

Linear variational Diophantine techniques in mass balance of chemical reactions

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Received 14 August 2001

Linear algebraic techniques based on minimization of thermodynamic functional and/or other constraints are illustrated for mass balance of chemical reactions that do not exhibit stoichiometrically unique solutions in the linear algebraic vector space. The techniques demonstrate elegant casting of chemical equations in terms of generalized linear Diophantine matrices and generalized elimination and variational schemes.

KEY WORDS: Diophantine techniques, balancing chemical reactions, linear variation, thermodynamic functional

1. Introduction

Mass balance of chemical reactions or commonly known as balancing of chemical reactions is a century-old problem that has received considerable attention both in chemical and mathematical literature [1–10]. Herndon [1] has written a nice and comprehensive review article on the subject recently. The mass balance of chemical reactions provides an excellent demonstrative and pedagogical example of interplay between chemical principles and mathematics. The mathematics involved can vary in complexity from simple trial and error techniques to sophisticated Diophantine equations [5] and generalized matrix inverses [6]. Although the first algebraic formulation dates back to 1878 by Bottomley [3], under the title of “indeterminate coefficients” technique, the topic has received considerable attention both in mathematical and chemical community continuously for several decades, the most recent one that I am aware of is due to Herndon [1] who has written a comprehensive review and a previous article [2] on the subject.

While it may seem that expressing mass balance in linear algebraic terms may complicate a simple inspection method, intuitive technique or other methods such as half-reactions, there are situations where linear algebra based methods may be more at-

tractive, especially to explain and resolve what may be seemingly paradoxical or infinite solutions to chemical reactions.

It is usually presumed that most of the common textbook chemical reactions are readily and easily balanced, and with the availability of mathematica and other software, this seems straightforward. A set of chemical reactions has been perplexing to chemists and has received particular attention in the literature [4,7]. Herndon [1] characterized these reactions as $n(\text{CM}) > 1$ chemical reactions, where $n(\text{CM})$ is the nullity of the coefficient matrix (CM) of the chemical reaction under consideration. These reactions are perplexing in that they exhibit infinite linearly independent solutions all of which satisfy the chemical balance, and yet they are not all chemically feasible solutions for a given set of experimental conditions. A unique solution is obtained by imposing a chemical constraint, namely, that reactants have to react only in certain proportions. This has led to the idea of "splitting Diophantine equations" by explicitly imposing a stoichiometric constraint. Sophisticated mathematical techniques such as generalized matrix inverses [6] have been considered for chemical balance reactions which exhibit unique balanced equations, that is $n(\text{CM}) = 1$. It seems, however, that a precise linear algebraic method based on variational principles may be appropriate to achieve the splitting of $n(\text{CM}) > 1$ chemical reactions. The thermodynamic minimization has been suggested in the chemical context [11] of treating analogous reactions, but a precise linear algebraic treatment that also combines the thermodynamics variational principles can be quite elegant and educational as we demonstrate here. It should also be emphasized that thermodynamic optimization [11,16] is applicable only when the chemical species are in chemical equilibrium. In other circumstances, other constraints have to be stipulated on the basis of experimental conditions, or kinetics consideration or consideration of mechanisms, catalysis, pH and so on.

It should also be noted that mass balance of chemical reactions constitutes linear equations in integers called Diophantine equations in the mathematical context [12–15] and the topic as such has received considerable attention in mathematics [12–14] and computer literature [15]. For example, the celebrated Hilbert's tenth problem seeks a technique for solving a general Diophantine equation, especially non-linear equations. It seems at present higher order Diophantine equations have not been solved. Diophantine equations find important applications in the encryption method [15], computer security through cryptosystems, which send a known transformation of a message as a secure cryptogram, which is back transformed by the receiver by a reciprocal transformation to decipher the message.

An objective of this article is to demonstrate a hybrid linear algebraic variational method for chemical reactions, which do not exhibit unique mass balance, that is, the nullity of the chemical coefficient matrix is greater than 1. The technique seems to be elegant in expressing and separating chemical reactions on the basis of thermodynamic optimization or other constraints derived on the basis of experimental conditions such as fixed initial stoichiometric proportions, kinetics or mechanistic considerations etc.

2. Basic linear algebraic techniques

It is well known [1–10] that all chemical reactions can be expressed in terms of a coefficient matrix CM, wherein the columns represent the reactants and products, and the rows represent the distinct atoms in the chemical reaction. To illustrate, the reaction



can be expressed by the CM matrix, which we represent by an $m \times n$ matrix \mathbf{A} , where the m rows correspond to the distinct elements, namely, Na, N, O, Fe, S and H, respectively, and the columns are the chemical species:

$$\mathbf{A} = \begin{bmatrix} 1 & 0 & 0 & -1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & -1 & 0 \\ 2 & 4 & 4 & -4 & -12 & -1 & -1 \\ 0 & 1 & 0 & 0 & -2 & 0 & 0 \\ 0 & 1 & 1 & -1 & -3 & 0 & 0 \\ 0 & 0 & 2 & -1 & 0 & 0 & -2 \end{bmatrix}. \quad (1)$$

