Chemical Reaction Stoichiometry (CRS): A Tutorial[*]

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1 Introduction

Chemical reaction stoichiometry (CRS) is a branch of chemical stoichiometry dealing with the constraints, in the form of chemical equations, placed on changes in the composition of a closed reacting system by the requirement for conservation of the amount of each atomic species and of the total charge. This simple conservation concept has far-reaching consequences for all of chemistry and chemical engineering, including reaction kinetics and reactor design, reaction equilibrium, and reaction "book-keeping" in general. If chemical equations are to be used to express this concept, it is important to have a universal, systematic method for generating a proper set for *any* system under consideration. However, many methods currently in use, particularly in introductory teaching, do not properly or fully exploit the concept, and may give incomplete or misleading results; their scope is very limited, rendering them obsolete for general use.

To understand the role played by CRS, we believe that it is desirable to study it in its own right, "uncontaminated" by implications stemming from such things as reaction networks, reaction mechanisms, and equilibrium. Conversely, CRS does not contribute to intrinsic predictive information for kinetics or equilibrium, but only provides constraints on any predictions.

The universal, systematic method we describe in this paper and implement on the web site is not new, and has been described extensively elsewhere (Smith and Missen, 1979; 1982, 1991). As an aid to the efficiency of learning about CRS, it builds on a student's existing knowledge of very basic material (in addition to the concept of atomic conservation): the representation of a chemical species by a molecular formula, and the solution of sets of linear algebraic equations. Since it uses elementary matrix operations for the latter, we call it the *matrix reduction method* (MRM); we remark that it employs only such basic matrix manipulations as those involved in the solution of sets of linear equations, and essentially uses a matrix only as a convenient tabular way of organizing the calculations. MRM can be implemented by hand-calculation, and, for convenience in complex cases, can be programmed for implementation by computer. A new Java applet for the latter is introduced in this tutorial, and is accessible for use interactively on the web site located at http://www.chemical-stoichiometry.net

In spite of a long history of the use of an algebraic method for the simplest situation in CRS, that of balancing a single specified reaction (method of Bottomley, 1878), there appears to be considerable resistance on the part of instructors to the use of such a method in CRS. The reasons given are: (1) that it emphasizes mathematics and not chemistry, (2) that, as a result, students don't learn about chemistry in the form of "oxidation numbers" and "half-reactions", and (3) that, if implemented by computer, it uses a "sledgehammer" to "crack the egg" of (in many cases) a relatively simple problem. In response, it can be argued that (1) students learn precisely what part of chemistry is involved in CRS (see also Olson, 1997), (2) other parts are extraneous to, and unnecessary for, CRS, and (3) use of computers and computer software is simply a matter of convenience to eliminate tedium for large-scale systems, but is not a necessity.

To overcome our suspicion of resistance on the part of many instructors, we are taking advantage of two advances in technology which may act as a catalyst to achieve adoption of MRM: ease of accessibility afforded by a web site on a global basis, and the interactive capability of a Java applet for implementation of the method.

The purpose of this tutorial is to provide a treatment of CRS as the basis for MRM. The tutorial first describes the nature and importance of CRS, and provides some historical background. It then shows the genesis of chemical equations from algebraic atom-balance equations. This is followed by a simple algorithm for the procedure used in MRM. Implementation of MRM by various means, including use of the Java applet, is illustrated with examples. The new Java applet itself, JSTOICH, is also described, with sections on "Getting Started", "Capabilities", and "Help." JSTOICH is intended to be both a teaching/learning tool and a user tool, and can be used interactively on the web site. Exercises are provided for the reader to gain experience in using MRM, particularly by implementation with JSTOICH. They also explore further aspects of CRS, including some examples of apparent confusion in the literature.

2 What is Chemical Reaction Stoichiometry (CRS)?

2.1 A definition

We define *chemical stoichiometry* as the constraints placed on the composition of a closed system by the requirement for conservation of the amount of each atomic species and of electronic charge. These constraints take the form of linear conservation equations, which may be expressed in the form of either linear algebraic atom- and charge-balance equations, or chemical equations. *Chemical reaction stoichiometry* (CRS) is concerned with the latter. The Java applet on the web site constructs chemical equations using as input only the molecular formulas of the species stated as being present in the system.

The term "chemical reaction" includes not only a chemical transformation, but also a phase change such as the vaporization of water. We are thus concerned with the stoichiometry of both single- and multiphase systems.

2.2 Why is CRS important?

Chemical reaction stoichiometry is an essential consideration in any situation involving change in chemical composition. Such situations include (1) reaction kinetics, (2) reaction equilibrium, and (3) reaction "book-keeping", as follows:

1. in reaction equilibrium:
    - CRS provides constraints on the optimization (minimization) of the appropriate thermodynamic objective function (*e.g.*, the Gibbs function, G); CRS expresses these constraints in the form of chemical equations, which may be used in the calculation of the equilibrium composition of the system (section 7.1.1)
    - CRS provides a means of obtaining species-related thermochemical data from a given set of reaction-related data (section 7.1.2)
2. in reaction kinetics:
    - CRS establishes the maximum or proper number of independent steps in a *reaction network* (or *kinetics scheme*) for a given system, *i.e.*, the maximum or proper number of independent rate laws (section 7.2.1)
    - CRS-like methods may be used to calculate, from a postulated reaction mechanism, the required number of independent steps in a corresponding reaction network (section 7.2.2)
    - each step in a reaction network or a reaction mechanism must be balanced.

3. in reaction "book-keeping":
    - CRS provides the framework to calculate the composition of a system subsequent to a given initial state; it provides both the minimum number of species amounts that must be specified to determine the system composition, and specific equations for its calculation
    - in general, for chemical process material balances, it provides the proper number of independent continuity or material balance equations, and a means to obtain specific sets of such equations

2.3 The central problem of CRS

The central problem of chemical reaction stoichiometry may be stated as follows:

Given a list of chemical species and their molecular formulas, obtain *a proper set* of independent chemical equations to represent the conservation of atomic species in terms of the molecular formulas of the system species. A *proper set* has the property that any other chemical equation can be obtained from members of this set by adding or subtracting multiples of them.

- The list of species, of number N, must contain all those of interest for the problem at hand.
- A species is distinguished by its molecular formula, its isomeric form, and the phase in which it is present. For example, $H_2O(\ell)$ and $H_2O(g)$ are distinct species, as are ethyl alcohol and dimethyl ether (each of which has the same molecular formula C_2H_6O).
- For the molecular formula of ionic species, charge is treated as an atomic species (denoted by p), with appropriate sign (+ or -).
- A set of chemical equations is *independent* if any one cannot be obtained by adding or subtracting multiples (*i.e.*, linear combinations) of the others.
- The number of equations in a proper set is the maximum number of independent chemical equations, R.

2.4 "Balancing chemical reactions"

Investigators and instructors often assume that a chemical system can be represented by a *single* reaction (reactant(s) → product(s)). They then proceed to "balance" this skeletal equation. Two aspects of this are (1) the procedure for carrying out the balancing, and (2) whether the reaction written can be "uniquely balanced". If it *can* be uniquely balanced, the original assumption is correct, and there is one corresponding chemical equation ($R = 1$). If it *cannot* be uniquely balanced, and if this is realized, the investigator may feel that there is no systematic way of proceeding: if $R > 1$, "no unique solution exists or the equation (*sic*) cannot be balanced" (Herndon, 1997). Such difficulties are commonly due to the methods used for balancing, which are inherently incapable of discovering the value of R, and of dealing with $R > 1$. The method described in this tutorial is free of any such difficulties.

2.5 Preliminary examples of sets of chemical equations

Example 1:
Consider the complete combustion of CH_4 (methane) to CO_2 and H_2O. This system is represented by the ordered list of species and elements:

$$\{(\mathrm{CH_4}, \mathrm{O_2}, \mathrm{CO_2}, \mathrm{H_2O}), (\mathrm{C}, \mathrm{O}, \mathrm{H})\} \tag{1}$$

A proper set of chemical equations consists of the single equation ($R = 1$)

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

Any other proper set consists of a multiple of this equation, and is not an independent set.

- Note the use of = to represent atomic species conservation in a chemical *equation*.
- For this example, as *is the case whenever* $R = 1$, = may be replaced by → to represent the corresponding overall reaction, or a kinetics scheme for the system.
- The above equation does not necessarily represent a reaction mechanism for the system.
- = may be replaced by $\rightleftharpoons$ to imply reaction equilibrium.

Example 2:
As a different (but related) example, consider the *partial* combustion of CH_4 to produce synthesis gas (CO and H_2) (H_2O and CO_2 are also formed). The system is represented as follows:

$$\{(CH_4, O_2, CO_2, H_2O, CO, H_2), (C, O, H)\} \tag{3}$$

A proper set of $R = 3$ chemical equations is:

$$\begin{aligned} CH_4 + 2O_2 &= CO_2 + 2H_2O && (4)\\ 2CO_2 &= O_2 + 2CO && (5)\\ CH_4 + O_2 &= CO_2 + 2H_2 && (6) \end{aligned}$$

The question we raise at this point (and answer below) is: How do we systematically determine such a set?

- These equations do not necessarily represent a system in reaction equilibrium ($\rightleftharpoons$).
- These equations do not necessarily represent steps in a reaction mechanism or in a reaction network ($\rightarrow$).
- In the case $R > 1$, if the $=$ sign is replaced by $\rightarrow$, the resulting set *may* represent a particular reaction network, in the sense that R is the number of independent rate laws required.
- These equations are independent, since the species H_2O, CO, and H_2 only appear in separate equations. The latter feature defines a *canonical* proper set. Each equation in a canonical set contains at most $M+1$ species (where M is the number of elements); a canonical set is purely a matter of convenience, with no essential chemical significance.
- The essential feature of a proper set of chemical equations for this system is that it consists of $R = 3$ independent equations.
- The proper set of equations (4), (5), (6) is not unique. Any one equation of the set may be replaced by an equation obtained by taking a nonzero multiple of it and adding a linear combination of the remaining equations, to form a different proper set. For example, equation (6) could be replaced by

$$CO_2 + H_2 = H_2O + CO \tag{7}$$

obtained from $\frac{1}{2}$[(4) + (5) - (6)]. The resulting set of equations {(4), (5), (7)} is also a proper set, but is not a canonical set. Canonical sets are not unique; for example, (5), (7), and the equation obtained from (5) + (6) also form a canonical set.

