Chemical Stoichiometry Using MATLAB

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Abstract

In beginning chemistry courses, students are taught a variety of techniques for balancing chemical equations. The determination of the stoichiometric coefficients in a chemical equation is mathematically equivalent to solving a system of linear algebraic equations, a problem for which MATLAB is ideally suited. Using MATLAB, it is possible to balance equations describing all kinds of chemical transformations, including acid-base reactions, redox reactions, electrochemical half-reactions, combustion reactions, and synthetic reactions. MATLAB is especially convenient for balancing chemical equations that are difficult to treat by traditional methods.

Introduction

A number of different techniques have traditionally been taught in beginning chemistry courses for balancing chemical reactions. Three methods are commonly found in introductory textbooks [1–3]:

- ***Inspection.*** In its simplest form, this method may be little more than intelligent guessing. For this reason, it is sometimes called the *trial-and-error method*. Students may be taught various rules of thumb that make the method more efficient. (e.g., "start with an element that appears in just one species on each side of the equation.")

- ***Half-Equation Method.*** This approach, also called the *ion-electron method*, is used for balancing oxidation-reduction (redox) reactions. The reaction is divided into two half reactions, one for oxidation, the other for reduction. These half reactions are balanced separately, then combined to form a balanced redox reaction.

- ***Oxidation Number Method.*** This is another approach for balancing redox reactions. The first step is to assign oxidation numbers to the elements involved in the reaction. The oxidation numbers are balanced, after which the anions, cations, and remaining elements are balanced by inspection.

There is a fourth method, which is arguably more general and powerful than the other three:

- ***Algebraic Method.*** The unbalanced chemical equation is used to define a system of linear equations, which can then be solved to yield the stoichiometric coefficients [4, 5].

The algebraic method has traditionally been less popular than the alternatives, probably because of the inconveniences related to solving systems of equations. However, modern mathematics software handle such systems with ease, making the algebraic method much more attractive.

A Simple Example

The algebraic method is perhaps best grasped by way of an example. The combustion of methane in oxygen can be represented by the chemical equation

$$x_1 CH_4 + x_2 O_2 \rightarrow x_3 CO_2 + x_4 H_2O$$

Our task is to determine the unknown coefficients x_1, x_2, x_3, and x_4. There are three elements involved in this reaction: carbon (C), hydrogen (H), and oxygen (O). A balance equation can be written for each of these elements:

$$\begin{aligned}
&\text{Carbon (C):}\ 1\cdot x_1 + 0\cdot x_2 = 1\cdot x_3 + 0\cdot x_4\\
&\text{Hydrogen (H):}\ 4\cdot x_1 + 0\cdot x_2 = 0\cdot x_3 + 2\cdot x_4\\
&\text{Oxygen (O):}\ 0\cdot x_1 + 2\cdot x_2 = 2\cdot x_3 + 1\cdot x_4
\end{aligned}$$

We write these as homogeneous equations, each having zero on its right hand side:

$$\begin{aligned}
&x_1 - x_3 = 0\\
&4x_1 - 2x_4 = 0\\
&2x_2 - 2x_3 - x_4 = 0
\end{aligned}$$

At this point, we have three equations in four unknowns. To complete the system, we define an auxiliary equation by arbitrarily choosing a value for one of the coefficients:

$$x_4 = 1$$

The complete system of equations can be written in matrix form as **Ax** = **b**, where

$$\mathbf{A} = \begin{bmatrix} 1 & 0 & -1 & 0 \\ 4 & 0 & 0 & -2 \\ 0 & 2 & -2 & -1 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \quad \mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix}, \quad \mathbf{b} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

Next we consider how this system can be solved using MATLAB.

The MATLAB Solution

MATLAB is a general-purpose mathematics program that was originally designed to solve problems involving matrices. (The name MATLAB is a contraction of *Matrix Laboratory*.) This program is ideally suited for solving matrix equations of the form **Ax** = **b**.

After starting MATLAB, we enter the matrix **A** and the column vector **b**. (In what follows, » is the MATLAB prompt.)

```
» A = [
1 0 -1 0
4 0 0 -2
0 2 -2 -1
0 0 0 1];
```

```
» b = [
0
0
0
1];
```

Next we compute **x** = $\mathbf{A}^{-1}\mathbf{b}$, in which $\mathbf{A}^{-1}$ is the inverse of **A**. The function inv() computes matrix inverses:

```
» x = inv(A)*b

x =

    0.5000
    1.0000
    0.5000
    1.0000
```

Finally, we note that the stoichiometric coefficients are usually chosen to be integers. Divide the vector **x** by its smallest value:

```
» x = x/0.5

x =

     1
     2
     1
     2
```

Thus, the balanced equation is

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Conservation of Mass and Charge

The reaction shown in the first example could easily be balanced by inspection. Not so with the following equation:

$$x_1Cr_2O_7^{2-} + x_2Fe^{2+} + x_3H^+ \rightarrow x_4Cr^{3+} + x_5Fe^{3+} + x_6H_2O$$

