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 **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 **A**.

3. At the end of these steps, the following are established:

   - the rank of the matrix **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.
$$\begin{array}{c} \\ \mathbf{A} = \end{array} \begin{array}{c} \begin{array}{cccccc} (1) & (2) & (3) & (4) & (5) & (6) \end{array} \\ \begin{pmatrix} 1 & 0 & 2 & 0 & 1 & 1 \\ 2 & 1 & 0 & 1 & 3 & 2 \\ 0 & 3 & 0 & 2 & 0 & 0 \\ -1 & 1 & 0 & 0 & -1 & 0 \end{pmatrix} \end{array} \tag{39}$$

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

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:

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

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

or, in conventional chemical form,

$$5ClO_3^- + 2H_3O^+ \quad = \quad Cl_2 + 3H_2O + 3ClO_3^- \tag{43}$$

$$8ClO_2^- + 8H_3O^+ \quad = \quad Cl_2 + 12H_2O + 6ClO_2 \tag{44}$$

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

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

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:

$$-1H^+ + 1OH^- + 1NO^+ + 0Tl^+ = 1NO_2^- \tag{47}$$
$$-1H^+ + 1OH^- + 2NO^+ + 0Tl^+ = 1N_2O_3 \tag{48}$$
$$0H^+ + 1OH^- + 1NO^+ + 0Tl^+ = 1HNO_2 \tag{49}$$
$$1H^+ + 1OH^- + 0NO^+ + 0Tl^+ = 1H_2O \tag{50}$$
$$-1H^+ + 1OH^- + 1NO^+ + 1Tl^+ = 1TlNO_2 \tag{51}$$

or, in conventional canonical form,

$$\mathrm{OH^- + NO^+} = \mathrm{H^+ + NO_2^-} \quad (52)$$

$$\mathrm{OH^- + 2NO^+} = \mathrm{H^+ + N_2O_3} \quad (53)$$

$$\mathrm{OH^- + NO^+} = \mathrm{HNO_2} \quad (54)$$

$$\mathrm{H^+ + OH^-} = \mathrm{H_2O} \quad (55)$$

$$\mathrm{OH^- + NO^+ + Tl^+} = \mathrm{H^+ + TlNO_2} \quad (56)$$

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

$$\begin{matrix} 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 2 & 2 & 1 & 1 & 0 \\ 4 & 0 & 0 & 2 & 0 & 2 \end{matrix} \quad (57)$$
   ```

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];
   TlNO2:=[0,2,1,1,0];
   ```

2. `transpose(array([Hplus,OHminus,H2O,NOplus,NO2minus,N2O3,HNO2,Tlplus,TlNO2]));`
   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

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

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.