Chemical Reaction Stoichiometry: A Key Link between Thermodynamics and Kinetics, and an Excel Implementation

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Abstract

Various special methods are generally taught for the construction of stoichiometric equations for simple reacting systems, including inspection, oxidation–reduction, and ion–electron approaches, which typically fall under the topic of "balancing a chemical equation". However, apart from the simplest cases described by single chemical equations, only matrix methods can express the Law of Conservation of Mass (LCM) by generating a set of multiple stoichiometric equations of the appropriate number.

Chemical Reaction Stoichiometry (CRS) represents the Law of Conservation of Mass (LCM) in the context of chemical reaction, both in and out of its chemical equilibrium state; it may be expressed as a set of linear equations involving the conservation of mass, of chemical elements, or of another appropriate quantity, for example chemical moieties or genetic units. CRS expresses this information in terms of a set of stoichiometric equations, which are equivalent representations of the LCM and have the appearance of, but are distinct from, actual chemical reaction mechanisms. These equations may be determined by algorithms implemented in symbolic mathematics programs or by purpose-specific computer programs. In order to provide a more generally accessible means of implementing the matrix method, we provide a Microsoft Excel implementation, XSTOICH, as a Supplementary file that contains many examples.

After first briefly reviewing the matrix method for the standard case based on a set of chemical species and their molecular formulae, we show how to incorporate complications arising from stoichiometric restrictions such as those imposed by a kinetic model of the system. The need for background mathematical knowledge is avoided by the provision of simple worked motivating examples in the text. The chemical motivation for more complex problems is made clear, and their solution is illustrated by means of the simple input procedures of XSTOICH.

Introduction

The Law of Conservation of Mass (LCM) is fundamental to chemistry. It applies to all closed chemical systems as well as to open flow systems (those with both inlets and exits) at steady state; we refer to both situations as *closed systems* in the following. The LCM can be expressed most directly by means of a set of linear equations involving the species amounts, representing the conservation of the atom types in the system (including the conservation of electronic charge, which is incorporated by imposing a value of zero for its conserved value). This is equivalent to requiring that changes in the amounts of the conserved quantities which accompany arbitrary changes in the species amounts from a given composition must always be zero. The LCM may equivalently be expressed in the form of "chemical equations", which have the appearance of, but are distinct from, actual chemical reaction mechanisms. Chemical Reaction Stoichiometry (CRS) is the study of the inter-relationships between the two expressions of the LCM. Although these inter-relationships can provide insights into the underlying chemical phenomena, the topic is not a component of traditional undergraduate chemistry pedagogy, in spite of the fact that it is based on the use of relatively simple mathematical manipulations.

In undergraduate chemistry education, reaction kinetics and equilibrium thermodynamics are two important topics, traditionally taught as separate subjects. However, they share the common link of the LCM. Not only must the overall reaction conserve mass, but each reaction that appears in a chemical kinetic description of a system must individually satisfy the LCM. The topics are further connected by the fact that reaction processes in a closed system under a given set of overall thermodynamic conditions (for example, specified temperature and pressure) evolve with time towards a unique chemical equilibrium composition. Although the details of a system's reaction mechanism and its kinetic description may be exceedingly complex or, indeed, even unknown, the equilibrium composition itself is independent of such considerations, and is determined by the global minimum of the system's Gibbs function. Thus, the calculation of chemical reaction equilibrium requires only species reference state

Gibbs energy information in conjunction with the specification of the LCM for the system and an appropriate chemical potential model. This also means that the limiting compositional state of any chemical kinetic model for such systems must coincide with the equilibrium composition. In addition, a link may be made from a chemical kinetic model to its implied LCM conservation equations using the concepts of Chemical Reaction Stoichiometry (CRS).

For the aforementioned reasons we believe that a focus on the pedagogical treatment of the topic of CRS itself would serve to unify the treatment of chemical equilibrium and of chemical kinetics within the field of chemistry and, by avoiding its duplication in each, provide a more efficient pedagogical approach to both topics. We also note in passing the increasing importance of CRS concepts in systems biology,[1,2] providing an additional field that could benefit from a common treatment of the topic.

