Chemical Equations are Actually Matrix Equations

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Chemists tend to think that chemical equations are unique to chemistry, and they are not used to thinking of chemical equations as the mathematical equations they really are. The mathematical aspects of chemical equations have been discussed in *this Journal* in connection with balancing chemical equations, but the objective of the following example is to illustrate the mathematical significance of the chemical equation.

Consider the following reaction:

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} = \mathrm{CO_2} \tag{1}$$

$$\begin{matrix} \mathrm{C} \\ \mathrm{O} \end{matrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \quad \begin{bmatrix} 0 \\ 2 \end{bmatrix} \quad \begin{bmatrix} 1 \\ 2 \end{bmatrix}$$

The three column matrices below the molecular formulas indicate that the molecular formulas are really ways of representing the column matrices that give the atomic compositions of the molecules. The upper integer of the matrix gives the number of carbon atoms and the lower integer gives the number of oxygen atoms.

The general representation of a chemical reaction is $0 = \Sigma\, \nu_i B_i$, where the stoichiometric numbers ν_i are positive for products and negative for reactants and B_i is the molecular formula for the ith reactant. Applying this relation to reaction 1 yields

$$0 = -1\mathrm{CO} - \tfrac{1}{2}\mathrm{O_2} + 1\mathrm{CO_2} \tag{2}$$

which is converted to reaction 1 by simply moving the negative terms to the left side of the equation. Now let us rewrite reaction 2 by replacing the molecular formulas by the corresponding column matrices.

$$-1\begin{bmatrix} 1 \\ 1 \end{bmatrix} - \tfrac{1}{2}\begin{bmatrix} 0 \\ 2 \end{bmatrix} + 1\begin{bmatrix} 1 \\ 2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{3}$$

Textbooks on linear algebra all show that eq 3 can be written in the form of a matrix product.

$$\begin{bmatrix} 1\ 0\ 1 \\ 1\ 2\ 2 \end{bmatrix} \begin{bmatrix} -1 \\ -\tfrac{1}{2} \\ +1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{4}$$

Notice that the stoichiometric numbers for reaction 2 form a column matrix in eq 4. You should make this matrix multiplication yourself to verify that it is correct. Equation 4 is the mathematician's way of writing the chemical equation for this particular chemical reaction. Equation 4 shows that the equal sign in eq 1 is the mathematician's equal sign.

Equation 4 is an example of the general equation[1]

$$\boldsymbol{A\nu} = \boldsymbol{0} \tag{5}$$

where $\boldsymbol{A}$ is the $C \times N$ conservation matrix (formula matrix), $\boldsymbol{\nu}$ is the $N \times R$ stoichiometric number matrix, and $\boldsymbol{0}$ is the $C \times R$ zero matrix. C is the number of components; in this case, C is the number of elements. N is the number of reactants. R is the number of independent reactions.

Equation 5 is important, because it can be applied to a system with any number of elements and any number of reactants. The $\boldsymbol{A}$ matrix for a system involving many reactants is readily written down. Actually $\boldsymbol{A}$ is simply made up of the coefficients of the conservation equations which apply to a system. $\boldsymbol{\nu}$ is the null space of matrix $\boldsymbol{A}$. The null space of a small matrix can be calculated by hand, but a computer is required for larger $\boldsymbol{A}$ matrices. When a system contains many reactants, a number of simultaneous independent reactions are required to describe all possible changes in chemical composition that are permitted by the element balances.

As an example of a system that requires more than one reaction to represent the changes that can take place, consider a system containing CO, CO_2, H_2, H_2O, and CH_4. The $\boldsymbol{A}$ matrix is

$$\begin{matrix} & \mathrm{CO} & \mathrm{CO_2} & \mathrm{H_2} & \mathrm{H_2O} & \mathrm{CH_4} \\ \mathrm{C} & 1 & 1 & 0 & 0 & 1 \\ \mathrm{O} & 1 & 2 & 0 & 1 & 0 \\ \mathrm{H} & 0 & 0 & 2 & 2 & 4 \end{matrix} \tag{6}$$

When we calculate the null space of this matrix, we find that eq 5 is

$$\begin{bmatrix} 1\,1\,0\,0\,1 \\ 1\,2\,0\,1\,0 \\ 0\,0\,2\,2\,4 \end{bmatrix} \begin{bmatrix} 1 & -2 \\ -1 & 1 \\ -1 & -2 \\ 1 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 0\,0 \\ 0\,0 \\ 0\,0 \end{bmatrix} \tag{7}$$

The $\boldsymbol{\nu}$ matrix shows that it takes two independent reactions to represent all possible changes in composition that can occur in the system; the stoichiometric numbers of the first reaction are given by the first column and the stoichiometric numbers of the second reaction are given by the second column. When the negative terms are moved to the left-hand side, the two independent reactions are

$$\mathrm{CO_2} + \mathrm{H_2} = \mathrm{CO} + \mathrm{H_2O} \tag{8}$$

$$2\mathrm{CO} + 2\mathrm{H_2} = \mathrm{CO_2} + \mathrm{CH_4} \tag{9}$$

The $\boldsymbol{\nu}$ matrix in eq 7 can be calculated by hand (although that is not described here), but larger systems can be treated by using a computer that can carry out matrix operations.

[1]Smith, W. R.; Missen, R. W. *Chemical Reaction Equilibrium Analysis*; Wiley: New York, 1982.