- Given an initial system composition, any subsequent compositional state must be in accordance with these equations.

2.6 Mathematical equivalent of the central problem of CRS

The *mathematical equivalent* of the central problem of CRS is:

For a specified formula matrix, $\mathbf{A} = (a_{ki})$, where a_{ki} is the subscript to element k in species i, find a set of stoichiometric coefficients, $\{\nu_{ij}\}$, where ν_{ij} is the coefficient of species i in chemical equation j. These coefficients form a set of stoichiometric vectors, $\{\boldsymbol{\nu}_j,\ j = 1, ..., R\}$, where R is the maximum number of linearly independent solutions of the linear equations (Smith and Missen, 1982, 1991, Chapter 2):

$$\mathbf{A}\boldsymbol{\nu} = 0 \tag{8}$$

For illustration, for Examples 1 and 2 above, the formula matrices are, respectively:

$$\mathbf{A}_1 = \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 2 & 2 & 1 \\ 4 & 0 & 0 & 2 \end{pmatrix} \tag{9}$$

$$\mathbf{A}_2 = \begin{pmatrix} 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 2 & 2 & 1 & 1 & 0 \\ 4 & 0 & 0 & 2 & 0 & 2 \end{pmatrix} \tag{10}$$

Each $\mathbf{A}$ is an $M \times N$ matrix in which each column represents a species (N columns) in the order originally listed, and each row represents an element (M rows) in the order listed. Each entry is the subscript to an element in the molecular formula of a species, and each column (vector) is a formula vector for a species. For example,

$$\begin{pmatrix} 1 \\ 0 \\ 4 \end{pmatrix}$$

is the formula vector for CH_4 in terms of the elements C, O, and H.

In section 3, we show how chemical equations arise from the atom- and charge-balance equations.

2.7 Historical Background

Historically, it is perhaps natural that writing chemical equations in a stoichiometric sense arose from observed chemical reactions. This is particularly self-evident when the reacting system can be accurately represented by 1 reaction (*e.g.*, $2SO_2 + O_2 \rightarrow 2\ SO_3$); CRS is then expressed by 1 equation ($R = 1$; $2SO_2 + O_2 = 2\ SO_3$). The case of $R = 1$ is an important and relatively common one in inorganic industrial processes, analytical chemistry and electrochemistry. Probably for this reason, together with its simplicity, there has been an over-emphasis on this case in chemical pedagogy. In this pedagogy, CRS is reduced to the chemical "game" of how to "balance" a *specified* chemical reaction in skeletal form. The existence of many (and continuing) papers in the literature attests to the "popularity" of this game.

More generally, a reacting system may be specified by a *set* of skeletal chemical reactions, or by a *set* of chemical species (without reactions), either set including information about the molecular formulas of the species involved. In either situation, two questions arise in CRS: (1) what is the maximum number (R) of independent chemical equations? and (2) how can a set of R independent equations be obtained? The *a priori* specification of $R = 1$ for a system may be an *underspecification*, a situation of which there are many examples in the literature, most of them not realized, but sometimes described as "reactions that can be balanced in an infinite number of ways".

For the simple case of $R = 1$, a sufficient method to balance a specified chemical reaction was given 120 years ago by Bottomley(1878). This is sometimes referred to as the method of undetermined coefficients or the "algebraic" method. It is equivalent, for $R = 1$, to the method used here (MRM) in the Java applet, and can be extended to cases of $R > 1$ to make it completely equivalent to MRM (Missen and Smith, 1998). Other methods used for a specified single reaction are: the method of inspection, the oxidation-number method (for inorganic and organic oxidation-reduction reactions), and the method of half-reactions (naturally tied to reactions in chemical cells). None of these methods addresses the question of the value of R, and the last two are inherently incapable of dealing with $R > 1$. Use of the method of inspection is "fair game" wherever it can be simply applied, but we consider the other two to be obsolete because of their limitations, which include their apparent inability to be programmed for computer implementation, and because the additional artifices of oxidation numbers and half-reactions are unnecessary (in spite of their value outside CRS).

Other methods have been proposed for $R > 1$. Wink(1994) has presented a computer spreadsheet procedure that has some aspects in common with MRM, but which is not a universal method. Weltin(1994) has presented a universal, systematic method that implements a Gram-Schmidt orthogonalization procedure (Noble and Daniel, 1977)(which is well beyond the understanding of most beginning students).

A number of authors have proposed computer programs for (1) $R = 1$, *i.e.*, for balancing a specified reaction in skeletal form, apparently all by means of the Bottomley method, and (2) $R \geq 1$, *i.e.*, for both determining R and generating a proper set of R equations. For $R = 1$, these include programs by Brown *et al.*(1972), Rosen(1977), Ramette(1995), and Campanario(1995). For $R \geq 1$, they include programs by Smith and Missen(1982, 1991), and by Betz *et al.*(1997), all of which utilize MRM. In addition, Smith and Missen(1997) have shown how computer algebra software, such as Mathematica[1] and Maple[2], can be used to implement MRM. The Java applet made available on the web site described in this paper is a universally available interactive program implementing MRM for $R \geq 1$.

3 From Atom-balance Equations to Chemical Equations

In a closed chemical system, the conservation of atomic species can be expressed as a set of atom-balance equations, one for each element:

$$\sum_{i=1}^{N} a_{ki} n_i = b_k; \quad k = 1, 2, \ldots, M \tag{11}$$

where n_i is the number of moles of species i, and b_k is the number of moles of element k. In vector-matrix notation, equation (11) may be written as

$$\mathbf{An} = \mathbf{b} \tag{12}$$

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[1] Mathematica is a registered trade mark of Wolfram Research Inc.

[2] Maple is a registered trade mark of Waterloo Maple Inc.

where $\mathbf{n}$ is the vector of species mole numbers and $\mathbf{b}$ is the vector of element mole numbers.

Equation (11) may be written alternatively so as to express the change from one compositional state to another. Thus, in a closed system, equation (11) becomes

$$\sum_{i=1}^{N} a_{ki}\delta n_i = 0; \quad k = 1, 2, \ldots, M \tag{13}$$

where δn_i is the change in mole number of species i between two compositional states. Equation (13) may be written as

$$\mathbf{A}\boldsymbol{\delta}\mathbf{n} = 0 \tag{14}$$

where $\boldsymbol{\delta}\mathbf{n}$ is the vector of species mole number changes. The maximum number of linearly independent atom-balance equations, which is the same as the maximum number of independent rows (or columns) in the matrix $\mathbf{A}$, is called *rank*($\mathbf{A}$).

Example 3:
We use the system of Example 1 to illustrate the genesis of a chemical equation from equation (11). Numbering the species in the order listed in Example 1 (CH_4=1, O_2=2, CO_2=3, H_2O=4), we write these equations for elements C, O, and H in turn as:

$$\begin{aligned} 1\delta n_1 + 0\delta n_2 + 1\delta n_3 + 0\delta n_4 &= 0 \qquad (15)\\ 0\delta n_1 + 2\delta n_2 + 2\delta n_3 + 1\delta n_4 &= 0 \qquad (16)\\ 4\delta n_1 + 0\delta n_2 + 0\delta n_3 + 2\delta n_4 &= 0 \qquad (17) \end{aligned}$$

The formula matrix $\mathbf{A}$ for this system is $\mathbf{A}_1$ in equation (9), and is also the coefficient matrix on the left side in equations (15) to (17). Equations (15)-(17) form a set of 3 equations in the 4 variables $\{\delta n_1, \delta n_2, \delta n_3, \delta n_4\}$; these 3 equations can be solved for any 3 variables in terms of the 4th variable as a free parameter.

Suppose we choose δn_4, corresponding to H_2O, as the free parameter. With this choice, we perform the usual manipulations to solve a set of linear equations (in this case, (15)-(17)). These manipulations are equivalent to elementary row operations on $\mathbf{A}$, as follows:

1. multiplying a row by a nonzero constant

2. adding a multiple of one row to another row
3. interchanging two rows

Carrying out these manipulations, we proceed as follows:

1. Add -4 times the first row to the third, to give

$$\begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 2 & 2 & 1 \\ 0 & 0 & -4 & 2 \end{pmatrix}$$

2. Multiply the second row by 1/2 to give

$$\begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 1 & 1/2 \\ 0 & 0 & -4 & 2 \end{pmatrix}$$

3. Multiply the third row by -1/4 to give

$$\begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 1 & 1/2 \\ 0 & 0 & 1 & -1/2 \end{pmatrix}$$

4. Add -1 times the third row to the first and second rows to give the final matrix $\mathbf{A}^*$:

$$\mathbf{A}^* = \begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & -1/2 \end{pmatrix} \tag{18}$$

This is called the unit matrix form (*reduced row-echelon form*) of **A**, and the method above is essentially Gauss-Jordan reduction (Noble and Daniel, 1977).