The commonest pedagogical application of the LCM in a system undergoing chemical change has been the calculation of the chemical equilibrium in closed systems, for which the LCM may be expressed in terms of sets of equations that have the superficial appearance of describing actual chemical reaction processes. This emphasis, and traditional applications to relatively simple systems that require only a single such equation, have both obscured their basic purpose and led to the teaching of a myriad of methods for "balancing a chemical equation", including "inspection", simple algebra,[3] the oxidation number method[4] and the half-reaction (or ion-electron) method.[5] Only the matrix method,[6] which we herein discuss, can be extended to the ubiquitous case of multi-reaction systems. This approach also addresses the core task of determining the appropriate number, R, of independent chemical equations that are required to implement the LCM; this number is a crucial aspect of chemical equilibrium problems.

The importance of chemical reaction stoichiometry (CRS) has been explored by one of us in many articles[6–11] and a website[12] that have advocated for an increased emphasis on the LCM itself and its application to both chemical reaction equilibrium and to chemical reaction kinetics. Software to implement the general matrix method for the LCM was first

published in the 1982 textbook of Smith and Missen,[6] and later (1989) by Missen and Smith[8] in the form of a BASIC program to generate a maximal set of chemical equations from the system's formula matrix. To the best of our knowledge, no other generally available current software provides this universality. However, in order to run the BASIC program in current Windows, Mac and Linux computers, it is necessary to install an emulator[13] which makes the program unacceptable for general use. The method was later coded as a web–based Java Applet, JSTOICH.[14] However, current security considerations mean that Java Applets are no longer accessible through web browsers, except under special circumstances.[15,16]

The purpose of this paper is to briefly describe the matrix method for CRS and to present its implementation in Microsoft VBA Excel, which is rather widely available and not subject to browser restrictions. The Excel program is made available as a supplement, XSTOICH, to this manuscript. Examples of its use are illustrated in the paper.

Although CRS is based upon the mathematics of sets of linear algebraic equations, the need for background knowledge in this area is avoided by the consideration of very simple worked examples, which are easily understood by first-year chemistry students. The chemical motivation for more complex problems is explained clearly, and their implementation is illustrated by simple input entries to XSTOICH.

The paper is organized as follows. In the next section, we briefly review the matrix method for the determination of a set of chemical equations consistent with the most general form of the LCM that arises when the set of species chemical formulae is specified. We proceed from the simple case of a one-equation system to the general case of multiple chemical equations, demonstrated in XSTOICH on examples. The subsequent section discusses the use of XSTOICH to consider less well-known LCM situations, in which restrictions are placed on its general form. These may arise either from explicit restrictions on the element conservation equations over and above the conservation of the elements, or from implicit restrictions arising from a specified set of chemical equations. In both cases, the restrictions must correspond to experimental observations.

The Matrix Method for a One–Reaction System

CRS implements the law of the conservation of mass (LCM) in a closed chemical system undergoing chemical change. It expresses the conservation of appropriate entities such as atomic elements, electronic charge, quantities such as group moieties in biological processes being transferred between molecules,[17] and the transfer of genetic information,[1,2] all of which will henceforth be referred to as "elements". The LCM is expressed in terms of the set of homogeneous linear algebraic equations arising from the requirement that changes in the species amounts must result in a net zero change in the amount of each conserved element in the system. This may be represented by a system of homogenous linear equations involving the changes in the species amounts (thus having their right sides equal to zero) and treated by the methods of linear algebra, most conveniently by the use of simple matrix manipulations.

The matrix method can be most straightforwardly derived by stating that there is zero change in the amount of each chemical element for any set of changes in the molar amounts of the chemical species involved in a closed system. In the case of a single-reaction system, this is the principle underlying the familiar "ICE method"[18,19] used in solving a chemical equilibrium problem involving a single reaction.

As an initial simple example, consider the system of coal (in the form of solid carbon), steam and synthesis gas ($C(s), H_2O, CO, H_2$). The 3×4 system formula matrix, $\mathbf{A}$, is shown in Fig. 1(a), where the numbers under the chemical formulae in the column headings represent the numbers of atoms per molecule of the type labelled at the left of the corresponding row; for example, a molecule of H_2O consists of two H atoms, one O atom and zero C atoms. $\mathbf{A}$ represents the formula matrix of the system of $N = 4$ species (heading the columns), requiring $M = 3$ linear equations (represented by the rows) involving arbitrary mole number changes, whose right sides are set to zero to indicate that the amount of each element is conserved.

