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

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

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:

$$1\delta n_1 + 0\delta n_2 + 1\delta n_3 + 0\delta n_4 = 0 \tag{15}$$

$$0\delta n_1 + 2\delta n_2 + 2\delta n_3 + 1\delta n_4 = 0 \tag{16}$$

$$4\delta n_1 + 0\delta n_2 + 0\delta n_3 + 2\delta n_4 = 0 \tag{17}$$

The formula matrix **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 **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 $\mathbf{A}$, 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 $\mathbf{A}$ 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,

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (34)$$

$$2CO_2 = O_2 + 2CO \quad (35)$$

$$CH_4 + O_2 = CO_2 + 2H_2 \quad (36)$$

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