Balancing chemical equations using linear algebra

Rune N. T. Thorsen - 201505509

August 15, 2020

Sometimes it can be a bit hard to balance a chemical equation. Using linear algebra and a calculator it can make such a task a lot easier.

1 A short recap of the maths involved

Suppose you have n different linear equations with n different variables. Furthermore, suppose that this set of equations can actuallæy be solved, meaning that you could correctly find the value of each of the n variables.

These equations could be written as follows:

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n &= b_1, \\ a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n &= b_2, \\ &\vdots \\ a_{n1}x_1 + a_{n2}x_2 + \cdots + a_{nn}x_n &= b_n. \end{aligned}$$

Now doing a notational trick (where the variables x_i is left out), one could write these in matrix form:

$$\left(\begin{array}{cccc|c} a_{11} & a_{12} & \cdots & a_{1n} & b_1 \\ a_{21} & a_{22} & \cdots & a_{2n} & b_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} & b_n \end{array}\right).$$

Let A be the matrix without the right hand side of each equation:

$$A = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix},$$

and b be the vector of values on the right hand side of each equation:

$$b = \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix}.$$

Now let I denote the identity matrix of size n:

$$I = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{pmatrix}.$$

In other words, I has the number 1 on each entry in it's diagonal going from the top left down to the bottom right and 0 on any other entry, with n columns and n rows.

If the matrix A can be brought to look like I, it is said to be *row equivalent* to I. Likewise I is row equivalent to A. It is written

$$A \sim I,$$

or

$$I \sim A$$

respectively.

Since the set of equations can be solved (ie. it is possible to find the value of each x_i), it is indeed true, that A is row equivalent to I.

Now let A^{-1} be the inverse matrix of A, such that:

$$A^{-1}A = I.$$

As it is implied above, it is indeed true, that

$$Ax = b.$$

Due to how linear algebra works, this means that if

$$A^{-1}A = I$$

then

$$A^{-1}b$$

will give a vector, c, where the i'th entry in c is equal to x_i.

If it is unknown if a set of linear equations can be solved, then you could compute the determinant of A, denoted $det(A)$ and if this is equal to 0, then the system of linear equations simply cannot be solved. If it can be solved however, then it is true, that

$$det(A) \neq 0.$$

2 Converting a chemical equation into a set of linear mathematical equations

In general a chemical equation will look like the following:

$$\mathrm{aA} \quad + \quad \mathrm{bB} \longrightarrow \mathrm{cC} \quad + \quad \mathrm{dD}.$$

Now it would be interesting to treat this like a set of linear mathematical equations.

In order to do this, we need to apply some rules:

1. When dealing with redox equations, if it takes place in an acidic or in a basic environment, then you should firstly always write H^+ or OH^- on the left side of the equation (H^+ for an acidic environment and OH^- for a basic environment) and H_2O on the right side of the equation,

2. Once the above rule has been followed, you must know all reactants and all products of the reaction,

3. As variables we will use the the coefficients of each species in the chemical equation,

4. A linear mathematical equation is made by letting the reaction arrow show where to put the equal sign,

5. There needs to be an equation for each distinct type of atom,

6. If the i'th chemical species (read from left to right in the chemical equation) contains k of the j'th atom in the chemical equation, then $a_{ji} = k$,
7. A helper equation is always needed, where the first coefficient is set to 1,
8. When dealing with redox equations, an equation is needed to deal with conservation of charge, where the charge of a chemical species is used as the coefficient of the species' coefficient,
9. Once all necessary equations have been generated, the chemical coefficients (the mathematical variables) and their respective (mathematical) coefficients should be moved to the left side of each equation, but the helper equation should not have it's 1 moved to the left side.

2.1 Balancing a normal chemical equations using linear algebra

In order to balance the chemical equation above, with arbitrary coefficients and compounds you should follow rules 2-7 and rule 9, since rule 1 and rule 8 only apply to redox reactions.