A maximal set of independent solutions of these equations can be found by a standard Gauss-Jordan elimination process[20] implemented in XSTOICH, of generating the diagonal

Row-Reduced Echelon Form (RREF) of $\mathbf{A}$, labelled as the matrix, $\mathbf{A}^*$, containing a leading 3×3 unit matrix, as depicted in Fig. 1(b). The RREF procedure consists of considering each row in turn, and adding (positive or negative) multiples of rows together, ("swapping" of rows is a special case of this), so as to produce a "1" in the column corresponding to the row and zeros in all other rows of that column. (This process may usefully be followed interactively and step-by-step on the RESHISH Matrix Calculator website[21]) At the termination of this process, the final column of the RREF matrix in Fig. 1(b) is a solution stoichiometric vector, $\boldsymbol{\nu}$, which may be interpreted as the relationship of the formula vector of the single "non-component species" listed in the header to the formula vectors of each of the prior header species (termed the "component species") with their corresponding unit vectors beneath them, in sequence, thus:

$$1 \times \begin{pmatrix} 2 \\ 0 \\ 0 \end{pmatrix} = 1 \times \begin{pmatrix} 2 \\ 1 \\ 0 \end{pmatrix} + 1 \times \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} - 1 \times \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} \tag{1}$$

or, replacing the formula vectors by their chemical names

$$1 \times \mathrm{H_2} = 1 \times \mathrm{H_2O} + 1 \times \mathrm{C(s)} - 1 \times \mathrm{CO} \tag{2}$$

which re-arranges to the more familiar chemical equation

$$\mathrm{C(s)} + \mathrm{H_2O} = \mathrm{CO} + \mathrm{H_2} \tag{3}$$

In general, the $\mathbf{A}^*$ matrix is comprised of a leading unit matrix of dimension C followed by a $C\times R$ stoichiometric matrix (a 3×1 vector in this case), where C represents the number of "components species" (or "basis chemical species") in the system and R represents the number of noncomponent species which may be produced from the component species by the R reactions. This example is a very simple one, since it has $R = 1$; note also that

(a)

A =		H_2O	C	CO	H_2
	H	2	0	0	2
	O	1	0	1	0
	C	0	1	1	0

(b)

A* =		H_2O	C	CO	H_2
	H	1	0	0	1
	O	0	1	0	1
	C	0	0	1	-1

Figure 1: (a) 3×4 formula matrix, $\mathbf{A}$, for the system involving coal, steam and synthesis gas (CO and H_2O). (b) $\mathbf{A}^*$, the RREF (Row-Reduced Echelon Form) of $\mathbf{A}$, with the resultant leading 3×3 unit matrix highlighted. Each column is headed by a species name, with each cell beneath it containing the number of atoms per molecule of the component species indicated in the corresponding left column. The final column is the stoichiometric vector, $\boldsymbol{\nu}$, for the (single) reaction producing the "non-component" species noted in its header from the prior component species. In this case, the number of reactions is $R = 1$.

$C = M$ in this case. Finally, note that we could have arranged the species columns in any order and would have arrived at the same resulting Eq. (1) (but the sets of component species and non-component species would be different). The astute reader will also notice that $R = N - C$ in this simple example, a result that carries over to the multiple reaction case. We shall see that the order of the columns affects the nature of the particular set of reactions that are generated when R is greater than 1.

The Universal Matrix Method (UMM)

Although simple chemical processes may be represented by a single chemical equation, most realistic cases result in multiple chemical equations. In elementary chemistry, these are sometimes characterised as being "difficult to solve" or having multiple solutions.[22] We believe that this characterization is pedagogically counterproductive since it emphasizes "single–reaction chemistry" (the notion that all reacting systems can be reduced to a single reaction);

in fact, every one of the possible "multiple solutions" can be written as a linear combination of a set of R independent chemical equations. The fundamental task of CRS is to find the values of C and R and to find a set of R independent chemical equations from the system formula matrix $\mathbf{A}$. The value of R is unique, but the set of independent chemical equations is not, with the only requirement being that the equations are "independent", that is, any individual equation cannot be obtained by a linear combination of the other members of the set.