Then the linear equations in integers expressing the mass balance become

$$\mathbf{AX} = 0, \quad (2)$$

where \mathbf{X} is a column vector of length n , which represents the solution of the chemical mass balance. The famous rank-nullity theorem of matrices determines when the solution of the matrix is unique and when it is not. That is, for the reactions where the nullity of the matrix expressed as

$$r = n - \text{rank}(\mathbf{A})$$

becomes more than or equal to 2, there are infinite ways of balancing the chemical reactions and each of which would represent a stoichiometrically different solution. For the common chemical reactions r becomes 1, which means any multiple of a set of balanced coefficients is also a solution. Since only the proportion of chemical masses matters, all such solutions are chemically equivalent. However, for reactions for which $r > 1$, there are infinite solutions with different chemical proportions. These reactions would be the topic of linear variational techniques.

It is interesting that r is always more than or equal to 2 if $n - m$ is more than or equal to 2; converse is not true since two rows of the matrix can become linearly dependent. These reactions are interesting from the standpoint that mathematically there may be infinite solutions but chemically one such solution or a linear multiple of such a solution can only be correct in a given chemical proportion or experimental condition, although other solutions may be appropriate in different experimental conditions.

It is well known that the solution for equation (2) can be readily obtained by the famous Gauss–Jordan or Gauss elimination method [17] which leads to a unique set of solutions for $r = 1$ given by

$$X_n = \prod_{i=1}^{n-1} a_{ii}, \quad a_{ii} \neq 0 \forall i, \quad (3)$$

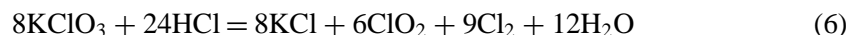
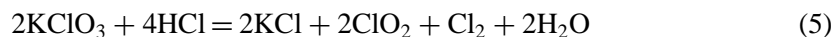
$$X_{n-1} = -a_{n-1,n} \prod_{i=1}^{n-2} a_{ii}, \quad a_{ii} \neq 0 \forall i, \quad (4)$$

$$X_{n-2} = -\frac{(a_{n-2,n-1}X_{n-1} + a_{n-2,n}X_n)}{a_{n-2,n-2}}, \quad (5)$$

$$X_i = -\frac{\sum_{j=i+1}^n a_{ij}X_j}{a_{ii}}, \quad (6)$$

where a_{ij} 's are the matrix elements of the Gauss-eliminated matrix obtained from starting with the CM matrix. Note that the above procedure assures integral solutions for all X_i 's. However, the mass balance cannot be achieved unless all X_i 's have the same sign. If some of them are positive and others are negative, the equation cannot be balanced. If one of the diagonal elements become zero in the final Gauss-eliminated matrix, the equation cannot be balanced. However, if a diagonal element becomes zero during the elimination procedure usually a permutation of the rows could circumvent the problem, but the final eliminated matrix cannot contain zero diagonal elements in order for the reaction to be balanced.

The cases for which $r \geq 2$ are quite interesting in that the standard Gauss elimination procedure needs to be generalized and thermodynamic or other constraints have to be imposed. There are many reactions of this kind, but the one that drew the author's attention [10] to this problem during his high school years is



One can make linear combination of any two of the above reactions and produce infinite solutions. The r value for the above reaction is $(6 - 4) = 2$, and thus, there are two linearly independent solutions according to the rank-nullity theorem.

The reactions such as the one shown above have been looked at in the literature using other techniques such as fixing the chemical proportion of the reactants combined with some experimental condition but it seems that the combination of variational method with matrix algebra may provide an elegant, general and interesting approach to the problem. That is, the Gauss elimination procedure is generalized as follows and then combined with the variational principle to minimize the thermodynamic variational

function or other schemes, which may be the Gibbs free energy if the system is under constant temperature and pressure constraints and equilibrium. Suppose we denote the variations of the n chemical species by dn_1, dn_2, \dots and then a thermodynamic functional L can be invoked as an extremum variable if the system is under equilibrium. The L function is a function of dn_1, dn_2, \dots and thermodynamic variables $V_1, V_2, V_3, \dots, V_t$. It is natural that L would be an extensive functional as the system is one of variable masses and L would have partial molar properties. As an example, for a system of two variables as pressure and temperature, L becomes the Gibbs free energy, and if the variables are volume and temperature, L becomes the Helmholtz function, but the formalism considered here is quite general to encompass both famous cases and any other optimization functional. The requirement of optimization is that $dL = 0$, and we have the variation expression:

$$dL = \sum_{i=1}^t \left(\frac{dL}{dV_i} \right) dV_i + \sum_{j=1}^n \left(\frac{dL}{dn_j} \right) dn_j, \quad (8)$$

and if we denote dL/dn_j by U_j , then L becomes an extremum when $dL = 0$. The constraint of constant variables $V_1, V_2, V_3, \dots, V_t$ results in the equations:

