

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, $\text{H}_2\text{O}(\ell)$ and $\text{H}_2\text{O}(g)$ are distinct species, as are ethyl alcohol and dimethyl ether (each of which has the same molecular formula $\text{C}_2\text{H}_6\text{O}$).
- 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) \rightarrow 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.

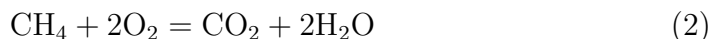
2.5 Preliminary examples of sets of chemical equations

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:

$$\{(\text{CH}_4, \text{O}_2, \text{CO}_2, \text{H}_2\text{O}), (\text{C}, \text{O}, \text{H})\} \quad (1)$$

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



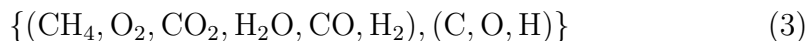
Any other proper set consists of a multiple of this equation, and is not an independent set.

- Note the use of $=$ to represent atomic species conservation in a chemical *equation*.

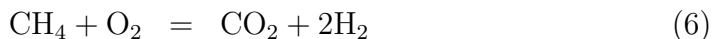
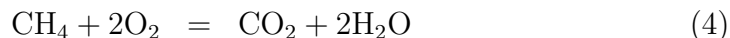
- For this example, as *is the case whenever* $R = 1$, $=$ may be replaced by \rightarrow to represent the corresponding overall reaction, or a kinetics scheme for the system.
- The above equation does not necessarily represent a reaction mechanism for the system.
- $=$ may be replaced by \rightleftharpoons 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:



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



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 non-zero 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



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, $\{\boldsymbol{\nu}_j, j = 1, \dots, R\}$, where R is the maximum number of linearly independent solutions of the linear equations (Smith and Missen, 1982, 1991, Chapter 2):

$$\mathbf{A}\boldsymbol{\nu} = 0 \quad (8)$$

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

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

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

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.*, $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$); CRS is then expressed by 1 equation ($R = 1$; $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$). 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 Camparano(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 Mathematica¹ and Maple², 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 $R \geq 1$.

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

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