chemical system that is conserved in the reaction. Charge is such a characteristic of ionic reactions that commonly occur in aqueous solution. It is introduced as another conserved quantity by adding a row for it to the formula matrix.

The "Breathalyzer" Reaction

Consider the example of the "Breathalyzer" (*8*) reaction of ethanol and dichromate to give chromium(III) ion and acetic acid. The formula matrix contains both water and hydrogen ions because the reaction is carried out in aqueous acid solution, and both species are available for the reaction.

$$\begin{array}{r|cccccc} \text{Substance} & Cr_2O_7^{2-} & C_2H_5OH & CH_3CO_2H & Cr^{3+} & H^+ & H_2O \\ \hline \text{Cr} & 2 & 0 & 0 & 1 & 0 & 0 \\ \text{O} & 7 & 1 & 2 & 0 & 0 & 1 \\ \text{C} & 0 & 2 & 2 & 0 & 0 & 0 \\ \text{H} & 0 & 6 & 4 & 0 & 1 & 2 \\ \text{Charge} & -2 & 0 & 0 & 3 & 1 & 0 \\ & 0 & 0 & 0 & 0 & 0 & 1 \end{array} = \mathbf{A}' \quad (7)$$

The inverse of this matrix gives the stoichiometric vector

$$\boldsymbol{\nu} = \begin{bmatrix} -2/11 \\ -3/11 \\ 3/11 \\ 4/11 \\ -16/11 \\ 1 \end{bmatrix} \quad (8)$$

from which we can write the chemical equation, first in crude form,

$$-2/11\,Cr_2O_7^{2-} - 3/11\,C_2H_5OH + 3/11\,CH_3CO_2H + 4/11\,Cr^{3+} - 16/11\,H + 1H_2O = 0 \quad (9)$$

and then after rearranging to conventional form:

$$16H^+ + 2Cr_2O_7^{2-} + 3C_2H_5OH = 3CH_3CO_2H + 4Cr^{3+} + 11H_2O \quad (10)$$

Systems with Multiple Chemical Equations

The examples cited thus far all contain a formula matrix that has one more column than row (i.e., $N - M = 1$). Associated with these is one solution to the equation $\mathbf{A}n = \mathbf{0}$. However, for many systems, $N - M > 1$, so two or more chemical equations will be obtained (*9*).

Reaction of Methane and Dioxygen

For example, the reaction of methane and dioxygen can give, among other products, carbon dioxide, hydrogen, and water, depending on the reaction conditions. Then there are five substances and three elements. To make a square matrix, two rows are added so that the lower right of the square matrix is an identity matrix.

$$\begin{array}{r|ccccc} & CH_4 & O_2 & CO_2 & H_2 & H_2O \\ \hline \text{C} & 1 & 0 & 1 & 0 & 0 \\ \text{H} & 4 & 0 & 0 & 2 & 2 \\ \text{O} & 0 & 2 & 2 & 0 & 1 \\ & 0 & 0 & 0 & 1 & 0 \\ & 0 & 0 & 0 & 0 & 1 \end{array} = \mathbf{A}' \quad (11)$$

$$\begin{bmatrix} 0 & 1/4 & 0 & -1/2 & -1/2 \\ -1 & 1/4 & 1/2 & -1/2 & -1 \\ 1 & -1/4 & 0 & 1/2 & 1/2 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} = (\mathbf{A}')^{-1} \quad (12)$$

$$\boldsymbol{\nu} = \begin{bmatrix} -1/2 & -1/2 \\ -1/2 & -1 \\ 1/2 & 1/2 \\ 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (13)$$

This corresponds to the following independent chemical equations.

$$CH_4 + O_2 = CO_2 + 2H_2 \quad (14)$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (15)$$

Experiments involving the reaction of methane and dioxygen may proceed to give both hydrogen and water as the hydrogen-containing products. Such a system would be described by a linear combination of these two independent solutions.

A Redox Reaction

Another example of a system that yields multiple equations was recently given by Riley and Richmond in *this Journal* (*10*). They discussed the special case of redox reactions involving aqueous hydrogen peroxide, which can act as either a reductant, to yield dioxygen, or an oxidant, to yield water. The "infinite number of balanced solutions" of their title arise from the infinite number of linear combinations of the system's two linearly independent chemical equations.

