Chemical Equations for Multireaction Systems

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Abstract: While the balanced chemical equations for a multireaction system are generally not unique, the minimum number of independent equations, *R*, is a characteristic property of the system. Deleting one nonspectator species from the system leads to a system with *R* reduced by one. In this way each system can be reduced to a single-reaction system and ultimately to a no-reaction system. The least number of chemical species that can be deleted to obtain a no-reaction system equals R. Every multireaction system, therefore, can be reduced to a number of single-reaction equations which can be balanced by any one of the standard techniques. Some examples are given where balancing by inspection is employed.

Everybody is aware of the fact that the combustion of kerosene produces not only CO_2 but also CO with possibly lethal consequences. The typical chemistry texts mention, of course, competing or consecutive reactions; however, in the section on stoichiometry and the balancing of reactions they invariably restrict the discussion to single reaction systems and ask the students to balance equations given in a skeletal form. The tacit implication is that every balancing problem has a unique solution. The students, and some teachers [1] as well, are then very surprised if they find a sizable number of equations for some chemical systems, all perfectly well-balanced, which are not just multiples of each other.

The minimum number of independent chemical equations, *R*, required to characterize a system of given chemical species is a unique property of the system. This number plays an important role in the phase rule and reaction kinetics. In chemical equilibria, it is the number of independent equilibrium constants of the system. If *R* is larger than one, the term independent means linearly independent in the mathematical sense; it does not imply chemical independence, as in most cases one deals with coupled, competing or consecutive reactions which have one or more chemical species in common. Any chemical process from the most elementary to the most complex is subject to the fundamental constraints of mass and charge conservation, which are expressed as balanced chemical equations. If *R* equals 1 the system is characterized by a unique balanced equation if we stay with the convention that the stoichiometric coefficients are the smallest integers consistent with the conservation requirements. Of course, any multiple of a balanced equation is also an equivalent, balanced equation. Herndon [2] has given an extensive review of methods to balance equations for *R* = 1. For *R* greater than 1, he states "no unique solution exists or the equation cannot be balanced." It is correct that the equations are not unique, but matrix based techniques [3–5] prove one can always generate a valid set of balanced equations. Smith and Missen have given on their web site [6] (http://www.chemical-stoichiometry.net) an excellent discussion of the matrix-reduction method to balance equations either by hand or, in a Java Applet available to any visitor, to let a computer balance the chemical equations for a given set of chemical species. Although matrix methods have the last word, the following discussion does not explicitly refer to the formula table and uses examples that can easily be balanced by inspection, including the case of *R* = 0 where no reaction between the given species is possible. It demonstrates a systematic approach to determine *R* and to find one or more valid set of balanced equations for multi-reaction systems.

The problem may be stated as follows. Given a list of *N* chemical species in a system, find the minimum number, *R*, of independent reactions and a set of balanced equations. It is convenient, but not necessary, that the equations be as simple as possible, that is, contain the smallest number of chemical species. These equations are called a canonical set. A canonical proper set satisfies the additional criterion that *R* species only appear in separate equations, assuring linear independence in a simple fashion. A species may be a reactant, a product, or a spectator species with a stoichiometric factor of zero. A system with *R* = 0 is a no reaction system (NRS) and consists only of spectators. We take advantage of two facts:

(a) *R* is the smallest number of species that can be deleted from the original list resulting in an NRS.

(b) The desired simple equations have at least R – 1 spectator species with zero stoichiometric coefficient or, equivalently, contain at most N – R + 1 chemical species.

(c) As a simple example, consider the system

$$\{C, O_2, CO, CO_2\} \qquad (1)$$
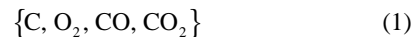
Obviously, if we delete just one species at a time, we still can form balanced equations; however, if we delete any two species, the remaining two are an NRS. We conclude that *R* = 2 and that each canonical equation has one zero and three nonzero coefficients. By inspection we find

