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A concise description of an old problem: application of matrices to obtain the balancing coefficients of chemical equations

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It is not difficult to balance chemical equations and thus it is hardly given more thoughts. However, there is a mathematical principle for the balancing of chemical equations and this principle may be used for automation. The balancing of chemical equation is carried out, by formulating a reaction matrix and the latter is used in a matrix equation. The matrix equation is then solved to obtain the balancing coefficients. The conventional matrix inverse method cannot always be used and hence the solution is obtained by row reduced operations. These operations and any matrix manipulation are carried out with Matlab. Further this novel method can be used to classify chemical equations as nonfeasible, unique and nonunique.

KEY WORDS: balancing equations, matrices

1. Introduction

Simple chemical equations are easy to balance but more time is required for other equations, particularly redox equations. In general, the balancing coefficients are obtained by trial and error [1]. Thus chemical equations are sometimes so easy to balance that it is hardly given more thought. However, there are chemical equations which take more time for balancing [2–4] and it happens that sometimes when it is difficult to obtain the balancing coefficient, questions such as: Does the chemical reaction occur?, are asked. Well, it is very important to note that there is no need for a chemical reaction to occur for its chemical equation to be balanced and more important it is not required for a chemical reaction to occur in case its chemical equation is balanced.

This paper illustrates the mathematical procedure of balancing chemical equations, using suitable examples, and the novel procedure used is based on fundamental laws. In fact a reaction matrix [5] is formulated and the latter is used in a matrix equation, which is then solved to obtain, if any, the balancing coefficients. Matrix manipulations are carried out using Matlab[1], where in-built commands perform the necessary operations.

[1] Matlab is a registered trademark.

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Other softwares [6] such as Mathematica or Maple can also be used. Further the characteristics of the reaction matrix formulated may be used to classify chemical reactions as nonfeasible, unique and non-unique.

2. Formulation of the reaction matrix

Consider a chemical equation such as:

$$c_1\,\mathrm{HgS} + c_2\,\mathrm{HCl} + c_3\,\mathrm{HNO_3} \;\rightarrow\; c_4\,\mathrm{H_2\,HgCl_4} + c_5\,\mathrm{NO} + c_6\,\mathrm{S} + c_7\,\mathrm{H_2O}.$$

It is required to obtain the values of the coefficients c_i $(i = 1, \ldots, 7)$ and in general the following principles are applied:

(a) The law of conservation of atom.

(b) The law of electrical neutrality.

Applying the conservation of atom to the above chemical equation, the following mathematical equations can be obtained:

- $c_1 = c_4$ (for Hg atom) or

$$1 \cdot c_1 + 0 \cdot c_2 + 0 \cdot c_3 + (-1) \cdot c_4 + 0 \cdot c_5 + 0 \cdot c_6 + 0 \cdot c_7 = 0;$$

- $c_1 = c_6$ (for S atom) or

$$1 \cdot c_1 + 0 \cdot c_2 + 0 \cdot c_3 + 0 \cdot c_4 + 0 \cdot c_5 + (-1) \cdot c_6 + 0 \cdot c_7 = 0;$$

- $c_2 + c_3 = 2 \cdot c_4 + 2 \cdot c_7$ (for H atom) or

$$1 \cdot c_1 + 0 \cdot c_2 + 1 \cdot c_3 + (-2) \cdot c_4 + 0 \cdot c_5 + 0 \cdot c_6 + (-2) \cdot c_7 = 0;$$

- $c_2 = 4 \cdot c_4$ (for Cl atom) or

$$0 \cdot c_1 + 1 \cdot c_2 + 0 \cdot c_3 + (-4) \cdot c_4 + 0 \cdot c_5 + 0 \cdot c_6 + 1 \cdot c_7 = 0;$$

- $c_3 = c_5$ (for N atom) or

$$0 \cdot c_1 + 0 \cdot c_2 + 1 \cdot c_3 + 0 \cdot c_4 + (-1) \cdot c_5 + 0 \cdot c_6 + 0 \cdot c_7 = 0;$$