In the case cited there are six chemical species (dichromate, hydrogen peroxide, dioxygen, chromium(III) ion, proton, and water) and four conserved items (Cr, O, and H atoms, and charge). The modified stoichiometric matrix becomes

$$\begin{array}{r|cccccc} \text{Substance} & Cr_2O_7^{2-} & H_2O_2 & O_2 & Cr^{3+} & H^+ & H_2O \\ \hline \text{Cr} & 2 & 0 & 0 & 1 & 0 & 0 \\ \text{O} & 7 & 2 & 2 & 0 & 0 & 1 \\ \text{H} & 0 & 2 & 0 & 0 & 1 & 2 \\ \text{Charge} & -2 & 0 & 0 & 3 & 1 & 0 \\ & 0 & 0 & 0 & 0 & 1 & 0 \\ & 0 & 0 & 0 & 0 & 0 & 1 \end{array} = \mathbf{A}' \quad (16)$$

The stoichiometric matrix that results has two solutions to the following chemical equation.

$$\nu = \begin{bmatrix} 1/8 & 0 \\ -1/2 & -1 \\ 1/16 & 1/2 \\ -1/4 & 0 \\ 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (17)$$

The conventional chemical equations that result are

$$2Cr_2O_7^{2-} + O_2 + 16H^+ = 8H_2O_2 + 4Cr^{3+} \quad (18)$$

$$2H_2O_2 = 2H_2O + O_2 \quad (19)$$

Any linear combination of these two equations will, of course, also be a balanced chemical equation.

Limitations—Systems That Yield Singular Matrices

The inversion method fails when the number of chemical substances equals the number of variables (usually the number of elements). In these cases, the formula matrix is square from the start, and it will have no inverse because the M rows of such a matrix are not linearly independent.

A Decomposition Reaction

An example is the decomposition of sodium chlorate to dioxygen and sodium chloride (eq 20), where the Na:Cl ratio is the same in the $NaClO_3$ reactant and the NaCl product.

$$2NaClO_3 = 2NaCl + 3O_2 \quad (20)$$

We could obtain this equation by considering only the Cl and the O. Then the Na would be used as a check, not as an independent element. In the terminology of linear algebra, one of the element rows is a linear combination of the others. In the formula matrix (eq 21), the Cl row is the same as the Na row.[2] One can, in principle, evade the problem by eliminating the element row that is dependent on the others, but this is awkward. Instead, such problems are best done by the conventional matrix method (*5, 6, 9*).

$$\begin{array}{c} \\ \text{Na} \\ \text{Cl} \\ \text{O} \end{array} \begin{array}{c} \begin{array}{ccc} NaClO_3 & NaCl & O_2 \end{array} \\ \begin{bmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 3 & 0 & 2 \end{bmatrix} \end{array} = \mathbf{A} \quad (21)$$

More Than One Equation

A similar problem with a singular matrix can arise for cases in which more than one equation can be obtained, but then the problem becomes the ordering of the chemical substances.[3] One must ensure that the first N substances form a linearly independent set with respect to the elements.

For example, if instead of the matrix presented in eq 11 for the oxidation of methane we had chosen a different matrix with a different ordering of substances (eq 22), there would be no inverse to the modified matrix $\mathbf{A}'$.[3] This does not mean one cannot obtain the chemical equations for the system. It just means that one must reorder the columns.

$$\begin{array}{c} \\ \text{C} \\ \text{H} \\ \text{O} \\ \\ \\ \end{array} \begin{array}{c} \begin{array}{ccccc} O_2 & H_2 & H_2O & CH_4 & CO_2 \end{array} \\ \begin{bmatrix} 0 & 0 & 0 & 1 & 1 \\ 0 & 2 & 2 & 4 & 0 \\ 2 & 0 & 1 & 0 & 2 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \end{array} = \mathbf{A}' \quad (22)$$

Appendix—Justification of the Method

The matrix description of a chemical reaction relies upon the fact that chemical elements are neither created nor destroyed in a chemical reaction (except nuclear reactions). Thus, for each element j,

$$\sum a_{ij} n_i = 0$$

where a_i is the amount of an element in a substance; and n_i is the coefficient for that substance in the chemical reaction.