The matrix $\mathbf{A}^*$ is equivalent to the set of equations

$$1\delta n_1 + 0\delta n_2 + 0\delta n_3 + \frac{1}{2}\delta n_4 = 0 \tag{19}$$

$$0\delta n_1 + 1\delta n_2 + 0\delta n_3 + 1\delta n_4 = 0 \tag{20}$$

$$0\delta n_1 + 0\delta n_2 + 1\delta n_3 - \frac{1}{2}\delta n_4 = 0 \tag{21}$$

or

$$\begin{pmatrix} \delta n_1 \\ \delta n_2 \\ \delta n_3 \\ \delta n_4 \end{pmatrix} \equiv \boldsymbol{\delta}\mathbf{n} = \begin{pmatrix} -1/2 \\ -1 \\ 1/2 \\ 1 \end{pmatrix} \delta n_4 \tag{22}$$

(Note that, in order to display a complete vector of unknowns on the left side of (22) containing all 4 unknowns, the trivial equation $\delta n_4 = \delta n_4$ has been added to equations (19) to (21).) Either the set of equations (19) to (21) or equation (22) represents the general solution of equations (15) to (17). To obtain a *chemical* equation, we replace the columns of the formula matrix **A** in equation (14) by the species names, and formally multiply the row vector of species names into the column vector of equation (22) to obtain

$$(\mathrm{CH_4}, \mathrm{O_2}, \mathrm{CO_2}, \mathrm{H_2O}) \begin{pmatrix} -1/2 \\ -1 \\ 1/2 \\ 1 \end{pmatrix} = 0 \tag{23}$$

or

$$-\frac{1}{2}\mathrm{CH_4} - 1\mathrm{O_2} + \frac{1}{2}\mathrm{CO_2} + 1\mathrm{H_2O} = 0 \tag{24}$$

or, as is usually written, on elimination of minus signs and fractions,

$$\mathrm{CH_4} + 2\mathrm{O_2} = \mathrm{CO_2} + 2\mathrm{H_2O} \tag{25}$$

which is the same as equation (2) in Example 1.

Example 3 illustrates a situation for which $R = 1$. In the next example, we illustrate the important case of $R > 1$.

Example 4:
We use the system of Example 2, for which the formula matrix is $\mathbf{A}_2$ in equation (10). Performing the same manipulations on $\mathbf{A}_2$ as in Example 3, we obtain the unit matrix form

$$\mathbf{A}_2^* = \begin{pmatrix} 1 & 0 & 0 & 1/2 & 0 & 1/2 \\ 0 & 1 & 0 & 1 & -1/2 & 1/2 \\ 0 & 0 & 1 & -1/2 & 1 & -1/2 \end{pmatrix} \tag{26}$$

Similarly, as in Example 3, the matrix $\mathbf{A}_2^*$ is equivalent to the set of equations

$$1\delta n_1 + 0\delta n_2 + 0\delta n_3 + \frac{1}{2}\delta n_4 + 0\delta n_5 + \frac{1}{2}\delta n_6 = 0 \tag{27}$$

$$0\delta n_1 + 1\delta n_2 + 0\delta n_3 + 1\delta n_4 - \frac{1}{2}\delta n_5 + \frac{1}{2}\delta n_6 = 0 \tag{28}$$

$$0\delta n_1 + 0\delta n_2 + 1\delta n_3 - \frac{1}{2}\delta n_4 + 1\delta n_5 - \frac{1}{2}\delta n_6 = 0 \tag{29}$$

or

$$\boldsymbol{\delta}\mathbf{n} = \begin{pmatrix} \delta n_1 \\ \delta n_2 \\ \delta n_3 \\ \delta n_4 \\ \delta n_5 \\ \delta n_6 \end{pmatrix} = \begin{pmatrix} -1/2 \\ -1 \\ 1/2 \\ 1 \\ 0 \\ 0 \end{pmatrix} \delta n_4 + \begin{pmatrix} 0 \\ 1/2 \\ -1 \\ 0 \\ 1 \\ 0 \end{pmatrix} \delta n_5 + \begin{pmatrix} -1/2 \\ -1/2 \\ 1/2 \\ 0 \\ 0 \\ 1 \end{pmatrix} \delta n_6 \tag{30}$$

Equation (30) is the general solution of equations (27)-(29), and is the counterpart of equation (22) for Example 3. $\{\delta n_4, \delta n_5, \delta n_6\}$ are free parameters, and each of the 3 vectors indicated is a solution of equations (27)-(29). Furthermore, these solutions are linearly independent, because of the nature of the final 3 entries in each vector. Each vector is used to construct a chemical equation, as in Example 3:

$$-\frac{1}{2}\mathrm{CH_4} - 1\mathrm{O_2} + \frac{1}{2}\mathrm{CO_2} + 1\mathrm{H_2O} + 0\mathrm{CO} + 0\mathrm{H_2} = 0 \tag{31}$$

$$0\mathrm{CH_4} + \frac{1}{2}\mathrm{O_2} - 1\mathrm{CO_2} + 0\mathrm{H_2O} + 1\mathrm{CO} + 0\mathrm{H_2} = 0 \tag{32}$$

$$-\frac{1}{2}\mathrm{CH_4} + -\frac{1}{2}\mathrm{O_2} + \frac{1}{2}\mathrm{CO_2} + 0\mathrm{H_2O} + 0\mathrm{CO} + 1\mathrm{H_2} = 0 \tag{33}$$

or, as is usually written,

$$\mathrm{CH_4} + 2\mathrm{O_2} = \mathrm{CO_2} + 2\mathrm{H_2O} \tag{34}$$

$$2\mathrm{CO_2} = \mathrm{O_2} + 2\mathrm{CO} \tag{35}$$

$$\mathrm{CH_4} + \mathrm{O_2} = \mathrm{CO_2} + 2\mathrm{H_2} \tag{36}$$

This set of 3 equations is the same set given in Example 2.

4 Universal, Systematic Method to Obtain Chemical Equations (MRM)

In Example 3, we note the existence of 1 free parameter among the 4 (=N) variables $\delta n_1, ..., \delta n_4$, arising from the difference between the number of variables and number of atom-balance equations relating them. This means that if we specify the value of 1 δn_i (or provide an additional independent equation relating the δn_i) from information outside stoichiometry, then we can determine the 3 remaining δn_i's from the atom-balance equations or from the chemical equations. The additional information may come from kinetics for a system not at equilibrium, or from thermodynamics for a system at equilibrium, or from chemical analysis.

In Example 4, the number of variables is 6, the number of equations is 3, and the number of free parameters is 6-3=3. In this case, if the values of any 3 of the variables are specified from information outside CRS (or if 3 additional independent equations are specified relating the variables), then we can use the equations of CRS to determine values of the 3 remaining variables. In each example, we also note that the number of free parameters is also equal to the proper number of chemical equations, R.

In general, the difference between the number of variables, N, and the number of independent equations relating them is called the *number of degrees of freedom*, F, of a problem; in CRS, this is the *number of stoichiometric degrees of freedom*, F_s. This is the number of additional items of information (additional independent equations outside stoichiometry, or values of some of the variables) that must be specified in order to fix the values of the entire set of variables. In this tutorial, we only consider the case $F_s = R$ (but see section 7.3). If $R = 1$, the number of stoichiometric degrees of freedom is $F_s = 1$.

The species, CH_4, O_2, CO_2, corresponding to δn_1, δn_2, δn_3 in equations (27)-(29), are called *component species*; these species correspond to the unit-vector columns of the reduced formula matrix $\mathbf{A}^*$ ($\mathbf{A}_2^*$ in this case). The remaining species, H_2O, CO, H_2, corresponding to δn_4, δn_5, δn_6, are called *noncomponent species*. Note that the choice of component and noncomponent species is arbitrary (to a certain extent). The number of component species is denoted by C, and is equal to the number of independent atom-balance equations. C is the rank of the matrix $\mathbf{A}$:

$$C = rank(\mathbf{A}) \tag{37}$$

Since $\mathbf{A}^*$ is obtained by performing elementary row operations on $\mathbf{A}$, $rank(\mathbf{A}^*) = rank(\mathbf{A})$. $C = rank(\mathbf{A}^*)$ is readily obtained by counting the number of 1's in the unit matrix portion of $\mathbf{A}^*$. Usually, $C = M$, but in general, $C \leq M$; the case $C < M$ occurs when the atom-balance equations are not linearly independent (see Example 6 below).

From the discussion above, it follows that

$$F_s = R = N - rank(\mathbf{A}) = N - C \tag{38}$$

We call the set of equations (34)-(36) a *canonical form* of the set of chemical equations for this system. In this form, each noncomponent species appears only once, and each equation can be regarded as representing the formation of 1 mole of a noncomponent species from the C component species. Note that this set can be formed directly from $\mathbf{A}_2^*$ in equation (26), without having to go through the formalism of equations (27)-(29), which are used here to justify the procedure and to illustrate the transition from atom-balance equations to chemical equations. In $\mathbf{A}_2^*$, the last 3 columns represent the noncomponent species, in the order listed originally. The entries in a given column are the coefficients of the component species, in the order listed, on the left side of a chemical equation in which 1 mole of the noncomponent species represented by the column appears on the right side.

We are now in a position to describe the matrix-reduction method (MRM) for generating chemical equations for a reacting system specified by a list of species. MRM is a *universal* and a *systematic* method: *universal* because it can be used for *any* chemical system ($R \geq 0$); and *systematic* because it can be described unambiguously in terms of a simple algorithm.

The procedure constructs a proper set of chemical equations that represents the chemical system. The system is defined by a specified list of chemical species, as represented by their molecular formulas. We emphasize that a proper set is *not* unique, but the number of equations in the set (R) *is* uniquely defined.

We summarize the procedure developed through examples in the previous section in terms of a hand-calculation implementation. The steps are as follows (Smith and Missen, 1979; 1982, 1991 Chapter 2):

1. Write the formula matrix $\mathbf{A}$ for the given system of N species and M elements, with each column identified at the top by the chemical species represented.

2. Form a unit matrix as large as possible in the upper-left portion of $\mathbf{A}$ by means of elementary row operations, and column interchange if necessary; if columns are interchanged, the designation of the species (at the top) must be interchanged also. The final result is a matrix $\mathbf{A}^*$, called the unit matrix form of $\mathbf{A}$.

3. At the end of these steps, the following are established:
    - the rank of the matrix $\mathbf{A}$, which is equal to C, the number of component species; this is the number of 1's on the principal diagonal of $\mathbf{A}^*$.
    - a set of component species is given by the C species above the columns of $\mathbf{A}^*$.
    - the maximum number of linearly independent chemical equations is given by $R = N - C$.
    - the coefficients of a proper set of chemical equations are obtained from the columns of the part of the matrix $\mathbf{A}^*$ to the right of the unit matrix; each column relates to the formation from the component species of one mole of the species whose designation heads that column, and the entries in the column refer to the stoichiometric coefficients of the component species in the order of the component species columns in the unit matrix.