- $3 \cdot c_3 = c_5 + c_7$ (for O atom) or

$$0 \cdot c_1 + 0 \cdot c_2 + 3 \cdot c_3 + 0 \cdot c_4 + (-1) \cdot c_5 + 0 \cdot c_6 + (-1) \cdot c_7 = 0.$$

These equations may be written in matrix form as

$$\begin{pmatrix} 1 & 0 & 0 & -1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 1 & 1 & -2 & 0 & 0 & -2 \\ 0 & 1 & 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 3 & 0 & -1 & 0 & -1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \\ c_7 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

or

$$\mathbf{RC} = 0. \tag{1}$$

Equation (1) is said to be the matrix equation where **R** is said to be the reaction matrix and **C** is a matrix of stoichiometric coefficients.

The reaction matrix can otherwise be obtained by considering that there are x distinct elements and y reactants and products in a reaction. The entry r_{ij} of the reaction matrix **R** is the number of atoms of type i in each compound ($1 \leqslant i \leqslant x$ and $1 \leqslant j \leqslant y$). Also r_{ij} takes positive or negative value according to whether it corresponds to a reactant or a product. For the chemical reaction given above, **R** can therefore be written as:

	HgS	HCl	HNO_3	H_2HgCl_4	NO	S	H_2O
Hg	1	0	0	–1	0	0	0
H	1	0	0	0	0	–1	0
S	0	1	1	–2	0	0	–2
Cl	0	1	0	–4	0	0	0
N	0	0	1	0	–1	0	0
O	0	0	3	0	–1	0	–1

Once the reaction matrix is formulated, it is used in the matrix equation and the latter has to be solved to obtain the balancing coefficients. However, solution of the matrix equation presents a major difficulty since the inverse of the reaction matrix **R** cannot always be obtained. Hence the conventional matrix inversion method cannot always be used. The solution may be obtained by row reduced operations and the general solution of equation (1) is $\mathbf{C} = (\mathbf{I} - \mathbf{R}')\mathbf{Z}$ [7,8], where:

(a) **Z** is an arbitrary vector;

(b) $\mathbf{R}'$ as to be computed.

$\mathbf{R}'$ can be computed as described below.

- Let the transpose of **R** be denoted by $\mathbf{R}^{\mathrm{t}}$ (command in Matlab is $\mathbf{R}^{\mathrm{t}} = \mathsf{transpose}(\mathbf{R})$).
- Let the row reduced from of **R** be **RR** (command in Matlab is $\mathbf{RR} = \mathsf{rref}(\mathbf{R})$).
- Let the row reduced form of $\mathbf{R}^{\mathrm{t}}$ be $\mathbf{RR}^{\mathrm{t}}$.
- $\mathbf{R}'$ is computed as $\mathbf{R}' = \mathbf{RR}^{\mathrm{t}} \times \mathbf{RR}$.

If the rank [9] of the reaction matrix is r, it is found that the rank of $\mathbf{I} - \mathbf{R}'$ is $p = y - r$. p is also said to be the *nullity* of the reaction matrix and the matrix is an $y \times y$ matrix with $y - r$ nonzero columns.

Further, using this procedure, it is possible to classify chemical reactions as:

(a) *Nonfeasible*, when $r = y$ and thus $\mathbf{C} = 0$.

(b) *Unique*, when $r = y - 1$.

(c) *Nonunique*, when $r \leqslant y - 2$.

For the chemical reaction given above, the computation of $\mathbf{R}'$ once the reaction matrix is formulated is carried out with Matlab as illustrated below. In this case $y = 7$; $\text{rank}(\mathbf{R}) = r = 6$. Thus chemical reaction classified as unique.