Symbolic algebra programs to perform the necessary matrix manipulations on the formula matrix are generally expensive and require some familiarity in use, while Microsoft Excel (and similar programs) are widely available (with some being free of charge) while still requiring some experience in data manipulation. We therefore introduce XSTOICH, a "universal" programmed method in Excel to perform the task.[6,7,9,12] In this method, the formula matrix $\mathbf{A}$ is transformed as in Fig. 1 by Gauss-Jordan elimination[21,23] to a "Row-Reduced Echelon form" (RREF), resulting in a matrix $\mathbf{A}^*$ consisting of a unit matrix followed by stoichiometric coefficient vector(s) from which a set of independent stoichiometric equations may be directly written. Since $\mathbf{A}^*$ is obtained from $\mathbf{A}$ by linear combinations of its rows, the matrices satisfy

$$\mathrm{rank}(\mathbf{A}^*) = \mathrm{rank}(\mathbf{A}) \tag{4}$$

where the rank of a matrix is its number of linearly independent rows or columns. (We remark that XSTOICH is configured to require the formula matrix $\mathbf{A}$ to be entered in its transposed form, that is, the columns contain the formula vectors.)

As a simple example of a multi–reaction system, consider the partial combustion of methane to produce synthesis gas, CO and H_2, together with CO_2 and H_2O. The 3×6 stoichiometric formula matrix for this system appears in Fig. 2(a). After Gauss–Jordan elimination, we observe in the RREF matrix $\mathbf{A}^*$ (Fig. 2(b)) that there is a leading 3×3 unit matrix, followed by three additional columns; rank($\mathbf{A}$) is readily determined by counting the

(a)

A =		CH_4	O_2	CO_2	H_2O	CO	H_2
	C	1	0	1	0	1	0
	O	0	2	2	1	1	0
	H	4	0	0	2	0	2

(b)

A* =		CH_4	O_2	CO_2	H_2O	CO	H_2
	C	1	0	0	0.5	0	0.5
	O	0	1	0	1	-0.5	0.5
	H	0	0	1	-0.5	1	-0.5

Figure 2: (a) Formula matrix, $\mathbf{A}$, for the partial combustion of methane to produce synthesis gas, CO and H_2, together with CO_2 and H_2O. (b) $\mathbf{A}^*$, the RREF (Row-Reduced Echelon Form) of $\mathbf{A}$, with the resultant initial unit matrix highlighted. The final three columns are the stoichiometric vectors, $\boldsymbol{\nu}_j$, for the $R = 3$ stoichiometric equations.

number of 1s in the unit matrix, three in this case. Each of the last three columns is a set of coefficient vectors (for the non-component species heading that column) corresponding to the reaction forming one mole of the non-component species from the prior component species indicated above the unit matrix. Thus, the chemical equation for the species H_2O is

$$1 \times H_2O = 0.5 \times CH_4 + 1 \times O_2 - 0.5 \times CO_2 \tag{5}$$

Multiplying by 2 and re-arranging, we obtain

$$CH_4 + 2O_2 = 2H_2O + CO_2 \tag{6}$$

The two remaining column vectors produce the equations

$$2CO_2 = 2CO + O_2 \tag{7}$$

$$CH_4 + O_2 = 2H_2 + CO_2 \tag{8}$$

The set of three chemical equations that we have obtained are not unique, and can be replaced by other sets which are linear combinations of the three equations we have found; however, the number of *three* independent stoichiometric equations for this system is unique. (As an exercise, the reader may re-run this example in the supplied program XSTOICH with different orderings of species and see what happens.)

Finally, a consequence of the operations used by RREF on $\mathbf{A}$ to obtain $\mathbf{A}^*$ is that the $M \times N$ formula matrix $\mathbf{A}$ and the $N \times R$ stoichiometric matrix $\boldsymbol{\nu}$ derived from it by the RREF procedure satisfy

$$\mathbf{A}\nu = \mathbf{0} \tag{9}$$

and the ranks of the matrices satisfy

$$\mathrm{rank}(\boldsymbol{\nu}) = N - \mathrm{rank}(\mathbf{A}) \tag{10}$$

If we let the species formulae stand for their formula vectors in Eq. (9), the equation can be expressed in the form:

$$\boldsymbol{A\nu} = \begin{pmatrix} \mathrm{CH_4} & \mathrm{O_2} & \mathrm{CO_2} & \mathrm{H_2O} & \mathrm{CO} & \mathrm{H_2} \end{pmatrix} \begin{pmatrix} 0.5 & 0 & 0.5 \\ 1 & -0.5 & 0.5 \\ -0.5 & 1 & -0.5 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \end{pmatrix} \tag{11}$$