This procedure can be implemented by hand-calculation (section 5.1) for most cases that a student or instructor will encounter. This includes virtually all cases of single-equation systems ($R = 1$), such as are provided by complicated redox reactions. Even for cases with $R > 1$, the procedure is still feasible for hand calculation.

For very complex systems involving many species and elements, the hand calculations involved become tedious, and it is then more convenient to use a computer implementation of the procedure. In section 5.2, we describe examples of the use of widely-available computer algebra software (Mathematica and Maple) for this task. The Java applet JSTOICH presented on the web site for the first time is also a computer implementation of MRM (section 6).

5 Implementations of MRM

5.1 Hand Calculation

Example 5:
This example illustrates the case of ionic species. Consider the system $\{(ClO_2^-, H_3O^+, Cl_2, H_2O, ClO_3^-, ClO_2), (Cl, O, H, p)\}$ (*cf.* Porter, 1985).

Proceeding as above, we obtain, with the columns numbered for the species in order,

1.

$$\mathbf{A} = \begin{array}{cccccc} (1) & (2) & (3) & (4) & (5) & (6) \\ \left(\begin{matrix} 1 \\ 2 \\ 0 \\ -1 \end{matrix}\right. & \begin{matrix} 0 \\ 1 \\ 3 \\ 1 \end{matrix} & \begin{matrix} 2 \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 1 \\ 2 \\ 0 \end{matrix} & \begin{matrix} 1 \\ 3 \\ 0 \\ -1 \end{matrix} & \left.\begin{matrix} 1 \\ 2 \\ 0 \\ 0 \end{matrix}\right) \end{array} \tag{39}$$

2.

$$\mathbf{A}^* = \begin{array}{cccccc} (1) & (2) & (3) & (4) & (5) & (6) \\ \left(\begin{matrix} 1 \\ 0 \\ 0 \\ 0 \end{matrix}\right. & \begin{matrix} 0 \\ 1 \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 1 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ 1 \end{matrix} & \begin{matrix} 10/6 \\ 2/3 \\ -1/3 \\ -1 \end{matrix} & \left.\begin{matrix} 4/3 \\ 4/3 \\ -1/6 \\ -2 \end{matrix}\right) \end{array} \tag{40}$$

3. rank($\mathbf{A}$) = rank($\mathbf{A}^*$)= $C = 4$
   component species: $ClO_2{}^-$, H_3O^+, Cl_2, H_2O
   noncomponent species: $ClO_3{}^-$, ClO_2

   $$R = N - C = 6 - 4 = 2$$

   the 2 equations in canonical form are:

   $$\frac{10}{6}Cl_2^- + \frac{2}{3}H_3O^+ - \frac{1}{3}Cl_2 - 1H_2O \;=\; 1ClO_3^- \tag{41}$$
   $$\frac{4}{3}ClO_2^- + \frac{4}{3}H_3O^+ - \frac{1}{6}Cl_2 - 2H_2O \;=\; 1ClO_2 \tag{42}$$

   or, in conventional chemical form,

   $$5ClO_3^- + 2H_3O^+ \;=\; Cl_2 + 3H_2O + 3ClO_3^- \tag{43}$$
   $$8ClO_2^- + 8H_3O^+ \;=\; Cl_2 + 12H_2O + 6ClO_2 \tag{44}$$

Example 6:
This example illustrates the case $C < M$ (the rank-deficient case). It also

illustrates the procedure in the case of an inconvenient choice of ordering of the species. It involves the complexation of Tl^+ by NO_2^- (Cobranchi and Eyring, 1991). Consider the system $\{(H^+, OH^-, H_2O, NO^+, NO_2^-, N_2O_3, HNO_2, Tl^+, TlNO_2), (H, O, N, Tl, p)\}$. Proceeding as above, we obtain

1.
$$\mathbf{A} = \begin{array}{c} \begin{array}{ccccccccc} (1) & (2) & (3) & (4) & (5) & (6) & (7) & (8) & (9) \end{array} \\ \left(\begin{array}{ccccccccc} 1 & 1 & 2 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 2 & 3 & 2 & 0 & 2 \\ 0 & 0 & 0 & 1 & 1 & 2 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 1 & -1 & 0 & 1 & -1 & 0 & 0 & 1 & 0 \end{array} \right) \end{array} \tag{45}$$

2.
$$\mathbf{A}^* = \begin{array}{c} \begin{array}{ccccccccc} (1) & (2) & (4) & (8) & (5) & (6) & (7) & (3) & (9) \end{array} \\ \left(\begin{array}{ccccccccc} 1 & 0 & 0 & 0 & -1 & -1 & 0 & 1 & -1 \\ 0 & 1 & 0 & 0 & 1 & 1 & 1 & 1 & 1 \\ 0 & 0 & 1 & 0 & 1 & 2 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right) \end{array} \tag{46}$$

3. $\text{rank}(\mathbf{A}) = \text{rank}(\mathbf{A}^*) = C = 4$
   component species: H^+, OH^-, NO^+, Tl^+
   noncomponent species: ${NO_2}^-$, N_2O_3, HNO_2, H_2O, $TlNO_2$

   $$R = N - C = 9 - 4 = 5$$

   the 5 equations in canonical form are:

   $$\begin{aligned} -1H^+ + 1OH^- + 1NO^+ + 0Tl^+ &= 1NO_2^- && (47) \\ -1H^+ + 1OH^- + 2NO^+ + 0Tl^+ &= 1N_2O_3 && (48) \\ 0H^+ + 1OH^- + 1NO^+ + 0Tl^+ &= 1HNO_2 && (49) \\ 1H^+ + 1OH^- + 0NO^+ + 0Tl^+ &= 1H_2O && (50) \\ -1H^+ + 1OH^- + 1NO^+ + 1Tl^+ &= 1TlNO_2 && (51) \end{aligned}$$

   or, in conventional canonical form,

   $$\begin{aligned} OH^- + NO^+ &= H^+ + NO_2^- && (52) \\ OH^- + 2NO^+ &= H^+ + N_2O_3 && (53) \end{aligned}$$

$$OH^- + NO^+ = HNO_2 \tag{54}$$
$$H^+ + OH^- = H_2O \tag{55}$$
$$OH^- + NO^+ + Tl^+ = H^+ + TlNO_2 \tag{56}$$

To obtain $\mathbf{A}^*$, we note that two column interchanges are made so that 1's may appear on the principal diagonal of the unit matrix: first, columns (3) and (4) are interchanged, and then columns(3) and (8). This is because of the particular ordering of species and elements chosen. For the order of elements chosen, the third species should contain N and the fourth species Tl. We note also that $\mathbf{A}$ (or $\mathbf{A}^*$) is not of full rank, as indicated by the row of zeros.

5.2 Computer Algebra Software

In this section, we illustrate the use of built-in commands in Mathematica and in Maple, examples of computer algebra software that can be used to implement CRS. We show only the commands and the resulting responses. A more detailed description is given by Smith and Missen (1997).

Example 7:
We use the system of Examples 2 and 4 to illustrate implementation by Mathematica in the following step-wise procedure:

1.
```
CH4 = {1,0,4}
O2 = {0,2,0}
CO2 = {1,2,0}
H2O = {0,1,2}
CO = {1,1,0}
H2 = {0,0,2}
```

2. `MatrixForm[Transpose[A={CH4,O2,CO2,H2O,CO,H2}]]`
   followed by the response

$$\begin{matrix} 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 2 & 2 & 1 & 1 & 0 \\ 4 & 0 & 0 & 2 & 0 & 2 \end{matrix} \tag{57}$$

3. `RowReduce[%]`
   followed by the response

$$\begin{array}{cccccc} 1 & 0 & 0 & 1/2 & 0 & 1/2 \\ 0 & 1 & 0 & 1 & -1/2 & 1/2 \\ 0 & 0 & 1 & -1/2 & 1 & -1/2 \end{array} \tag{58}$$

The final matrix indicates that $C = 3$ and $R = 6 - 3 = 3$. The final 3 columns of the matrix provide the coefficients in the chemical equations (31)-(33), which may be simplified to equations (34)-(36), as in Example 4.

Example 8:
We use the system of Example 6 to illustrate implementation by Maple.

1.
```
with(linalg):
Hplus:=[1,0,0,0,1];
OHMinus:=[1,1,0,0,-1];
H2O:=[2,1,0,0,0];
NOplus:=[0,1,1,0,1];
NO2minus:=[0,2,1,0,-1];
N2O3:=[0,3,2,0,0];
HNO2:=[1,2,1,0,0];
Tlplus:=[0,0,0,1,1];
T1NO2:=[0,2,1,1,0];
```

2.
```
transpose(array([Hplus,OHminus,H2O,NOplus,NO2minus,N2O3,HNO2,
Tlplus,T1NO2]));
```
   followed by the response

$$\begin{array}{ccccccccc} 1 & 1 & 2 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 2 & 3 & 2 & 0 & 2 \\ 0 & 0 & 0 & 1 & 1 & 2 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 1 & -1 & 0 & 1 & -1 & 0 & 0 & 1 & 0 \end{array} \tag{59}$$

3. `rref(");`
   followed by the response

$$\begin{matrix} 1 & 0 & 1 & 0 & -1 & -1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 & 1 & 1 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 & 2 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{matrix} \tag{60}$$

We identify the component species from the standard unit vectors in columns 1, 2, 4, and 8, corresponding to H^+, OH^-, NO^+, and Tl^+, respectively. Similarly, the noncomponent species, from columns 3, 5, 6, 7, and 9, are H_2O, NO_2^-, N_2O_3, HNO_2, and $TlNO_2$. From the entries in each of these five columns, we obtain the 5 chemical equations, corresponding to each noncomponent species in turn, leading to equations (52) to (56), as in Example 6.