$$2C + O_2 = 2CO \qquad (1a)$$

$$C + O_2 = CO_2 \qquad (1b)$$

$$C + CO_2 = 2CO \qquad (1c)$$

$$2CO + O_2 = 2CO_2 \qquad (1d)$$
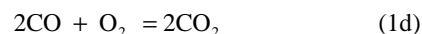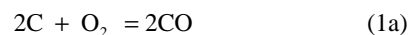
These four equations are not independent, but any two are. We can chose any pair as basis reactions and express the others as linear combinations of these two. For example if equations 1a and 1b are taken as basic, they are linearly independent because equation 1a contains the species CO not occurring in equation 1b, which in turn contains CO_2 that is not part of equation 1a. The other two equations, however,

$$(1c) = (1a) - (1b)$$

$$(1d) = 2\ (1b) - (1a)$$

are dependent on the chosen basis. Depending on the reaction conditions, chemical considerations may give preference to a particular choice of two basis reactions but the other two, or for that matter any other linear combination of the basis reactions, yields perfectly balanced chemical equations. For example:

$$C + 3CO_2\ =\ 4CO + O_2 \qquad (1e)$$
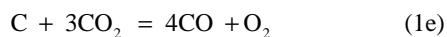
involves all four species. It is in fact (1e) = 2(1a) – 3(1b).

Consider the incomplete combustion of methane [6]. The six species are:

$$\{CH_4,\ O_2,\ CO_2,\ H_2O,\ CO,\ H_2\}$$
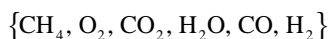
Clearly, if you leave out the first three species, the remaining system $\{H_2O, CO, H_2\}$ is an NRS. On the other hand, if you delete CH_4, H_2O, and H_2, the remainder $\{O_2, CO_2, CO\}$ still supports a reaction and one additional species must be deleted to reach an NRS. Deleting only any two species leaves systems that support a chemical reaction. As R is the smallest number of species deleted to get an NRS, it follows that R = 3. Each equation in the canonical set contains at most four species or has at least two species with zero stoichiometric coefficients. There are 6 over 4, which equals (6 × 5)/(1 × 2) = 15 ways, to select four species. Each choice supports one balanced equation. They are, however, not all different as some include a spectator species and the equations effectively contain only three species as in the two cases
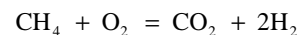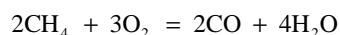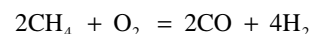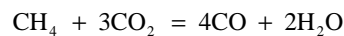
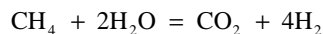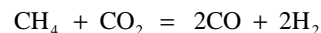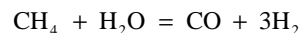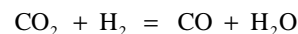$$O_2 + 2H_2\ =\ 2H_2O \qquad (2a)$$

$$2CO + O_2\ =\ 2CO_2 \qquad (2b)$$
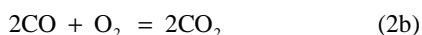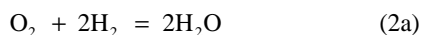
each appearing three times in the 15 possible canonical equations. That leaves 11 different equations. The third independent equation must be one that involves CH_4, for example

$$CH_4 + 2O_2\ =\ 2H_2O + CO_2 \qquad (2c)$$
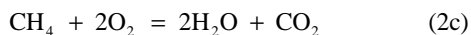
Of course, there are many ways, 11 over 3 (which equals (11 × 10 × 9)/(1 × 2 × 3) = 165) to be exact, by which three canonical proper equations may be selected from the 11 different equations, some of which appear chemically more

appropriate then others. The remaining equations in the complete set are:

$$CO_2 + H_2\ =\ CO + H_2O$$

$$CH_4 + H_2O\ =\ CO + 3H_2$$

$$CH_4 + CO_2\ =\ 2CO + 2H_2$$

$$CH_4 + 2H_2O\ =\ CO_2 + 4H_2$$

$$CH_4 + 3CO_2\ =\ 4CO + 2H_2O$$

$$2CH_4 + O_2\ =\ 2CO + 4H_2$$

$$2CH_4 + 3O_2\ =\ 2CO + 4H_2O$$

$$CH_4 + O_2\ =\ CO_2 + 2H_2$$

Any set of three equations fully characterizes the system as any other equation may be expressed as a linear combination of these basis equations. It is not necessary to generate all of them. In fact, the matrix methods are designed to produce only R independent equations. Which particular set is obtained depends on the order by which the chemical species are entered. This ambiguity clearly indicates that, as Smith and Missen [6] have observed, a canonical proper set is purely a matter of convenience with no essential chemical significance.