At first glance, it might appear that this equation cannot be balanced algebraically because there are six unknown stoichiometric coefficients but only four elements to conserve (Cr, O, Fe, and H). However, charge must be conserved as well, giving rise to another balance equation. That, plus an auxiliary equation setting the value of one coefficient, yields six equations in six unknowns:

Chromium (Cr): $2x_1 - x_4 = 0$
Oxygen (O): $7x_1 - x_6 = 0$
Iron (Fe): $x_2 - x_5 = 0$
Hydrogen (H): $x_3 - 2x_6 = 0$
Charge (+): $-2x_1 + 2x_2 + x_3 - 3x_4 - 3x_5 = 0$
(*): $x_6 = 1$

From these equations we obtain

$$A = \begin{bmatrix} 2 & 0 & 0 & -1 & 0 & 0 \\ 7 & 0 & 0 & 0 & 0 & -1 \\ 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & 0 & -2 \\ -2 & 2 & 1 & -3 & -3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad b = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

Using MATLAB, the unknown stoichiometric coefficients are quickly determined. First we enter **A** and **b**:

```
»  A = [
2 0 0 -1 0 0
7 0 0 0 0 -1
0 1 0 0 -1 0
0 0 1 0 0 -2
-2 2 1 -3 -3 0
0 0 0 0 0 1];

» b = [
0
0
0
0
0
1];
```

Next we solve the system, this time using the left division operator (\) instead of the inv() function. The left division operator uses LU factorization rather than matrix inversion, and is the preferred method of solution:

```
» x = A\b

x =

    0.1429
    0.8571
    2.0000
    0.2857
    0.8571
    1.0000
```

We divide by the smallest value of **x** to obtain integral coefficients. In the this case, the smallest value is found in the first element, designated by x(1):

```
» x = x/x(1)

x =

    1.0000
    6.0000
   14.0000
    2.0000
    6.0000
    7.0000
```

Thus we obtain

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

A DifficultRedox Reaction

The oxidation number and half-reaction methods are normally recommended for balancing redox reactions. However, neither method works well on the following reaction [6]:

$$x_1P_2I_4 + x_2P_4 + x_3H_2O \rightarrow x_4PH_4I + x_5H_3PO_4$$

What makes this reaction difficult is that phosphorus appears in four different oxidation states. Nevertheless, we can easily balance this reaction using MATLAB:

```
» A = [
2 4 0 -1 -1
4 0 0 -1 0
0 0 2 -4 -3
0 0 1 0 -4
0 0 0 0 1
];

» b = [
0
0
0
0
1];

» x = A\b

x =

    0.3125
    0.4062
    4.0000
    1.2500
    1.0000
```

We divide by the first element of **x** to obtain integral coefficients:

```
» x = x/x(1)

x =

    1.0000
    1.3000
   12.8000
    4.0000
    3.2000
```

This does not yield integral coefficients, but multiplying by 10 will do the trick:

```
» x = x * 10

x =

    10
    13
   128
    40
    32
```

The balanced equation is

$$10\,P_2I_4 + 13\,P_4 + 128\,H_2O \rightarrow 40\,PH_4I + 32\,H_3PO_4$$

Underdetermined Systems

Some reactions cannot be balanced by the algebraic method as presented here. One such reaction is the oxidation of hydrogen peroxide by permanganate ion in acid solutions:

$$x_1MnO_4^- + x_2H_2O_2 + x_3H^+ \rightarrow x_4Mn^{2+} + x_5O_2 + x_6H_2O$$

This equation contains six unknowns. We can write four independent balances and an auxiliary equation, giving a total of five equations. Thus the system is underdetermined, having infinitely many solutions [6, 7]:

$$\begin{aligned}
&2\,MnO_4^- + 3\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 4\,O_2 + 6\,H_2O\\
&2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O\\
&2\,MnO_4^- + 7\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 6\,O_2 + 10\,H_2O\\
&\qquad\vdots\\
&2\,MnO_4^- + (5+2n)\,H_2O_2 + 3H^+ \rightarrow 2\,Mn^{2+} + (5+n)\,O_2 + (8+2n)\,H_2O
\end{aligned}$$

The problem here is that there are really two chemical reactions occurring independently. One reaction is the reduction of permanganate ion, the other is the disproportionation of hydrogen peroxide [7, 8]:

$$\begin{aligned}
&2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O\\
&2\,H_2O_2 \rightarrow O_2 + 2\,H_2O
\end{aligned}$$

Summary

The procedure for balancing a chemical equation with MATLAB may be summarized as follows:

1. Write the chemical equation showing the n unknown coefficients $x_1, x_2, \ldots, x_n$.

2. Write a balance equation for each of $(n - 1)$ conserved quantities (elements and charge).

3. Write an auxiliary equation setting the value of one of the unknowns.

4. Express the system in the form $\mathbf{Ax} = \mathbf{b}$.

5. Start MATLAB and enter the matrix **A** and column vector **b**.

6. Solve the system $\mathbf{Ax} = \mathbf{b}$ for **x** using either the inv() function or the left division operator (\).
7. If necessary, scale **x** to obtain integral coefficients.

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