6 Java Applet JSTOICH

6.1 Getting Started

JSTOICH is a Java applet; your browser must be capable of running Java classes (incorporated, for example, in Netscape version 3.0 or later, and in Internet Explorer version 3.0 or later).

To implement JSTOICH, the steps are as follows:

1. - Enter the number of species and number of elements in the initial window (Figure 1).
   - Click the **Next** button.

   A new window will appear for the entry of the species names and their molecular formulas in a table (Figure 2).

2. - Enter the species names in the first column as indicated, using any desired notation (*e.g.*, H2O(g) for gaseous water and H2O(l) for liquid water; i-C4H8 for isobutene, *etc.*).
   - Enter the names of the elements across the top row of the table, using any desired notation (*e.g.*, Na for sodium, H for hydrogen, *etc.*).

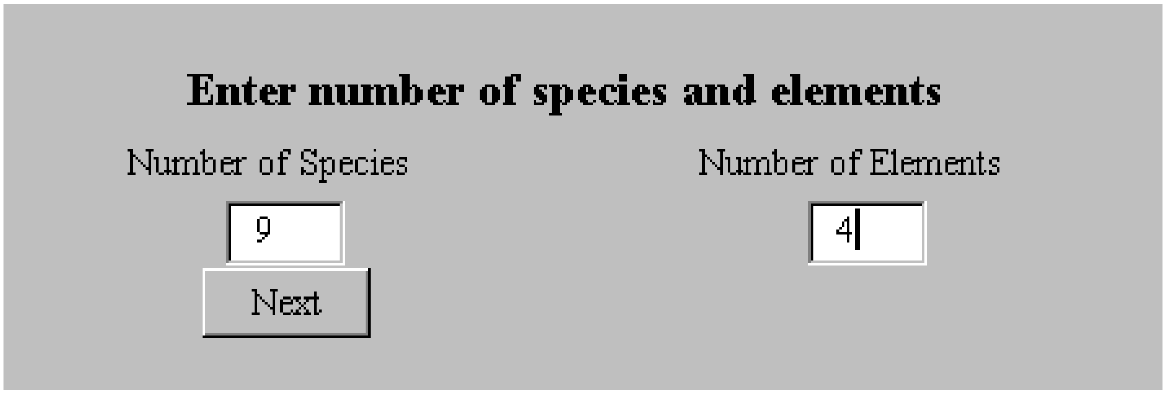


Figure 1: Java applet window for entering number of species and elements

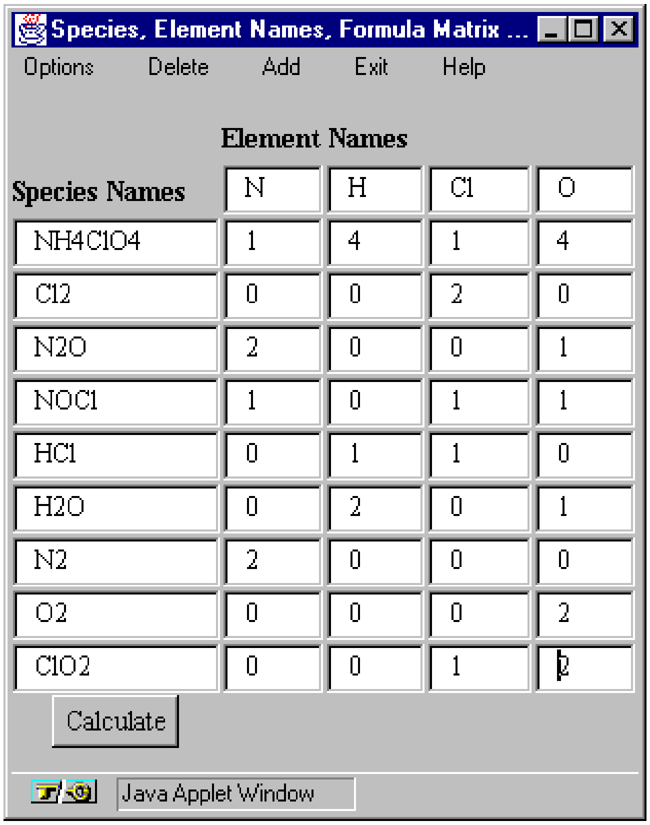
- Enter the (total) subscripts to each of the elements for each species in the row of the table to the right of its name (*e.g.*, for H_2O, enter 2 for H, 1 for O, and 0 for any other element in the system; for $(CH_3)_2CO$ enter 3 for C, 6 for H, 1 for O, and 0 for any other element in the system.)
- Click the **Calculate** button.

The window is over-written with the results of the calculation (Figure 3).

3. The window contains:
    - C, the number of components
    - R, the number of independent chemical equations in a proper set
    - a list of any chemically inert species (those that are not contained in any chemical equation), if any
    - a proper set of chemical equations in conventional canonical chemical form.
    - the component species indicated in the equations in blue, and the noncomponent species indicated in the usual text color, typically black.

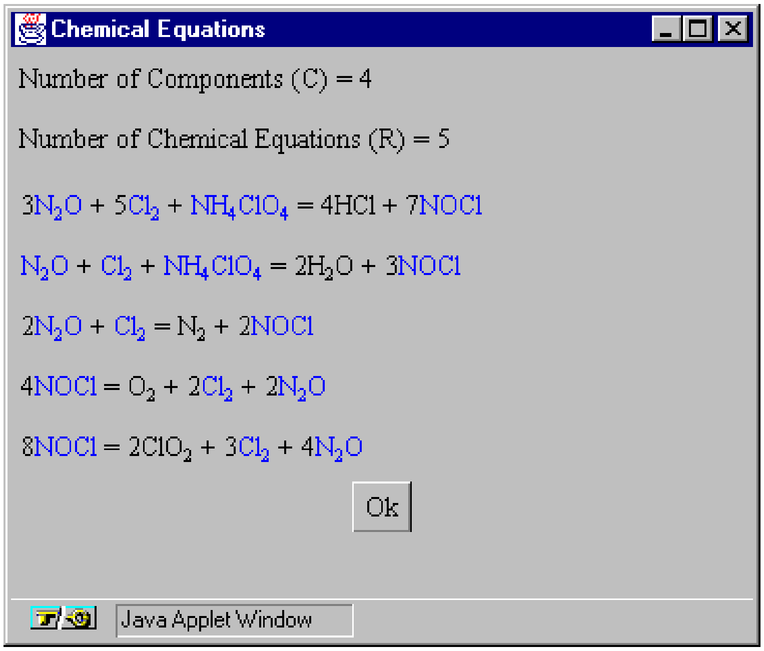
    Click on the **Ok** button to close the window.

4. To terminate JSTOICH, choose the **Exit** item on the menu bar of the window under Step 2 above.



	Element Names			
Species Names	N	H	Cl	O
NH4ClO4	1	4	1	4
Cl2	0	0	2	0
N2O	2	0	0	1
NOCl	1	0	1	1
HCl	0	1	1	0
H2O	0	2	0	1
N2	2	0	0	0
O2	0	0	0	2
ClO2	0	0	1	2

Figure 2: Java applet window for entering species names and formulas



Number of Components (C) = 4

Number of Chemical Equations (R) = 5

$3N_2O + 5Cl_2 + NH_4ClO_4 = 4HCl + 7NOCl$

$N_2O + Cl_2 + NH_4ClO_4 = 2H_2O + 3NOCl$

$2N_2O + Cl_2 = N_2 + 2NOCl$

$4NOCl = O_2 + 2Cl_2 + 2N_2O$

$8NOCl = 2ClO_2 + 3Cl_2 + 4N_2O$

Figure 3: Java applet window containing results of the calculation

Example 9:
Figures 1-3 show the three windows for the example problem (Segraves and Wickersham, 1991): $\{(NH_4ClO_4, Cl_2, N_2O, NOCl, HCl, H_2O, N_2, O_2, ClO_2), (N, H, Cl, O)\}$, relating to the explosion of ammonium perchlorate. The component species are NH_4ClO_4, Cl_2, N_2O, and NOCl.

6.2 Capabilities

JSTOICH:

- allows any number of species, N
- allows any number of elements, M
- allows for:
  - inert species
  - multiphase system
  - charged species

  - problem modification by addition of a species or element to a given list
  - problem modification by deletion of a species or element from a given list

6.3 Help File for JSTOICH

Optional actions may be performed by clicking on any of the items in the menu bar of the final window, as follows:

- **Options:**
  - Enter zero values:
    instead of entering 0 values for element subscripts, only the non-zero ones need be entered; this option fills in the remaining entries with zeros.
- **Delete:**
  - Clear all matrix entries:
    All the species formulas are erased from the table.
  - Clear all entries:
    The species names and formulas, and the element names are erased from the table.
  - Species:
    A row in the table is deleted corresponding to the selected species.
  - Element:
    A column in the table is deleted corresponding to the selected element.
- **Add:**
  - Species:
    A row in the table is added for an additional species
  - Element:
    A column in the table is added for an additional element
- **Exit:**

  - The Java applet is terminated.

- **Help:**
  - Instructions are given to perform specific tasks (displays this file).

Some Additional Hints:

- After entering each element name, pressing the Enter key will move the cursor to the next element.

- The cursor (arrow) keys allow you to move around the cells of the table for the species and element names, and their formulas.

- For systems involving charged species, enter a symbol for the protonic charge (*e.g.*, "p") and enter the signed charge of each species in the corresponding column of the table for its formula; *e.g.*, for H+ the charge is 1; for OH-, the charge is -1. The charge entry for a neutral species is 0.

- You can save the output windows of the applet to a file in the usual way. For example, to insert CRS output into a wordprocessor in Windows (*e.g.*, Word or WordPerfect), do the following:
  1. When the appropriate window of the applet is active (as indicated by the highlighted bar at its top), press Alt-Print Scrn to copy its contents to the Windows Clipboard.
  2. In the wordprocessor, place the cursor at the desired location and press Control-V.

7 Outline of Applications of CRS

In this section, we first expand on section 2.2 about the importance of CRS in chemical equililibrium (7.1) and kinetics (7.2). We then briefly note two aspects of CRS (not treated in this tutorial) for advanced study (7.3 and 7.4).