where the matrix of numbers is the stoichiometric matrix, constructed from $\mathbf{A}^*$ by appending the negative of a unit matrix below the right–most part of $\mathbf{A}^*$. The notation in Eq. (11) follows the usual matrix multiplication rules, where on the left side, the row of species names is a $1 \times N$ ($N = 6$ in this case) row vector is multiplied into the columns of the $N \times R$ ($R = 3$ in this case) stoichiometric matrix, yielding a $1 \times R$ row vector of linear combinations of

species names, with each linear combination set equal to the corresponding zero in the row vector on the right side.

Stoichiometric Restrictions: Explicit and Implicit

A complication arises when constraints are imposed on the reactions undergone by a chemical system over and above the conservation of the elements; these typically arise either from experimental observations or are imposed by a kinetic model. When these constraints are equivalent to specifications of linear combinations of species mole numbers, we call these constraints "stoichiometric restrictions".

Stoichiometric restrictions may arise either explicitly or implicitly. In the former case, one or more additional independent conservation equations on the species mole numbers are imposed, and the goal is to derive a modified system formula matrix $\mathbf{A}'$ that takes the restriction(s) into account. A stoichiometric matrix is then derived by the UMM in the usual way from $\mathbf{A}'$.

A general result from linear algebra[20] states that for an arbitrary matrix pair $(\mathbf{A}, \boldsymbol{\nu}')$ satisfying Eq. (9), their ranks satisfy

$$\text{rank}(\boldsymbol{\nu}') \leq N - \text{rank}(\mathbf{A}) \tag{12}$$

where N is the number of columns of $\mathbf{A}$. rank($\boldsymbol{\nu}'$) is called the *number of stoichiometric degrees of freedom*, F_s, which is the number of values of appropriate species mole numbers (or independent conditions to obtain them) that must be specified in order to determine the values of the remaining mole numbers (see also Smith and Missen,[6] Section 2.4.3). A matrix pair ($\mathbf{A}$, $\boldsymbol{\nu}'$) satisfying Eq. (12) as an equality is said to be *stoichiometrically compatible*. As noted, the RREF procedure in the implementation of the UMM always produces such a matrix pair (see Eq. (10)), in which case rank($\boldsymbol{\nu}'$) is of maximal rank R for the given $\mathbf{A}$

matrix, where

$$R = N - \text{rank}(\mathbf{A}) \tag{13}$$

.

In the case of stoichiometric restrictions, the left side of Eq. (12) is strictly less than the right side and the difference is defined to be the number of stoichiometric restrictions, r, given by

$$r = N - \text{rank}(\mathbf{A}) - \text{rank}(\boldsymbol{\nu}') \tag{14}$$

Explicit restriction example

An example of an explicit restriction[10] occurs for the reaction with potassium permanganate used in the analytical determination of hydrogen peroxide. Without restrictions, application of the UMM for this system with $N = 7$ shows that rank($\mathbf{A}$)=5, indicating that every possible reaction is described by a linear combination of the two ($F_s = N - \text{rank}(\mathbf{A}) = 7 - 5 = 2$) stoichiometric equations

$$6\text{H}_2\text{SO}_4 + 4\text{KMnO}_4 = 5\text{O}_2 + 6\text{H}_2\text{O} + 4\text{MnSO}_4 + 2\text{K}_2\text{SO}_4 \tag{15}$$

$$\text{O}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{O}_2 \tag{16}$$

which allow for KMnO_4 and H_2O_2 to react in any ratio.

However, it is known experimentally that peroxide and permanganate always react in the fixed ratio of 5/2.[24] This can be expressed as the following explicit restriction on their mole number changes, Δn_i:

$$2\Delta n(\text{H}_2\text{O}_2) = 5\Delta n(\text{KMnO}_4) \tag{17}$$

This can be expressed by inserting an additional row into the system formula matrix (see Fig. 3(a)), which represents the revised conservation equations in a matrix $\mathbf{A}'$ with rank equal to 6. The UMM then gives the single (from $F_s = N - \text{rank}(\mathbf{A}') = 7 - 6$) stoichiometric

equation

$$2\mathrm{KMnO_4} + 5\mathrm{H_2O_2} + 3\mathrm{H_2SO_4} = \mathrm{K_2SO_4} + 2\mathrm{MnSO_4} + 8\mathrm{H_2O} + 5\mathrm{O_2} \tag{18}$$

as indicated in Fig. 3(b), corresponding to the indicated stoichiometric matrix (a vector in this case), $\boldsymbol{\nu}'$ of rank 1.

