• *Задачи* • *Problems* •

BALANCING OF A COMPLEX REDOX EQUATION USING THE TECHNIQUE OF MATERIAL BALANCE

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Abstract. The technique of material balance method or algebraic method was used for balancing of a complex redox equation depending of five degrees of freedom. Although that there are some criticisms that the method is founded on „mathematics, not chemistry“ and that when several elements are involved in an equation the balancing is laborious, sometimes the material balance method is the unique possibility for successful balancing of such complex redox equations.

Keywords: material balance method, conservation matrix, complex redox equation

In his paper entitled „Unbalanced Chemical Equations“ Jensen [1] has noted that the equation

$$a\mathrm{NH4ClO_4} + b\mathrm{HNO_3} + c\mathrm{HCl} + d\mathrm{H_2O} \rightarrow e\mathrm{HClO_4{\cdot}2H_2O} + f\mathrm{N2O} + g\mathrm{NO} + h\mathrm{NO_2} + i\mathrm{Cl_2}$$

which summarizes the experimentally observed facts for production of perchloric acid is „an excellent example of the usefulness of the technique of the material balance.“ The above redox equation involves four chemical elements and nine chemical compounds. Its stoichiometric coefficients taken as variables are solution of the system described [1]. Jensen has determined that the system depends on five parameters (five degrees of freedom). He has proposed four equations of material balance of the chemical elements and pointed out that „no single unique lowest whole number solution is possible“ but, unfortunately, he has not given at least one set of numeral values of the coefficients.

The aim of the present paper is to examine the possible solutions of the system and to propose some of them by means of the algebraic method.

The conservation of atoms can be expressed by a conservation matrix A [2] with a row for each element and a column for each species. Every column gives the number of atoms of the elements in a particular chemical species. The matrix elements, corresponding to the species on the right side of the equation, are negative. For the concrete equation, the system $A\vec{x} = \vec{0}$ can be expressed as

$$\begin{pmatrix} 1 & 1 & 0 & 0 & 0 & -2 & -1 & -1 & 0 \\ 4 & 1 & 1 & 2 & -5 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & -1 & 0 & 0 & 0 & -2 \\ 4 & 3 & 0 & 1 & -6 & -1 & -1 & -2 & 0 \end{pmatrix} \times \begin{pmatrix} a \\ b \\ c \\ d \\ e \\ f \\ g \\ h \\ i \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

Using the Gaussian Elimination Method, the system can be transformed into the following equivalent system

$$\begin{pmatrix} 1 & 1 & 0 & 0 & 0 & -2 & -1 & -1 & 0 \\ 0 & 1 & -1 & 0 & 1 & -2 & -1 & -1 & 2 \\ 0 & 0 & 1 & -1 & 5 & -5 & -2 & -1 & -2 \\ 0 & 0 & 0 & 0 & -8 & 8 & 3 & 1 & -2 \end{pmatrix} \times \begin{pmatrix} a \\ b \\ c \\ d \\ e \\ f \\ g \\ h \\ i \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

Since the rank of the system matrix is equal to four and the number of the unknown stoichiometric coefficients is nine, the solution of the system really depends on five independent parameters (five of the stoichiometric coefficients) which can be given various values keeping definite limiting conditions. This determines obtaining of infinite sets of non multiple coefficients [3-6]. The theory of linear algebraic equations gives a possibility to specify which of the stoichiometric coefficients can be parameters. It could be found calculating all determinants (in this example four columns and four rows because the rank is equal to four) forming by corresponding columns of the matrix for the respective coefficients (four in the present example). All possible combinations of parameters are 126. When the determinant is different from zero, then the other five coefficients (which columns of the matrix do not take part in the determinant) can be parameters. If the determinant is equal to zero, the coefficients which columns are included in it cannot be explicitly derived by the other five coefficients and these five coefficients cannot be parameters (13 combinations), namely *e,f,g,h,i; a,b,f,g,h; a,b,c,d,i; a,b,c,d,e; a,b,c,e,i; a,b,d,e,i; a,c,d,e,i; b,c,d,e,i; b,c,e,f,g; a,c,e,h,i; a,c,e,g,i; c,d,g,h,i; a,c,e,f,i.*