7.1 Applications in Chemical Equilibrium

7.1.1 Computation of chemical equilibrium

CRS may be used in the calculation of the chemical equilibrium composition of a system (for example, at fixed T and P) using a so-called *stoichiometric* formulation (Smith and Missen, 1982, 1991, Chapter 6). Such an algorithm employs a complete set of R linearly independent chemical equations representing the law of conservation of mass and charge for the system, and then solves the set of nonlinear equations:

$$\Delta G_j \equiv \sum_{i=1}^{N} \nu_{ij}\mu_i = 0; j = 1, 2, \ldots, R \tag{61}$$

where ΔG_j is the change in the Gibbs function for chemical equation j, and μ_i is the chemical potential of species i. Equation (61) can be rewritten in terms of equilibrium constants. If we set

$$\mu_i = \mu_i^0(T, P^0, X^0) + RT \ln a_i \tag{62}$$

where $\mu_i^0(T, P^0, X^0)$ (henceforth denoted by $\mu_i^0(T)$) is the *standard chemical potential* of species i at the system T, standard-state pressure P^0, and standard-state composition X^0, and a_i is the *activity* of species i, (61) may be written as

$$\Delta G_j^0 = -RT \ln K_{aj}; j = 1, 2, \ldots, R \tag{63}$$

where ΔG_j^0 is the standard change in the Gibbs function for chemical equation j and K_{aj} is the corresponding equilibrium constant:

$$\Delta G_j^0 = \sum_{i=1}^{N} \nu_{ij}\mu_i^0(T) \tag{64}$$

$$K_{aj} = \Pi_{i=1}^{N} a_i^{\nu_{ij}}; j = 1, 2, \ldots, R \tag{65}$$

It is important to note that *any* proper set of chemical equations may be used in the stoichiometric formulation (however, especially for large systems, there are computational considerations in set selection; see Smith and Missen, 1982, 1991, section 6.4, for details).

7.1.2 Species data (μ_i^0) from equilibrium constant data ($\Delta G_j^0, K_{aj}$)

In addition to the stoichiometric formulation of the chemical equilibrium problem, there is a *nonstoichiometric* formulation, which minimizes the total system Gibbs function, G, subject to the mass- and charge-balance constraints, solving the problem:

$$\min\ G \equiv \sum_{i=1}^{N} n_i \mu_i \tag{66}$$

$$\text{such that} \quad \sum_{i=1}^{N} a_{ki} n_i = b_k; k = 1, 2, \ldots M \tag{67}$$

Algorithms using the nonstoichiometric formulation are often referred to as "free-energy minimization algorithms", although this term is misleading, since *any* chemical equilibrium algorithm can be viewed as solving a minimization problem (equations (61) are a set of necessary conditions satisfied at the minimum of G).

An algorithm of either type may be used for any given problem, provided that the appropriate data are available. For a stoichiometric algorithm, the required thermochemical data are the quantities ΔG_j^0 (or K_{aj}); for a nonstoichiometric algorithm, the corresponding data are the standard chemical potentials of each species, $\mu_i^0(T)$. For a large number of species, the latter quantities have been determined and are available in tabular form (*e.g.*, JANAF, 1985). However, for many systems (for example, many biochemical and geochemical systems), data are only available in the form of ΔG_j^0 or K_{aj}. An apparent conclusion (*e.g.*, Björnbom, 1975, 1978; Anderson and Crerar, 1993, pp.517-518; Nordstrom and Nunoz, 1994, p. 401) is that nonstoichiometric algorithms cannot be used in such cases. This conclusion is not valid; methods of linear algebra like those used in MRM can be used to calculate a set of $\mu_i^0(T)$ from a set of ΔG_j^0 or K_{aj} (Smith, 1976, 1978; Smith and Missen, 1982, 1991, section 9.4; Cheluget *et al.*, 1987).

The key to calculating a set of $\mu_i^0(T)$ from a set of ΔG_j^0 or K_{aj} is the realization that equations (64) can be considered to be a set of R linear equations in the N unknown quantities $\mu_i^0(T)$. Thus, *any* solution of these equations may be used in a nonstoichiometric (or even in a stoichiometric) algorithm. We say that such a set is *consistent with* the set of ΔG_j^0 or K_{aj}. We show how to carry out the procedure using a method based on MRM by means of a simple example (Smith and Missen, 1982, 1991, pp. 216-217).

Example 10:
For the system $\{(H_3PO_4, H_2PO_4^-, HPO_4^{2-}, PO_3^{3-}, H^+, OH^-, H_2O), (H,O,P,p)\}$, suppose that data are given in the form

$$\begin{aligned} H_3PO_4 &= H_2PO_4^- + H^+;\ K_1 && (68)\\ H_2PO_4^- &= HPO_4^{2-} + H^+;\ K_2 && (69)\\ HPO_4^{2-} &= PO_4^{3-} + H^+;\ K_3 && (70)\\ H_2O &= OH^- + H^+;\ K_4 = K_w/a_{H_2O} && (71) \end{aligned}$$

where K_1 to K_4 are the equilibrium constants for the reactions as written, and K_w is the ion-product for water. To find a consistent $\{\mu_i^0\}$ for the seven species of the system, we first calculate $\Delta G_j^0 \equiv -RT\ln K_j$ and form the matrix

$$(\mathbf{N}^T, -\mathbf{\Delta G}^0) = \begin{array}{c} \begin{array}{cccccccc} (1) & (2) & (3) & (4) & (5) & (6) & (7) & \end{array} \\ \left(\begin{array}{cccccccc} -1 & 1 & 0 & 0 & 1 & 0 & 0 & -\Delta G_1^0 \\ 0 & -1 & 1 & 0 & 1 & 0 & 0 & -\Delta G_2^0 \\ 0 & 0 & -1 & 1 & 1 & 0 & 0 & -\Delta G_3^0 \\ 0 & 0 & 0 & 0 & 1 & 1 & -1 & -\Delta G_4^0 \end{array}\right) \end{array}$$

The unit matrix form of this is

$$\begin{array}{c} \begin{array}{cccccccc} (1) & (2) & (3) & (6) & (5) & (4) & (7) & \end{array} \\ \left(\begin{array}{cccccccl} 1 & 0 & 0 & 0 & -3 & -1 & 0 & \Delta G_1^0 + \Delta G_2^0 + \Delta G_4^0 \\ 0 & 1 & 0 & 0 & -2 & -1 & 0 & \Delta G_2^0 + \Delta G_3^0 \\ 0 & 0 & 1 & 0 & -1 & -1 & 0 & \Delta G_3^0 \\ 0 & 0 & 0 & 1 & 1 & 0 & -1 & -\Delta G_4^0 \end{array}\right) \end{array}$$

A consistent $\{\mu_i^0\}$ with the species ordered as specified is $\{\Delta G_1^0 + \Delta G_2^0 + \Delta G_3^0, \Delta G_2^0 + \Delta G_3^0, 0, 0, -\Delta G_4^0, 0\}$. If we write the R (=4) stoichiometric equations represented by the first N (=7) entries in each of the rows of the unit matrix form, we see that the method in effect sets standard chemical potentials for R noncomponent species (here H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and OH^-) relative to a set of C (=3) component species (here H^+, PO_4^{3-}, and H_2O), which are assigned zero values. This is analogous to the usual assignment of standard chemical potentials relative to the elements, the "ultimate" components.

7.2 Applications in Chemical Kinetics

7.2.1 Number of independent steps (F_s) in a reaction network

A *reaction network* or *kinetics scheme* is a representation of the sequence of events or of a reaction pathway in a reacting system. It takes the form of a set of chemical *reactions* involving only "observable" species (that is, excluding reactive intermediates, such as free radicals). The set of reactions may involve reversible steps, and steps in series and/or parallel. The maximum number of independent steps in a reaction network, F_s, is an experimentally determined quantity. F_s is the number of stoichiometric degrees of freedom of the system. From CRS, the maximum value of F_s is R. A role of the network is to enable calculation of the complete compositional state of the reaction system, say, as a function of time. The information is in the form of a rate law for each step (obtained experimentally), including values of the rate parameters, such as order of reaction and Arrhenius parameters.

To illustrate reaction networks, consider the important process for making ethylene (C_2H_4) by dehydrogenation of ethane (C_2H_6). The simplest reaction network for this is the single step

$$C_2H_6 \rightarrow C_2H_4 + H_2 \tag{72}$$

If methane (CH_4) is formed in addition in significant amount as an "observed" species, we can expand (72) as a two-step network:

$$\begin{aligned} C_2H_6 &\rightarrow C_2H_4 + H_2 & (73)\\ C_2H_6 + H_2 &\rightarrow 2CH_4 & (74) \end{aligned}$$

In either case of (72) or (73) and (74), we do not *necessarily* imply that reaction takes place in the manner indicated.

Reaction (72) corresponds to the single chemical equation ($R = 1$) that we obtain (*e.g.*, by MRM) for the system $\{(C_2H_6, H_2, C_2H_4), (C,H)\}$:

$$C_2H_6 = C_2H_4 + H_2 \tag{75}$$

The set of reactions (73) and (74) corresponds to the set of chemical equations ($R = 2$) that we obtain for the system $\{(C_2H_6, H_2, C_2H_4, CH_4), (C,H)\}$:

$$\begin{aligned} C_2H_6 &= C_2H_4 + H_2 & (76)\\ C_2H_6 + H_2 &= 2CH_4 & (77) \end{aligned}$$

7.2.2 Determination of F_s implied by a reaction mechanism using CRS

A *reaction mechanism* is a more detailed representation of the sequence of events or reaction pathway than is a reaction network. The set of chemical reactions in a mechanism, called *elementary steps*, involves not only "observable" species, but also transient species or reactive intermediates, whose concentrations remain very small. (The number of elementary steps in a reaction mechanism may be greater than the value of R corresponding to the complete species list including the transient species.) Each step is postulated to represent an actual encounter between molecular species so as to react to form other species. We may call the observable species *major species*, and the reactive intermediates, whether molecular species or molecular fragments such as free radicals, *minor species*.

