

### 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:

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

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

$$\mathbf{A}\mathbf{n} = \mathbf{b} \quad (12)$$

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

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

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

$$\mathbf{A}\delta\mathbf{n} = 0 \quad (14)$$

where  $\delta\mathbf{n}$  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 ( $\text{CH}_4=1$ ,  $\text{O}_2=2$ ,  $\text{CO}_2=3$ ,  $\text{H}_2\text{O}=4$ ), we write these equations for elements C, O, and H in turn as:

$$1\delta n_1 + 0\delta n_2 + 1\delta n_3 + 0\delta n_4 = 0 \quad (15)$$

$$0\delta n_1 + 2\delta n_2 + 2\delta n_3 + 1\delta n_4 = 0 \quad (16)$$

$$4\delta n_1 + 0\delta n_2 + 0\delta n_3 + 2\delta n_4 = 0 \quad (17)$$

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  $\delta n_4$ , corresponding to  $\text{H}_2\text{O}$ , 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  $\mathbf{A}^*$ :

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

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

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

$$0\delta n_1 + 1\delta n_2 + 0\delta n_3 + 1\delta n_4 = 0 \quad (20)$$

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

or

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

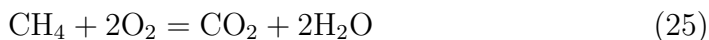
(Note that, in order to display a complete vector of unknowns on the left side of (22) containing all 4 unknowns, the trivial equation  $\delta n_4 = \delta n_4$  has been added to equations (19) to (21).) Either the set of equations (19) to (21) or equation (22) represents the general solution of equations (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

$$(\text{CH}_4, \text{O}_2, \text{CO}_2, \text{H}_2\text{O}) \begin{pmatrix} -1/2 \\ -1 \\ 1/2 \\ 1 \end{pmatrix} = 0 \quad (23)$$

or

$$-\frac{1}{2}\text{CH}_4 - 1\text{O}_2 + \frac{1}{2}\text{CO}_2 + 1\text{H}_2\text{O} = 0 \quad (24)$$

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



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

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

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

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

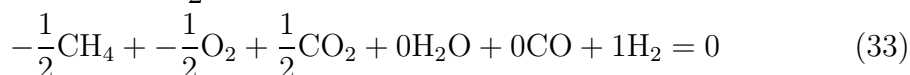
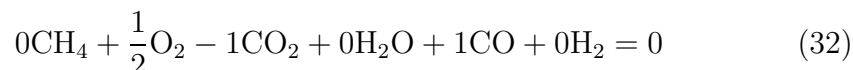
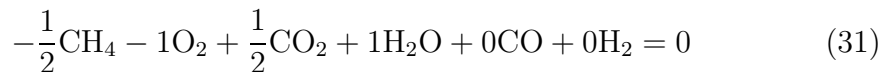
$$0\delta n_1 + 1\delta n_2 + 0\delta n_3 + 1\delta n_4 - \frac{1}{2}\delta n_5 + \frac{1}{2}\delta n_6 = 0 \quad (28)$$

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

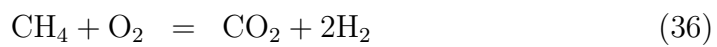
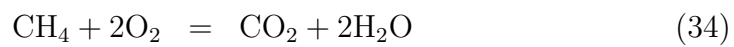
or

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

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:



or, as is usually written,



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