$$\mathbf{R}^{\text{t}} = \begin{pmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 3 \\ -1 & 0 & -2 & -4 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & -1 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -2 & 0 & 0 & -1 \end{pmatrix}, \quad \mathbf{RR} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & -0.75 \\ 0 & 1 & 0 & 0 & 0 & 0 & -3 \\ 0 & 0 & 1 & 0 & 0 & 0 & -0.50 \\ 0 & 0 & 0 & 1 & 0 & 0 & -0.75 \\ 0 & 0 & 0 & 0 & 1 & 0 & -0.50 \\ 0 & 0 & 0 & 0 & 0 & 1 & -0.75 \end{pmatrix},$$

$$\mathbf{RR}^{\text{t}} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad \mathbf{R}' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & -0.75 \\ 0 & 1 & 0 & 0 & 0 & -3 \\ 0 & 0 & 1 & 0 & 0 & -0.5 \\ 0 & 0 & 0 & 1 & 0 & -0.75 \\ 0 & 0 & 0 & 0 & 1 & -0.5 \\ 0 & 0 & 0 & 0 & 0 & -0.75 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\mathbf{I} - \mathbf{R}' = \frac{1}{4} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 3 \\ 0 & 0 & 0 & 0 & 0 & 12 \\ 0 & 0 & 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 & 3 \\ 0 & 0 & 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 & 3 \\ 0 & 0 & 0 & 0 & 0 & 4 \end{pmatrix}.$$

Thus the balancing coefficients correspond to the column vector (3 12 2 3 2 3 4), taking the arbitrary column vector $\mathbf{Z}$ to be (0 0 0 0 0 1).

Further examples are given and on the basis of the characteristics of the reaction matrix, the chemical equations are classified as:

(a) Unique.

(b) Nonfeasible.

(c) Nonunique.

3. Unique case

Consider a chemical equation such as:

$$c_1\, MnO_4^- + c_2\, H^+ + c_3\, Fe^{2+} \;\rightarrow\; c_4\, Mn^{2+} + c_5\, H_2O + c_6\, Fe^{3+}.$$

The reaction matrix **R**, after making use of law of conservation of atom and law of electrical neutrality, can therefore be written as:

$$R = \begin{pmatrix} 1 & 0 & 0 & -1 & 0 & 0 \\ 4 & 0 & 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 & -2 & 0 \\ 0 & 0 & 1 & 0 & 0 & -1 \\ -1 & 1 & 2 & -2 & 0 & -3 \end{pmatrix}.$$

$y = 6$; $\operatorname{rank}(\mathbf{R}) = r = 5$. Thus chemical reaction classified as unique.

$$\mathbf{R}^{\mathrm{t}} = \begin{pmatrix} 1 & 4 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 2 \\ -1 & 0 & 0 & 0 & -2 \\ 0 & -1 & -2 & 0 & 0 \\ 0 & 0 & 0 & -1 & -3 \end{pmatrix}, \qquad \mathbf{RR} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & -0.2 \\ 0 & 1 & 0 & 0 & 0 & -1.6 \\ 0 & 0 & 1 & 0 & 0 & -1.0 \\ 0 & 0 & 0 & 1 & 0 & -0.2 \\ 0 & 0 & 0 & 0 & 1 & -0.8 \end{pmatrix},$$

$$\mathbf{RR}^{\mathrm{t}} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \qquad \mathbf{R}' = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & -0.2 \\ 0 & 1 & 0 & 0 & 0 & -1.6 \\ 0 & 0 & 1 & 0 & 0 & -1.0 \\ 0 & 0 & 0 & 1 & 0 & -0.2 \\ 0 & 0 & 0 & 0 & 1 & -0.8 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\mathbf{I} - \mathbf{R}' = \frac{1}{5} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 8 \\ 0 & 0 & 0 & 0 & 0 & 5 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 4 \\ 0 & 0 & 0 & 0 & 0 & 5 \end{pmatrix}.$$

Hence it is possible to balance this chemical equation in a unique way and the balancing coefficients correspond to the column vector (1 8 5 1 4 5), taking the arbitrary column vector **Z** to be (0 0 0 0 0 1).