Rule 2 is automatically followed in this case.
Rule 3 dictates, that you will have 4 coefficients in each equation; a, b, c and d.
If we let each of the 4 chemical species be a single atom, except for B, which we let be equal to B_2, then we need 4 equations, one for each distinct type of atom, in accordance with rule 5. In accordance with rule 4 and 6, we let the 4 equations be[1]:

$$\begin{aligned}
1 \cdot a + 0 \cdot b &= 0 \cdot c + 0 \cdot d && \text{for atom A,}\\
0 \cdot a + 2 \cdot b &= 0 \cdot c + 0 \cdot d && \text{for atom B,}\\
0 \cdot a + 0 \cdot b &= 1 \cdot c + 0 \cdot d && \text{for atom C,}\\
0 \cdot a + 0 \cdot b &= 0 \cdot c + 1 \cdot d && \text{for atom D.}
\end{aligned}$$

Now you need to fulfill rule 7 and thus a 5'th equation is needed:

$$1 \cdot a + 0 \cdot b = 0 \cdot c + 0 \cdot d + 1.$$

Once this is done all that is left is for you to fulfill the last rule, rule number 9. And thus your set of equations should become:

$$\begin{aligned}
1 \cdot a + 0 \cdot b + 0 \cdot c + 0 \cdot d &= 0,\\
0 \cdot a + 2 \cdot b + 0 \cdot c + 0 \cdot d &= 0,\\
0 \cdot a + 0 \cdot b - 1 \cdot c + 0 \cdot d &= 0,\\
0 \cdot a + 0 \cdot b + 0 \cdot c - 1 \cdot d &= 0,\\
1 \cdot a + 0 \cdot b + 0 \cdot c + 0 \cdot d &= 1.
\end{aligned}$$

Now if you let the right side of equation l be the l'th entry in the vector b from before and fill the coefficients into a matrix, like you did in A before, then this checmical equation can be checked for solutions as described in section 1[2]. If solutions for this chemcical equation exists it can be found as described in section 1[3]. Once a solution has been found, it may be necessary to multiply each of the coefficients found with some constant, so as to make sure that there is only integers present in the resulting chemical equation.

[1] Of course not all sets of equations generated following the rules will be this simple.

[2] Please note that even if the set of equations can be solved, this does most certainly not mean, that the chemical reaction can necessarily occur – there can be rules in chemistry that are not accounted for, that can prohibit the reaction from occuringt.

[3] Note that due to how matrix multiplication works, if the helper equation is set to be the m'th equation in the matrix, then the solution vector c, from section 1, will have the same entries as the m'th column in the inverse matrix.

2.2 Balancing a redox reaction using linear algebra

In order to balance a redox reaction, you first need to modify the chemical equation, in accordance with rule 1.

Let's say that the chemical equation looks like the following:

$$\mathrm{aA^+} \quad + \quad \mathrm{bB} \longrightarrow \mathrm{cC} \quad + \quad \mathrm{dD^+}.$$

Then it should be changed to

$$\begin{cases} \mathrm{eH^+} \quad + \quad \mathrm{aA^+} \quad + \quad \mathrm{bB} \longrightarrow \mathrm{cC} \quad + \quad \mathrm{dD^+} \quad + \quad \mathrm{fH_2O} & \text{for an acidic environment,} \\ \mathrm{eOH^-} \quad + \quad \mathrm{aA^+} \quad + \quad \mathrm{bB} \longrightarrow \mathrm{cC} \quad + \quad \mathrm{dD^+} \quad + \quad \mathrm{fH_2O} & \text{for a basic environment.} \end{cases}$$

The rules 2-7 is now applied and the same equations as before arises, with the exception that now there is also variables for the species that was added by applying rule 1, which also leads to two more equations due to rule 5.

Rule 8 now has to be followed. A new linear equation is made with the k'th coefficient set to the charge of the k'th chemical species.

Lastly rule 9 has to be followed once again.

Once all this is done the chemical equation can again be balanced using the method described in section 1.