This system thus exhibits one stoichiometric restriction, from Eq. (14):

$$r = N - \mathrm{rank}(\mathbf{A}) - \mathrm{rank}(\boldsymbol{\nu}') = 7 - 5 - 1 \tag{19}$$

(a)

A′ =		O_2	H_2O	H_2SO_4	$KMnO_4$	H_2O_2	K_2SO_4	$MnSO_4$
	O	2	1	4	4	2	4	4
	H	0	2	2	0	2	0	0
	S	0	0	1	0	0	1	1
	K	0	0	0	1	0	2	0
	Mn	0	0	0	1	0	0	1
	$H_2O_2/KMnO_4$	0	0	0	5	-2	0	0

(b)

A′* =	O_2	H_2O	H_2SO_4	$KMnO_4$	H_2O_2	K_2SO_4	$MnSO_4$
	1	0	0	0	0	0	-2.5
	0	1	0	0	0	0	-4
	0	0	1	0	0	0	1.5
	0	0	0	1	0	0	1
	0	0	0	0	1	0	2.5
	0	0	0	0	0	1	-0.5

Figure 3: (a) Modified formula matrix $\mathbf{A}'$ for the reaction between H2O2 and $KMnO_4$, with the final added constraint row representing the 5/2 relation between the molar amounts of H_2O_2 and $KMnO_4$. (b) The RREF reduction of $\mathbf{A}'$ to its RREF $\mathbf{A}'*$, with the highlighted leading unit matrix followed by the single stoichiometric vector, ν', in the final column.

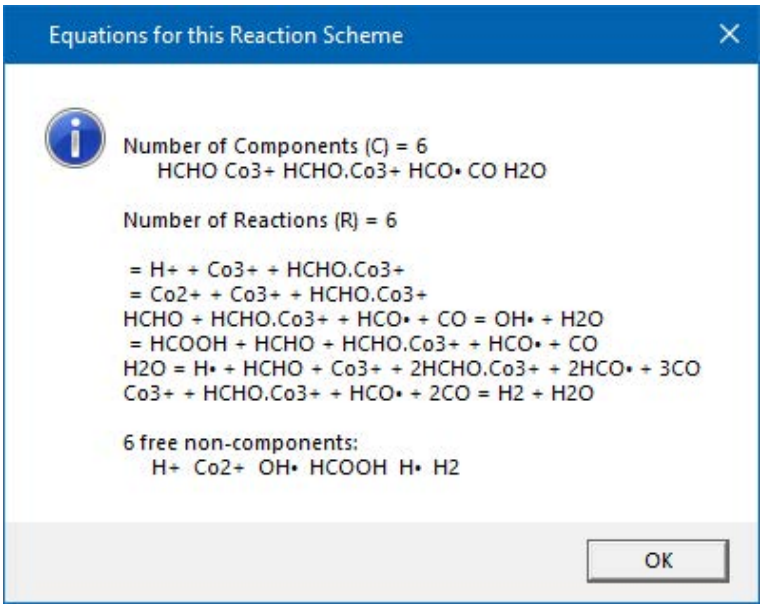
Implicit restriction example

We have seen that in the absence of restrictions, Eq. (10) holds for the ranks of the formula matrix and its stoichiometric matrix of maximum rank. However, a stoichiometric matrix $\boldsymbol{\nu}'$ may be specified, for example corresponding to a reaction mechanism. Our goal is to examine $\boldsymbol{\nu}'$ to discover whether or not it implies (one or more) stoichiometric restrictions, and if so, to determine a modified formula matrix $\mathbf{A}'$ that incorporates the restriction(s).