$$dL = \sum_{j=1}^n \left(\frac{dL}{dn_j} \right) dn_j = 0. \quad (9)$$

For independent variations dn_k this will result in $(dL/dn_k) = 0$ for $k = 1, 2, 3, \dots, (n - m)$, which resolves the chemical balance equation into $n - m$ linearly independent equations. To illustrate, the reaction



which has an r value of 2 and, thus, infinite stoichiometrically independent solutions yields the following equations for the extremal functional L :

$$-3U_1 + U_2 + 3U_3 = 0, \quad -2U_2 + 3U_4 = 0. \quad (11)$$

We can generalize the variational scheme with an $m \times n$ Diophantine matrix. The CM matrix \mathbf{A} for such reactions can be partitioned into an $m \times m$ square matrix and a residual $m \times (n - m)$ matrix. The $m \times m$ matrix is Gauss-eliminated as follows:

$$\left[\begin{array}{cccc|ccc} a_{11} & a_{12} & \dots & a_{1m} & a_{1,m+1} & \dots & a_{1n} \\ 0 & a_{21} & \dots & a_{2m} & a_{2,m+1} & \dots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & a_{mm} & a_{m,m+1} & \dots & a_{mn} \end{array} \right] \begin{bmatrix} dn_1 \\ dn_2 \\ \vdots \\ dn_n \end{bmatrix} = 0. \quad (12)$$

This results in the following solutions:

$$\begin{aligned} dn_m &= -\frac{1}{a_{mm}} \sum_{j=m+1}^n a_{mj} dn_j, \\ dn_{m-1} &= -\frac{1}{a_{m-1,m-1}} \left(\sum_{j=m+1}^n a_{m-1,j} dn_j \right) - \frac{a_{m-1,m}}{a_{m-1,m-1}} dn_m, \\ &\dots \end{aligned} \quad (13)$$

Thus, it can be seen that

$$a_{mm} U_m \left(\prod_{k=1}^m a_{kk} \right) dn_m = U_m \left(\prod_{k=1}^m a_{kk} \right) \sum_{j=m+1}^n a_{mj} dn_j. \quad (14)$$

The condition that dL should be 0 is equivalent to the matrix equation

$$(U_1 \quad U_2 \quad \dots \quad U_n) \mathbf{B} \begin{pmatrix} dn_{m+1} \\ dn_{m+2} \\ \vdots \\ dn_n \end{pmatrix} = 0, \quad (15)$$

where \mathbf{B} is a matrix of order $n \times (n - m)$ satisfying the following relations to the Gauss-eliminated reaction matrix \mathbf{A} :

$$\begin{aligned} b_{ml} &= -\frac{a_{m,m+l} \prod_{k=1}^m a_{kk}}{a_{mm}}, \\ b_{il} &= -\frac{a_{i,m+l}}{a_{ii}} \prod_{k=1}^m a_{kk} - \frac{1}{a_{ii}} \sum_{j=i+1}^n a_{ij} b_{jl}, \quad i < m, \\ b_{il} &= \prod_{k=1}^m a_{kk}, \quad i = m + l, \quad i > m, \\ b_{il} &= 0, \quad i \neq m + l, \quad i > m, \\ l &= 1, 2, 3, \dots, n - m. \end{aligned} \quad (16)$$

The above expressions represent the solutions obtained by seeking a generalized Gaussian elimination followed by recursive back substitution combined with the thermodynamic variational conditions. The latter conditions lead to the fact that the columns of the matrix \mathbf{B} contain the $(n - m)$ stoichiometrically independent solutions for the original chemical equation, which has infinite mathematical solutions. It should be emphasized that the optimization of a thermodynamic functional L is appropriate only when the system is in equilibrium. For other dynamical situations other constraints have to be sought such as initial stoichiometric proportions, catalysts, and other experimental conditions. Such conditions can then be mathematically transformed and the unique solution for those conditions can be sought.

3. Conclusion

While the century-old problem of chemical balance can be solved by many standard techniques such as half-reaction method, the elegant linear Diophantine matrix formulation becomes especially useful in cases where the reaction matrices lead to infinite stoichiometrically independent solutions. In addition to explaining the paradox of infinite solutions in precise mathematical terms, the cases provide models for the generalization of Gaussian elimination to other linear systems with infinite solutions. The technique also represents solutions to linear Diophantine equations with infinite solutions or cases with nullity of the associated linear Diophantine matrix is more than one. For the chemical species the unique set of stoichiometrically independent linear equations can be obtained by stipulating thermodynamic variational principles if the system is in equilibrium or other constraints determined on the basis of experimental conditions. The techniques outlined are valid for applications in other fields also, where such linear Diophantine equations with infinite solutions arise.

Acknowledgment

The work at UC Davis was supported by US National Science Foundation grant CHE9814056, and the work at LLNL was carried out under the auspices of US DOE under contract number W-7405-Eng-48.

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