4. Nonfeasible case

Consider a chemical equation such as:

$$c_1\,\mathrm{NO_2} + c_2\,\mathrm{H_2O} \;\rightarrow\; c_3\,\mathrm{HNO_3}.$$

The reaction matrix **R** can therefore be written as:

$$\mathbf{R} = \begin{pmatrix} 1 & 0 & -1 \\ 2 & 1 & -3 \\ 0 & 2 & -3 \end{pmatrix}.$$

$y = 3$; $\text{rank}(\mathbf{R}) = r = 3$. Thus chemical reaction classified as nonfeasible. It is interesting to note that only elementary reactions do really occur. Complicated chemical reactions usually represent overall reactions. A nonfeasible equation means that the species given cannot for an overall reaction equation. We have:

$$\mathbf{R}^{\mathrm{t}} = \begin{pmatrix} 1 & 2 & 0 \\ 0 & 1 & 2 \\ -1 & -3 & -1 \end{pmatrix}, \quad \mathbf{RR} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{RR}^{\mathrm{t}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\mathbf{R}' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{I} - \mathbf{R}' = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

Hence it is not possible to balance this chemical equation.

5. Nonunique case

Consider a chemical equation such as:

$$c_1\,\mathrm{NaClO_3} + c_2\,\mathrm{HCl} \rightarrow c_3\,\mathrm{NaCl} + c_4\,\mathrm{ClO_2} + c_5\,\mathrm{Cl_2} + c_6\,\mathrm{H_2O}.$$

The reaction matrix **R** can therefore be written as:

$$\mathbf{R} = \begin{pmatrix} 1 & 0 & -1 & 0 & 0 & 0 \\ 1 & 1 & -1 & -1 & -2 & 0 \\ 3 & 0 & 0 & -2 & 0 & -1 \\ 0 & 1 & 0 & 0 & 0 & -2 \end{pmatrix}.$$

$y = 6$; $\text{rank}(\mathbf{R}) = r = 4$. Thus chemical reaction classified as nonunique. We have:

$$\mathbf{R}^{\mathrm{t}} = \begin{pmatrix} 1 & 1 & 3 & 0 \\ 0 & 1 & 0 & 1 \\ -1 & -1 & 0 & 0 \\ 0 & -1 & -2 & 0 \\ 0 & -2 & 0 & 0 \\ 0 & 0 & -1 & -2 \end{pmatrix}, \quad \mathbf{RR} = \begin{pmatrix} 1 & 0 & 0 & 0 & 1.33 & -1.67 \\ 0 & 1 & 0 & 0 & 0 & -2 \\ 0 & 0 & 1 & 0 & 1.33 & -1.67 \\ 0 & 0 & 0 & 1 & 2 & -2 \end{pmatrix},$$

$$\mathbf{RR}^{\mathrm{t}} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad \mathbf{R}' = \begin{pmatrix} 1 & 0 & 0 & 0 & 1.33 & -1.67 \\ 0 & 1 & 0 & 0 & 0 & -2 \\ 0 & 0 & 1 & 0 & 1.33 & -1.67 \\ 0 & 0 & 0 & 1 & 2 & -2 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\mathbf{I}-\mathbf{R}'=\frac{1}{3}\begin{pmatrix}0&0&0&0&-4&5\\0&0&0&0&0&6\\0&0&0&0&-4&5\\0&0&0&0&6&6\\0&0&0&0&3&0\\0&0&0&0&0&3\end{pmatrix}.$$

Hence it is not possible to balance this chemical equation in a unique way. If the arbitrary column vector is taken to be (0 0 0 0 0 1), then the set of balancing coefficients corresponds to (5 6 5 6 0 3) and if the arbitrary column vector is taken to be (1 1 1 1 1 1), then the set of balancing coefficients corresponds to (1 6 1 0 3 3). Further a linear combination of these balancing coefficients lead to (6 12 6 6 3 6) and the latter can also be used to balance the equation.

6. Conclusion

This paper deals with applications of matrices for the balancing of chemical equations. It illustrates the mathematical principle, which can be automated, for the balancing of chemical equations and the method can even be applied to ionic equations. The method used deals with the formulation of a reaction matrix and by analysing the characteristics of the reaction matrix, the feasibility of balancing a chemical equation can be known.

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