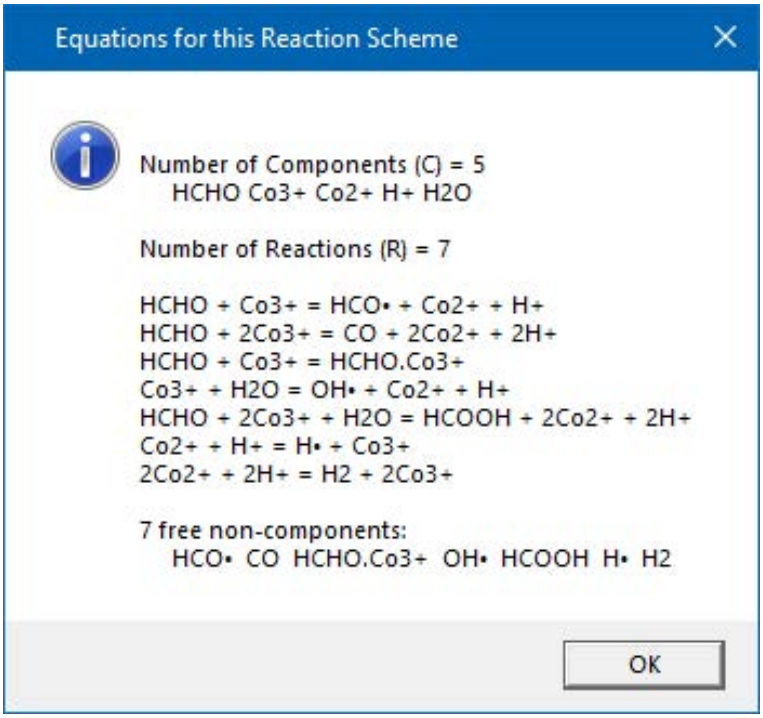
As an example, we examine a proposed reaction mechanism[25] for the aqueous–phase oxidation of formaldehyde (HCHO) catalysed by cobaltic ion. The 12×8 stoichiometric reaction matrix, $\boldsymbol{\nu}'$, describing this mechanism is given in the accompanying Supplementary Information Excel worksheet. XSTOICH yields the result in Fig. 4(a), demonstrating that $\mathrm{rank}(\boldsymbol{\nu}') = 6$ and $\mathrm{rank}(\mathbf{A}') = 6$. (Note: in XSTOICH, (i) the primed symbol is used for the numbers of mass-balance components and stoichiometric equations resulting from restrictions; (ii) the missing left entries for the first, second and fourth stoichiometric equations represent arbitrary constants, depending on the initial concentrations of the species on the right sides.) However, comparing the situation when the original 12×5 formula matrix, $\mathbf{A}$, is run in XSTOICH, we obtain $\mathrm{rank}(\mathbf{A}) = 5$, and $\mathrm{rank}(\boldsymbol{\nu}) = 7$, as in Fig. 4(b). Thus, the stoichiometric matrix $\boldsymbol{\nu}'$ indicates the presence of one stoichiometric restriction, since from Eq. (14):

$$r = N - \mathrm{rank}(\mathbf{A}) - \mathrm{rank}(\boldsymbol{\nu}') = 12 - 5 - 6 = 1 \tag{20}$$

This example shows that the reaction mechanism restricts the possible changes in the system composition to those described by the conservation matrix $\mathbf{A}'$. It is important to verify that when such a restriction is discovered, it be verified by experiment.



(a)



(b)

Figure 4: (a) XSTOICH output from specifying the stoichiometric reaction matrix of the aqueous-phase oxidation of formaldehyde (HCHO) catalysed by cobaltic ion. (b) XSTOICH output from specifying the formula matrix of the aqueous-phase oxidation of formaldehyde (HCHO) catalysed by cobaltic ion.

Conclusions

Chemical Reaction Stoichiometry (CRS) connects reaction kinetics and chemical equilibrium; this connection provides a link that we recommend be exploited in the teaching of both topics. A maximal set of independent stoichiometric equations may be determined from the system formula matrix through its algebraic manipulation, for which a programmed matrix reduction method must be used to treat the general multi–reaction case. When a stoichiometric matrix is specified, the matrix method can determine if it implies any "hidden" mass conservation equations. Such additional conservation equations must be consistent with experimental observations.

Supplementary Material

A Microsoft Excel macro–based program, XSTOICH.xlsm for implementing the Universal Matrix Method of chemical stoichiometry, is supplied. The user must provide a transposed formula matrix, consisting of N rows of species with M columns representing the contributing elements (which may be chemical elements, reaction equations, or lists of other conserved entities). Numerous example matrices are given and solved in the Excel worksheet.

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