Reaction Stoichiometry

Consider a typical chemical reaction such as, for example, the combustion of heptane. In this reaction, heptane (C_7H_{16}), in the presence of oxygen (O_2), reacts to produce carbon dioxide (CO_2) and water (H_2O) according to the following reaction equation:

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O \tag{1}$$

This equation tells us what substances are reacting and which ones are being produced. The coefficients in a balanced reaction equation define the **mole ratios** among the substances that react and are produced. That is, the stoichiometric coefficients in the chemical reaction equation (1 for C_7H_{16}, 11 for O_2, and so on) tell us about the **relative number** of atoms of the various chemical species that react and are produced.

But how do we determine these stoichiometric coefficients? Well, in most cases, this is done by simply writing a series of balance equations for the individual elements involved in the reaction -- since, **in a chemical reaction, the number of atoms of each element must be conserved**. Then, by solving the resultant linear equations, we can easily determine the coefficients needed to properly balance the chemical reaction.

For example, let's assume that we do not know the stoichiometric coefficients for the combustion of heptane. In this case, we write the reaction equation with unknown coefficients as

$$a_1C_7H_{16} + a_2O_2 \rightarrow a_3CO_2 + a_4H_2O \tag{2}$$

and our goal is to determine the four unknown coefficients, a_1 through a_4. To do this, we write a balance for each element in the reaction, or

$$\text{moles of element x in products} \;-\; \text{moles of element x in reactants} \;=\; 0 \tag{3}$$

Now, doing this for each chemical element for the given reaction gives:

$$\text{C balance:} \quad a_3 - 7a_1 = 0 \tag{4a}$$

$$\text{O balance:} \quad 2a_3 + a_4 - 2a_2 = 0 \tag{4b}$$

$$\text{H balance:} \quad 2a_4 - 16a_1 = 0 \tag{4c}$$

This gives three independent equations -- but we have four unknowns!!! However, since the stoichiometric coefficients represent **mole ratios**, we are free to normalize one of the coefficients as desired, where this is usually done so that integer coefficients result for all the other unknowns (since, on an elemental basis, we must have an integer number of atoms involved in the reaction). Thus, for our 4^{th} independent equation, we will set $a_1 = \alpha$, where α is a variable integer that can be modified, as needed, to give integer solutions for all the stoichiometric coefficients.

The above four equations, in matrix form, give

$$\begin{bmatrix} -7 & 0 & 1 & 0 \\ 0 & -2 & 2 & 1 \\ -16 & 0 & 0 & 2 \\ 1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ \alpha \end{bmatrix} \tag{5}$$

and the solution to this system, with α set to some integer, should give the desired coefficients of the balanced reaction equation.

To see this, we can solve this system in Matlab (with $\alpha = 1$) to give:

```
>>    A = [-7 0 1 0;0 -2 2 1;-16 0 0 2;1 0 0 0];
      b = [0 0 0 1]';
      a = A\b

a =

     1
    11
     7
     8
```

and, clearly, this is the correct solution for the current problem [compare these results to the coefficients in eqn. (1)].

As another (rather random) example, consider the following reaction (taken from the 7th Ed. of ***Basic Principles and Calculations in Chemical Engineering*** by Himmelblau and Riggs):

$$a_1 As_2S_3 + a_2 H_2O + a_3 HNO_3 \rightarrow a_4 NO + a_5 H_3AsO_4 + a_6 H_2SO_4 \tag{6}$$

Performing the individual element balances gives:

N balance: $a_4 - a_3 = 0$ (7a)

O balance: $a_4 + 4a_5 + 4a_6 - a_2 - 3a_3 = 0$ (7b)

H balance: $3a_5 + 2a_6 - 2a_2 - a_3 = 0$ (7c)

As balance: $a_5 - 2a_1 = 0$ (7d)

S balance: $a_6 - 3a_1 = 0$ (7e)

These equations, along with the normalization $a_1 = \alpha$, gives a system of six equations with six unknowns. Writing these in matrix form gives

$$\begin{bmatrix} 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & -1 & -3 & 1 & 4 & 4 \\ 0 & -2 & -1 & 0 & 3 & 2 \\ -2 & 0 & 0 & 0 & 1 & 0 \\ -3 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \\ a_6 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \alpha \end{bmatrix} \tag{8}$$

and, when implemented into Matlab with $\alpha = 1$, we have

```
>>    A = [ 0 0 -1 1 0 0; 0 -1 -3 1 4 4; 0 -2 -1 0 3 2;
           -2 0  0 0 1 0;-3  0  0 0 0 1; 1  0  0 0 0 0];
      b = [0 0 0 0 0 1]';
      a = A\b
```

```
a =
    1.0000
    1.3333
    9.3333
    9.3333
    2.0000
    3.0000
```

Now, although this is a correct solution, not all the stoichiometric coefficients are integers. However, with values like 1.3333 and 9.3333, we can convert these to integers by simply re-normalizing to $a_1 = \alpha = 3$. Doing this in Matlab gives

```
>>    b = [0 0 0 0 0 3]';
      a = A\b

a =
    3.0000
    4.0000
   28.0000
   28.0000
    6.0000
    9.0000
```

Thus, the properly balanced reaction equation for this example is

$$3\,As_2S_3 + 4\,H_2O + 28\,HNO_3 \rightarrow 28\,NO + 6\,H_3AsO_4 + 9\,H_2SO_4 \tag{9}$$

From a broader view, the reaction stoichiometry applications illustrated here lead to a system of linear algebraic equations that could be easily solved within Matlab with the backslash operator. Thus, since the solution procedure is so simple, the challenge here (as in most real problems) becomes the proper setup of the pertinent equations and the analysis and use of the Matlab results. Hopefully, this application in balancing chemical reaction equations will serve as another example of how to work with a variety of similar problem scenarios that you may encounter!