For a systematic approach, in any given list of species we drop all spectator species. If this results in an empty set, the list represented an NRS. If this is not the case, we can assign any one of the nonspectator species to a canonical equation. Eliminating this species from the list results in a reduced list with the value of R reduced by one. Applying this step recursively, eventually we arrive at an NRS. The immediately preceding list represents a single reaction system and a balanced equation can be found by any one of the standard methods. The least depth of nesting to reach an NRS is the number of independent reactions, R. Eliminating one species of the balanced equation from the original list leads to a reduced problem with R reduced by one. The same process is then applied until R proper canonical equations are generated.

In the calculation of the equilibrium composition of a system, it makes no difference which set of equations is taken as basic. At constant temperature and pressure, the equilibrium corresponds to the universal minimum of the Gibbs free energy, subject to the constraint of the mass and charge conservation [7]. If the system is at equilibrium with respect to R independent reactions, it is also at equilibrium with respect to any linear combination of these reactions. One might prefer to select as basic reactions those for which thermodynamic data are directly available, but again, if the data are available for a basic set, they can be easily derived for any other allowed process which need not be part of the canonical set.
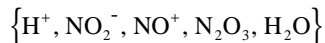
The equilibrium in a multireaction system, the complexation of thallium ion with nitric ion has been discussed by Cobranchi and Eyring [8]. The list of the chemical species is:

$$\{H^+, NO_2^-, HNO_2, NO^+, N_2O_3, Tl^+, TlNO_2, OH^-, H_2O\}$$
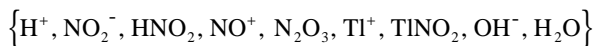
Inspection of the list immediately suggests the reactions:

$$Tl^+ + NO_2^- = TlNO_2 \qquad (3a)$$

$$H^+ + NO_2^- = HNO_2 \qquad (3b)$$

$$H^+ + OH^- = H_2O \qquad (3c)$$

If we delete either Tl^+ or $TlNO_2$ as unique to equation 3a, the other becomes a spectator species; therefore, we can drop both from the list. NO_2^- is common to equations 3a and 3b and H^+ is common to equations 3b and 3c. That leaves HNO_2 as unique to equation 3b. We still can select either OH^- or H_2O as the unique species in equation 3c. If we assign OH^- to equation 3c, the reduced list becomes:
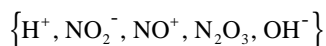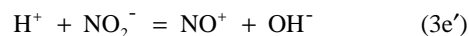
$$\{H^+, NO_2^-, NO^+, N_2O_3, H_2O\}$$

which contains

$$NO_2^- + NO^+ = N_2O_3 \qquad (3d)$$

and

$$2 H^+ + NO_2^- = H_2O + NO^+ \qquad (3e)$$

If we assign H_2O to equation 3c then

$$\{H^+, NO_2^-, NO^+, N_2O_3, OH^-\}$$

contains equation 3d and

$$H^+ + NO_2^- = NO^+ + OH^- \qquad (3e')$$

Nesting is five levels deep and the $R = 5$ equations, 3a to 3d and either 3e or 3e′, fully characterize this system. The system therefore requires five independent equilibrium constants.

The two rules on which the present approach is based are an extension of the fact that for a single reaction system without spectator species the elimination of any one species leads to a no reaction system. They allow us to determine the number of independent reactions, R, required to fully characterize the system. This number is unique. The choice of basis reactions for $R > 1$, however, is not unique, except if the reactions are not only mathematically independent but also chemically independent; that is, they have no chemical species in common. It is comforting to know that any set of R independent balanced equations represents a valid choice. The method discussed is not in any way tied to a particular method of balancing equations. Any appropriate technique: inspection, oxidation numbers, etc. will do, but without a systematic approach chemical intuition is unable to establish the value of R reliably. To be aware of the implications will, hopefully, prevent possible confusion in $R > 1$ systems.

References

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