A postulated reaction mechanism (Rice and Herzfeld, 1934) for ethane decomposition to ethylene involves the following five steps:

$$\begin{aligned} C_2H_6 &\rightarrow 2CH_3^\bullet & (78)\\ CH_3^\bullet + C_2H_6 &\rightarrow CH_4 + C_2H_5^\bullet & (79)\\ C_2H_5^\bullet &\rightarrow C_2H_4 + H^\bullet & (80)\\ H^\bullet + C_2H_6 &\rightarrow H_2 + C_2H_5^\bullet & (81)\\ H^\bullet + C_2H_5^\bullet &\rightarrow C_2H_6 & (82)\end{aligned}$$

where $CH_3^\bullet$, $C_2H_5^\bullet$ and $H^\bullet$ are free radicals (minor species); the reaction mechanism also involves CH_4, which may be considered to be either a minor species (case (a)) or a major species (case (b)).

We can use the techniques of CRS (*i.e.*, MRM) to construct the reactions of a network from those of the mechanism, and simultaneously to determine F_s. This is done by linearly combining the steps of the mechanism so as to eliminate the minor species, by means of the following procedure, analogous to that used in MRM:

1. Write the stoichiometric coefficients of the mechanism in a matrix $\mathbf{N}$, with the rows corresponding to the reaction steps and the columns corresponding to the species. Label the rows and columns of the matrix, and place the minor species in the *initial* columns of the matrix.

2. Use elementary row operations to produce a unit matrix as large as possible in the upper left hand corner of $\mathbf{N}$, resulting in a matrix $\mathbf{N}^*$.

3. The reactions of the network are contained in the bottom-most rows of $\mathbf{N}^*$, those that do not involve the minor species (there are zero entries for these species in those rows).

4. The value of F_s is given by the number of reactions of the resulting reaction network.

For the above mechanism, the steps are as follows:

1.

$$\mathbf{N} = \begin{array}{cccccccc} & CH_3^\bullet & C_2H_5^\bullet & H^\bullet & CH_4 & C_2H_6 & H_2 & C_2H_4 \\ R_1 & 2 & 0 & 0 & 0 & -1 & 0 & 0 \\ R_2 & -1 & 1 & 0 & 1 & -1 & 0 & 0 \\ R_3 & 0 & -1 & 1 & 0 & 0 & 0 & -1 \\ R_4 & 0 & 1 & -1 & 0 & -1 & 1 & 0 \\ R_5 & 0 & -1 & -1 & 0 & 1 & 0 & 0 \end{array}$$

2.

$$\mathbf{N}^* = \begin{array}{cccccccc} & CH_3^\bullet & C_2H_5^\bullet & H^\bullet & CH_4 & C_2H_6 & H_2 & C_2H_4 \\ R_1 & 1 & 0 & 0 & 0 & 0 & -1/2 & -1/2 \\ R_2 & 0 & 1 & 0 & 0 & 0 & -1/2 & -1 \\ R_3 & 0 & 0 & 1 & 0 & 0 & -1/2 & 0 \\ R_4 & 0 & 0 & 0 & 1 & 0 & -1 & -1/2 \\ R_5 & 0 & 0 & 0 & 0 & 1 & -1 & -1 \end{array}$$

3. The rows in $\mathbf{N}^*$ may be interpreted to provide the following five reactions, which are necessarily not elementary steps:

$$CH_3^\bullet - 1/2H_2 - 1/2C_2H_4 \to 0; \quad \text{or} \quad CH_3^\bullet \to 1/2H_2 + 1/2C_2H_4 \tag{83}$$

$$C_2H_5^\bullet - 1/2H_2 - C_2H_4 \to 0; \quad \text{or} \quad C_2H_5^\bullet \to 1/2H_2 + C_2H_4 \tag{84}$$

$$H^\bullet - 1/2H_2 \to 0; \quad \text{or} \quad H^\bullet \to 1/2H_2 \tag{85}$$

$$CH_4 - H_2 - 1/2CH_4 \to 0; \quad \text{or} \quad CH_4 \to H_2 + 1/2CH_4 \tag{86}$$

$$C_2H_6 - H_2 - C_2H_4 \to 0; \quad \text{or} \quad C_2H_6 \to H_2 + C_2H_4 \tag{87}$$

In case (a), if CH_4 is a minor species (as probably intended for this mechanism), the single reaction of the network is contained in the last row, which is the same as reaction (72) in section 7.2.1, and corresponds to the overall reaction stoichiometry in equation (75); that is, $F_s = R = 1$. In case (b), if CH_4 is a major species, the reaction network is contained in the last 2 rows, and these are equivalent to reactions (73) and (74) in section 7.2.1 (with (86=(73) - (74)), or to the overall stoichiometry of equations (76) and (77), with the equation corresponding to (86) given by (76) - (77); that is, $F_s = R = 2$.

7.3 Stoichiometric Restrictions

In this tutorial, as a general introduction to CRS, we assume that there are no restrictions on the allowable changes in composition on reaction other than the atom-balance constraints. This means that $F_s = R$. However, the composition of a reacting system may be further restricted in ways that stoichiometry itself cannot predict (but it can take such restrictions into account, see below). For example, with $R > 1$, two reactants may combine in a particular ratio, or a particular reaction may effectively be prevented from taking place by lack of an appropriate catalyst. We refer to any such restriction as a *stoichiometric restriction*, and its existence can only be discovered by experiment. Each stoichiometric restriction has the effect of reducing F_s by 1, but has no effect on R, which refers to the general (unrestricted) solution. If r is the number of stoichiometric restrictions,

$$F_s = R - r = N - C - r \tag{88}$$

Once the number and nature of the r stoichiometric restrictions are known, a stoichiometric analysis can proceed as described in this tutorial by appropriate modification of the system formula matrix. The procedure is described by Smith and Missen (1982, 1991, *pp.* 29–36)

7.4 From Chemical Equations to Atom-balance Equations

Just as a proper set of chemical equations can be generated from a given formula matrix, a (proper) formula matrix can also be generated from a given set of chemical equations. This is useful if the only information available concerning a system is in the form of a such a set of chemical equations. This set of equations corresponds to a given *stoichiometric matrix*. The mathematical basis is the same in both cases (whether starting from a formula matrix or from a stoichiometric matrix). The procedure is described by Smith and Missen (1982, 1991, section 2.4.5).

8 Exercises

1. (a) For each of the following systems, determine the values of C and of R, and a proper set of chemical equations in conventional canonical form. List the component species and the noncomponent species separately.
    i. {(P_2I_4, P_4, H_2O, PH_4I, H_3PO_4), (P, I, H, O)}(Carrano, 1978).
    ii. {(O_2, $(CH_3)_3COH$, CO_2, H_2O, CH_3COCH_3, CH_3COOH), (O, C, H)}, relating to the oxidation of *t*-butyl alchohol (Missen, 1970).
    iii. {(OH^-, O_2, e^-, H_2O, O_3), (H, O, p)}, relating to the reduction half reaction for ozone (Olson, 1997).
    iv. {(CH_4, O_2, CO_2, H_2O, CO, H_2, N_2), (C, O, H, N_2)}, relating to the partial combustion of CH_4 with *air*; *cf.* Example 7.
    v. {(C(*gr*), CO(*g*), CO_2(*g*), Zn(*g*), Zn(*l*), ZnO(*s*)), (C, O, Zn)}, relating to the production of zinc metal (Denbigh, 1981, pp. 191-193).
    vi. {($[Cr(N_2H_4CO)_6]_4[Cr(CN)_6]_3$, $KMnO_4$, H_2SO_4, $K_2Cr_2O_7$, $MnSO_4$, CO_2, KNO_3, K_2SO_4, H_2O), (Cr, N, H, C, O, K, Mn, S)}, described as an "incredibly challenging" redox system (Stout, 1995).
    vii. {(O_2(*g*), H_2O(*g*), CH_4(*g*), CO(*g*), CO_2(*g*), H_2(*g*), N_2(*g*), CHO(*g*), CH_2O(*g*), OH(*g*), Fe(*s*), FeO(*s*), Fe_3O_4(*s*), C(*gr*), CaO(*s*), $CaCO_3$(*s*)), (O, H, C, Fe, Ca, N_2)}, a blast furnace system (Madeley and Toguri, 1973a, 1973b).
    viii. {($Fe(C_2O_4)^+$, $Fe(C_2O_4)_2{}^-$, $Fe(C_2O_4)_3{}^{3-}$, Fe^{3+}, $SO_4{}^{2-}$, $HSO_4{}^-$, H^+, $HC_2O_4{}^-$, $H_2C_2O_4$, $C_2O_4{}^{2-}$), (C, Fe, H, O, S, p)} (Swinnerton and Miller, 1959).

ix. {(CH_4, CH_3D, CH_2D_2, CHD_3, CD_4), (C, H, D)}, relating to isotopic exchange among the deuteromethanes (Apse and Missen, 1967).

x. {(C_2H_4, C_3H_6, C_4H_8, C_5H_{10}, C_6H_{12}), (C, H)}, relating to the oligomerization of C_2H_4.

xi. {($H_2O(l)$, $C_2H_6O(l)$, $C_2H_4O_2(l)$, $C_4H_8O_2(l)$, $H_2O(g)$, $C_2H_6O(g)$, $C_2H_4O_2(g)$, $C_4,H_8O_2(g)$, $(C_2H_4O_2)_2(g)$), (C, H, O)}, relating to the liquid-vapor esterification of ethyl alchohol with acetic acid, and allowing for the presence of acetic acid dimer in the vapor phase (Sanderson and Chien,1973).

xii. {(O_2, H_2O, H_2SO_4, $KMnO_4$, H_2O_2, K_2SO_4, $MnSO_4$), (O, H, S, K, Mn)} (Missen and Smith,1990).

(b) For each system in (a), change the order of the species and the order of the elements, and repeat.