When all of the M elements and N substances are included, this becomes a series of M simultaneous equations with N elements. All add to zero, and the corresponding matrix description is

$$\mathbf{A}\boldsymbol{\nu} = \mathbf{0}$$

where $\mathbf{A}$ has M rows and N columns; and $\boldsymbol{\nu}$ has N rows and a number of columns equal to the number of independent solutions of the equation.

One can add to the bottom of matrix $\mathbf{A}$ rows that make a square matrix $\mathbf{A}'$,

$$\mathbf{A}' = \begin{bmatrix} \mathbf{A} \\ \mathbf{0}\ \mathbf{I} \end{bmatrix}$$

so that $\mathbf{I}$ is the identity matrix and $\mathbf{0}$ is a zero matrix as needed to make $\mathbf{A}'$ square. These additional rows correspond chemically to fixing the coefficient of one of the chemical substances equal to 1, which is chemically reasonable.

The inverse of $\mathbf{A}'$, if it exists, is a matrix that yields the identity matrix when multiplied by $\mathbf{A}'$,

$$(\mathbf{A}') \times (\mathbf{A}')^{-1} = \mathbf{I} = \begin{bmatrix} 1 & 0 & \dots & 0 & 0 \\ 0 & 1 & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & 1 & 0 \\ 0 & 0 & \dots & 0 & 1 \end{bmatrix}$$

The last $N - M$ columns of this matrix contain N rows of zeros. This means that the last $N - M$ columns of the matrix $(\mathbf{A}')^{-1}$, when multiplied by the first M rows of $\mathbf{A}'$, yield a zero matrix. Of course, the first M rows of $\mathbf{A}'$ are the original formula matrix $\mathbf{A}$. Thus, the last $N - M$ columns of $(\mathbf{A}')^{-1}$ are solutions of $\mathbf{A}\boldsymbol{\nu} = \mathbf{0}$.

Literature Cited

1. Parker, O. J.; Breneman, G. L. *Spreadsheet Chemistry*; Prentice Hall: Englewood Cliffs, 1991.
2. (a) Parker, O. J.; Breneman, G. L. *J. Chem. Educ.* **1990**, *67*, A5. (b) Sundheim, B. R. *J. Chem. Educ.* **1990**, *67*, A300.
3. Alberty, R. A. *J. Chem. Educ.* **1991**, *68*, 984.
4. Schneider, D. R.; Reklaitis, G. V. *Chem. Eng. Sci.* **1975**, *30*, 243.
5. Smith, W. R.; Missen, R. W. *Chemical Reaction Equilibrium Analysis: Theory and Algorithms*; Wiley: New York, 1982.
6. Smith, W. R.; Missen, R. W. *Chem. Eng. Educ.* **1979**, *13*, 26.
7. This is handled as an arithmetic function (/Tools | Advanced Math | Invert) that is called from the menu in *Quattro Pro* (*Quattro Pro 4.0 User's Guide*; Borland: Scotts Valley, 1992). A similar strategy is followed in Lotus 1-2-3, whereas Excel uses an array function ("=MINVERSE(array)"), Microsoft Excel 4.0 Function Reference, Microsoft, Redmond, WA, 1992).
8. Labianca, D. A. *J. Chem. Educ.* **1990**, *67*, 259.
9. Missen, R. W.; Smith, W. R. *J. Chem. Educ.* **1989**, *66*, 217; (Erratum *J. Chem. Educ.* **1989**, *66*, 534).
10. Riley, J.; Richmond, T. G. *J. Chem. Educ.* **1992**, *69*, 114. See also, Missen, R. W.; Smith, W. R. *J. Chem. Educ.* **1990**, *67*, 876.

[2] In many other cases the row that is linearly dependent on the others is much less obvious.

[3] I am grateful to a reviewer for pointing out this problem.