Then, if the coefficients d,e, f,g,i (the determinant of the other four coefficients is different from zero) are chosen as parameters the solution of the system is:

$$a = -d - 2e + 3f + g - 2i$$
$$b = d + 10e - 9f - 3g + 4i$$
$$c = d + 3e - 3f - g + 4i$$
$$h = 8e - 8f - 3g + 2i$$

Since the stoichometric coefficients are always positive, the following limiting conditions

$$-d - 2e + 3f + g - 2i > 0$$
$$d + 10e - 9f - 3g + 4i > 0$$
$$d + 3e - 3f - g + 4i > 0$$
$$8e - 8f - 3g + 2i > 0$$

must be taken into account. When these limiting conditions are kept, one set of parameter values is $d = 2$, $e = 12$, $f = 8$, $g = 5$, $i = 1$. Then the values of the other four coefficients are $a = 1$, $b = 39$, $c = 13$, $h = 19$. It must be noted that the numerous limiting conditions make the process of determination of the parameter's values rather time consuming.

Other sets of coefficients are $a = 1$, $b = 63$, $c = 23$, $d = 5$, $e = 20$, $f = 10$, $g = 20$, $h = 24$, $i = 2$; $a = 9$, $b = 33$, $c = 9$, $d = 1$, $e = 16$, $f = 8$, $g = 20$, $h = 6$, $i = 1$.

Using the last set of parameters, the balanced equation is

$$9NH_4ClO_4 + 33HNO_3 + 9HCl + H_2O \rightarrow 16HClO_4 \cdot 2H_2O + 8N_2O + 20NO + 6NO_2 + Cl_2$$

Although the material balance method is based on the law of conservation of mass, it is less frequently used technique [1]. The major criticisms of the material balance method are that it is founded on „mathematics, not chemistry“ and that it is difficult to solve sets of linear algebraic equations [3,4]. It is true that when several chemical elements are involved in an equation, the material balance method can be laborious. A simplification that permits to reduce the number of linear algebraic equations (more often to one or two) was recently proposed by Atanassova [7]. However, sometimes (as in the present case) the application of material balance method in its not simplified form (regardless of its complexity) is the unique possibility to balance similar complex redox equations.

REFERENCES
1. Jensen, W.J. Unbalanced Chemical Equations. *J. Chem. Educ*. **64**, 646 (1987).
2. Campanario, J.M. Automatic 'Balancing' of Chemical Equations. *Computers Chem.* **19**, 85-90 (1995).
3. Kolb, D. More on Balancing Redox Equations. *J. Chem. Educ*. **56**, 181-184 (1979).
4. Olson, J.A. An Analysis of the Algebraic Method for Balancing Chemical Reactions. *J. Chem. Educ.* **74**, 538-542 (1997).
5. Missen, R.W., W.R. Smith. The Permanganate-Peroxide Reaction: Illustration of a Stoichiometric Restriction. *J. Chem. Educ*. **67**, 876-877 (1990).
6. Subramanian, R., N.K. Goh, L.S. Chia. The Relationship between the Number of Elements and the Number of Independent Equations of Elemental Balance in Inorganic Chemical Equations. *J. Chem. Educ*. **72**, 894 (1995).
7. Atanassova, M. An Alternative Method for Oxidation-Reduction Reaction Balancing. *Chemistry* **18**, 280-285 (2009) [In Bulgarian].

ИЗПОЛЗВАНЕ НА МЕТОДА НА МАТЕРИАЛНИЯ БАЛАНС ЗА ИЗРАВНЯВАНЕ НА СЛОЖНО РЕДОКС УРАВНЕНИЕ

Резюме. Методът на материалния баланс или алгебричният метод беше използван за изравняване на сложно редокс уравнение, което зависи от пет независими променливи (има пет степени на свобода). Въпреки критиките, че методът се основава на „математика, а не на химия“, и че когато уравнението включва няколко химични елемента изравняването е трудно, този метод предлага единствена възможност за успешно изравняване на сложни редокс уравнения.

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