2. (a) For a system of N species and $rank(\mathbf{A}) = C$, what is the apparent maximum number of proper sets of chemical equations in canonical form?

   (b) Under what circumstances would the actual number of proper sets in canonical form be less than the apparent maximum number in (a)?

   (c) How would the actual number be determined, if it is less than the apparent maximum number?

   (d) For the system in Example 2, what is the number of proper sets of chemical equations in canonical form?

3. For the system in Example 9, Segraves and Wickersham (1991) wrote the chemical equation

$$\begin{aligned} 10NH_4ClO_4 &= 2.5Cl_2 + 2N_2O + 2.5NOCl + 1.5HCl + 19.25H_2O \\ &\quad +1.75N_2 + 7.125O_2 + ClO_2 \qquad \text{(A)} \end{aligned}$$

They noted, however, that “different...conditions could make almost any overall decomposition possible...there is no one overall decomposition reaction...” In comparison with the result given in Example 9, what are the implications of writing a single equation such as (A)? Explain.

4. The system in Exercise 1.(a)xii is the basis for "wet" chemical analysis for H_2O_2 in aqueous solution. The stoichiometry in this case is expressed by the chemical equation

   $$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2 \quad (B)$$

   In comparison with the result obtained in Exercise 1.(a)xii, what is the implication of writing (B)? (Missen and Smith, 1990).

5. In section 2.5 of the tutorial, it is noted that a proper set of chemical equations for a reacting system is not unique, and that any one equation of the set may be replaced by an equation obtained by taking a nonzero multiple of it and adding a linear combination of the remaining equations, to form a different proper set. For the system in Example 2, replace the set of equations (4), (5), and (6) by (4a) = (4) + (5), (5a) = (4) + (6), and (6a) = (5) + 3(6). Is the set (4a), (5a), and (6a) a proper set of chemical equations? Explain.

6. McBride and Adams(1984) give the following (skeletal) reaction for the production of perchloric acid from ammonium perchlorate:

   $$\begin{aligned} NH_4ClO_4 + HNO_3 + HCl + H_2O \quad \rightarrow \quad & HClO_4 \cdot 2H_2O + N_2O + NO \\ & +NO_2 + Cl_2 \end{aligned}$$

   They state that "The equation(*sic*) has been left unbalanced because no solution that has ever been produced satisfies the observed results. It is quite an exercise to balance it at all." What is the answer to this apparent dilemma? (Their statement has also been discussed by Jensen, 1987).

7. Ferguson(1996) has posed the problem of balancing the following skeletal reaction to his High School chemistry students:

   $$KClO_3 + HCl \rightarrow KCl + H_2O + Cl_2 + ClO_2$$

   After giving a table of many sets of coefficients for achieving this, and indicating that more exist, he concluded that the correct answer is

   $$2KClO_3 + 4HCl \rightarrow 2KCl + 2H_2O + Cl_2 + 2ClO_2$$

This results from his reasoning that, in addition to atom-balances, "transfer of electrons...needs to be balanced," thus requiring an excursion into consideration of balancing redox reactions. Is Ferguson's reasoning correct? Explain quantitatively.

8. In a kinetics investigation of the vapor-phase oxidation of CH_4 over a certain catalyst in a differential flow reactor, Spencer and Pereira (1987) obtained a reaction network consisting of two steps in series, in which CH_4 first oxidizes to HCHO, followed by further oxidation of HCHO to CO, together with a third step in parallel in which CH_4 oxidizes to CO_2:

$$\begin{aligned} \mathrm{CH_4 + O_2} &\rightarrow \mathrm{HCHO + H_2O} \\ \mathrm{HCHO} + \frac{1}{2}\mathrm{O_2} &\rightarrow \mathrm{CO + H_2O} \\ \mathrm{CH_4 + 2O_2} &\rightarrow \mathrm{CO_2 + 2H_2O} \end{aligned}$$

   (a) Does this reaction network correspond stoichiometrically to a proper set of chemical equations? Justify your answer.

   (b) What is the minimum number of species whose concentrations must be measured, so that the concentrations of all other species may be calculated? Explain.

   (c) What is the minimum number of species reaction rates, r_i, from which all other species rates can be calculated? Relate all other species rates to a particular chosen minimum set. What is the most efficacious way of choosing a minimum set?
   (Based on examples given by Missen *et al.*, 1999, Chapter 5.)

9. In a kinetics investigation of the catalytic vapor-phase oxidation of benzene (with *air*) to maleic anhydride ($C_4H_2O_3$) in a flow reactor, Vaidyanathan and Doraiswamy(1968) stated that the "reaction scheme...may be stoichiometrically represented as":

$$\begin{aligned} \mathrm{C_6H_6} + \frac{9}{2}\mathrm{O_2} &\rightarrow \mathrm{C_4H_2O_3 + 2CO_2 + 2H_2O} \\ \mathrm{C_4H_2O_3 + 3O_2} &\rightarrow \mathrm{4CO_2 + H_2O} \\ \mathrm{C_6H_6} + \frac{15}{2}\mathrm{O_2} &\rightarrow \mathrm{6CO_2 + 3H_2O} \end{aligned}$$

(a) Is a corresponding set of three chemical *equations* a proper set? Justify your answer. Is the first of these an allowable equation?

(b) The authors used partial pressure (p_i) as a measure of concentration. They reported p_i for 4 species. How many of these are independent as a minimum set? Choosing a set of this number of species and their p_i, relate the partial pressures of *all* other species to these p_i.

(c) Similarly, what is a minimum set of species reaction rates r_i? Relate all other species rates to a particular chosen minimum set. (Based on a problem given by Missen *et al.* (1999), chapter 5.)

10. A possible free-radical chain mechanism for the thermal decomposition of acetaldehyde (to CH_4 and CO) is the Rice-Herzfeld mechanism (Laidler and Liu, 1967):

$$\begin{aligned} CH_3CHO &\rightarrow CH_3^\bullet + CHO^\bullet && (89)\\ CHO^\bullet &\rightarrow CO + H^\bullet && (90)\\ H^\bullet + CH_3CHO &\rightarrow CH_3CO^\bullet + H_2 && (91)\\ CH_3^\bullet + CH_3CHO &\rightarrow CH_4 + CH_3CO^\bullet && (92)\\ CH_3CO^\bullet &\rightarrow CH_3^\bullet + CO && (93)\\ 2CH_3^\bullet &\rightarrow C_2H_6 && (94) \end{aligned}$$

Find a kinetics scheme for each of the following cases:

(a) H_2 and C_2H_6, in addition to the free radical species, are *minor* species.

(b) H_2 and C_2H_6 , but not the free radical species, are *major* species.

11. The first step in the extraction of Ti from titania (TiO_2) may be the chlorination of the oxide to produce the tetrachloride, in the absence of carbon to lower the partial pressure of O_2. Kubashewski and Alcock (1979) give equilibrium data in the form of ΔG^0 for three reactions as follows:

$$\begin{aligned} C(s) + \frac{1}{2}O_2(g) &= CO(g);\ \Delta G_1^0 = -111,700 - 87.65T && (95)\\ C(s) + O_2(g) &= CO_2(g);\ \Delta G_2^0 = -394,100 - 0.84T && (96) \end{aligned}$$

$$TiO_2(s) + 2Cl_2(g) \quad = \quad TiCl_4(g) + O_2(g); \tag{97}$$

$$\Delta G_3^0 = 161,100 - 56.5T \tag{98}$$

where ΔG^0 is in J and T is in K. Using these data, obtain a consistent set of the standard chemical potentials (μ^0) of the species at 1000K; *i.e.*, for the species in the system represented by $\{(O_2, H_2O, H_2SO_4, KMnO_4, H_2O_2, K_2SO_4, MnSO_4), (O, H, S, K, Mn)\}$.

Nomenclature

Latin letters

a_i	activity of species i
a_{ki}	subscript to element k in molecular formula of species i
$\mathbf{A}$	formula matrix: the $(M \times N)$ matrix whose entries are a_{ki}
$\mathbf{A}^*$	unit matrix or row-reduced echelon form of $\mathbf{A}$
b_k	number of moles of element k
$\mathbf{b}$	element-abundance vector with entries b_k
C	number of component species; number of linearly independent atom-balance equations
CRS	chemical reaction stoichiometry
F	number of degrees of freedom
F_s	number of stoichiometric degrees of freedom
G	Gibbs function
ΔG_j	change in Gibbs function for chemical equation j
ΔG_j^0	standard change in Gibbs function for chemical equation j
K_{aj}	equilibrium constant for chemical equation j
K_w	equilibrium constant for water dissociation
M	number of elements
MRM	matrix reduction method
$\mathbf{n}$	species-abundance vector with entries n_i
n_i	number of moles of species i
δn_i	change in number of moles of species i
$\boldsymbol{\delta}\mathbf{n}$	species-abundance-change vector with entries δn_i
N	number of species
$\mathbf{N}$	stoichiometric matrix with elements ν_{ij}
$\mathbf{N}^*$	reduced stoichiometric matrix obtained from the matrix $\mathbf{N}$
p	(protonic) charge
P	pressure
P^0	standard-state pressure
r	number of stoichiometric restrictions
R	maximum or proper number of linearly independent chemical equations
T	temperature (absolute)
X^0	standard-state composition

Greek letters

μ_i	chemical potential of species i

$\mu_i^0(T, P^0, X^0)$	standard chemical potential of species i at the system T, the standard-state pressure P^0, and the standard-state composition X^0
$\mu_i^0(T)$	standard chemical potential of species i at the system T (arguments P^0, X^0 are suppressed)
ν_i	stoichiometric coefficient of species i in a single chemical equation
ν_{ij}	stoichiometric coefficient of species i in chemical equation j
$\boldsymbol{\nu}$	stoichiometric vector with entries ν_i in a single chemical equation

Subscripts

i, j, k	dummy indices

Other symbols

$=$	denotes chemical equation
$\rightarrow$	denotes irreversible chemical reaction
$\rightleftharpoons$	denotes reaction at equilibrium
T	as superscript, denotes transpose of a vector

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