• *Задачи* •
• *Problems* •

A MODIFIED FORM OF THE MATERIAL BALANCE METHOD APPLIED TO REDOX EQUATIONS DEPENDING ON TWO DEGREES OF FREEDOM

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Abstract. A modified material balance technique of balancing redox equations depending on two degrees of freedom (two independent parameters) with infinite sets of non multiple coefficients was proposed. Such an approach permits to decrease the number of the linear algebraic equations and gives a possibility to solve the stoichiometric problems faster and easier.

Keywords: redox equations, material balance method, infinite sets of non-multiple stoichiometric coefficients

The problem for balancing redox chemical equations is an important part of the chemical education. Although Missen and Smith [1] have pointed out that the expression "balancing a chemical equation" is not correct, it has acquired popularity and is used extensively in the chemical literature. There are a large number of papers devoted to the balancing of chemical equations. A historical background of the problem is given by Risteski [2,3]. Several methods (the oxidation number method, the half reactions method, the material balance method, the inspection method) have been proposed for chemical equations balancing. Examples are described in [4-16]. However, no particular method could be given preference [6]. And yet, the method known as the material balance method (the algebraic method) is far more general in comparison with the other methods [8] because it is based on the law of conservation of mass firstly established by Lavoisier in 1789. It states that the total mass remains constant during a chemical reaction. Therefore, the balanced equation must obey the law of conservation of mass by having the same number of atoms on each side of the equation. When the material balance method is used, the coefficients of the unbalanced equation are represented as variables. An equation of balance for each element has to be written down. These equations can be solved using any of the methods available for solution of linear algebraic equations. Most often in the redox equations the number of reactants and products exceeds the number of chemical elements by one. However, there are equations in which the number of chemical elements is equal to the number of compounds or even the number of chemical elements exceeds the number of compounds. All this equations depend on one degree of freedom (one independent parameter) and can be balanced with one set of stoichiometric coefficients only. Examples are given below:

$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ (four elements; five compounds)

$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$ (four elements; four compounds)

$Ca(ClO)_2 + 2NaNO_2 \rightarrow CaCl_2 + 2NaNO_3$ (five elements; four compounds)

When the number of reactants and products exceeds the number of chemical elements by two or more i.e. the degrees of freedom are two or more, such equations can be balanced by infinite sets of non multiple stoichiometric coefficients. The possibility to balance redox equations with various sets of coefficients has been explained with the fact that the overall equation, as written, does not represent a unique reaction but is a sum of two or more simultaneous competing reactions [6,12-14,16].

The conservation of atoms can be expressed by a conservation matrix with a row for each element and a column for each species [14]. 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. The construction of a conservation matrix representing the system of linear algebraic equations of a complex redox equation with five degrees of freedom was recently shown by Petkova et al. [17]. Jensen [18] has pointed out the usefulness of the technique of material balance for balancing such chemical equations, but he has noted that it is less frequently used technique. The major criticisms are that the method is founded on "mathematics, not chemistry" and that when it is necessary to solve a set of several linear algebraic equations it can be laborious [6,9]. That is why, the proposal for modification of the material balance technique, permitting to reduce the number of the linear equations (most often to one or two that can be solved quite easy), will make the method more attractive and applicable, especially for equations with two degrees of freedom all the more that the other very popular methods (the oxidation number method and the half-reaction method) permit to obtain only one set of non multiple coefficients balancing such equations [13]. Most often the number of the linear algebraic equations, showing the element conservation, can be reduced significantly representing as variables not all coefficients but only those before the reactants on the left side of the equation. Then the coefficients of the products on the right side of the equation can be derived explicitly from those on the left side.

The advantage of the proposed modified method to the original method can be shown by their comparison for balancing of the skeletal equation

$$\mathrm{Li} + \mathrm{HN_3} \rightarrow \mathrm{LiN_3} + \mathrm{NH_3} + \mathrm{N_2}$$

in which the number of chemical compounds is five and the number of chemical elements is three (i.e., the equation depends on two degrees of freedom).

The original method requires representing as variables all stoichiometric coefficients. If these coefficients are a, b, c, d and e, the equation can be described as

$$a\mathrm{Li} + b\mathrm{HN_3} \rightarrow c\mathrm{LiN_3} + d\mathrm{NH_3} + e\mathrm{N_2}$$

Three linear equations giving the conservation of the three elements can be written down, namely

$$\begin{aligned} &\mathrm{Li}:\ a = c \\ &\mathrm{H}:\ b = 3d \\ &\mathrm{N}:\ 3b = 3c + d + 2e \end{aligned}$$

The solution of the system gives $c = a = \frac{8}{3}d - \frac{2}{3}e$. If d and e are given various values keeping the condition $4d > e$, (the stoichiometric coefficients must be positive), infinite sets of not multiple coefficients can be determined. Following this approach three sets of coefficients are given below: if $d = 1$ and $e = 1$,

$$c = a = \frac{8}{3} - \frac{2}{3} = 2 \text{ and } b = 3d = 3.$$

The balanced equation is

$$2\mathrm{Li} + 3\mathrm{HN_3} \rightarrow 2\mathrm{LiN_3} + \mathrm{NH_3} + \mathrm{N_2};$$

if $d = 2$ and $e = 1$,

$$c = a = \frac{16}{3} - \frac{2}{3} = \frac{14}{3}$$

and $b = 3d = 6$. The integer values of the coefficients before Li, HN_3, LiN_3, NH_3 and N_2 are 4, 18, 14, 6 and 3, respectively. The balanced equation is

$$4\mathrm{Li} + 18\mathrm{HN_3} \rightarrow 14\mathrm{LiN_3} + 6\mathrm{NH_3} + 3\mathrm{N_2}$$

if $d = 1$ and $e = 2$,

$$c = a = \frac{8}{3} - \frac{4}{3} = \frac{4}{3}$$

and $b = 3d = 3$. The integer values of the coefficients before Li, HN_3, LiN_3, NH_3 and N_2 are 4, 9, 4, 3 and 6, respectively. The balanced equation is

$$4\mathrm{Li} + 9\mathrm{HN_3} \rightarrow 4\mathrm{LiN_3} + 3\mathrm{NH_3} + 6\mathrm{N_2}$$

Other sets of non multiple coefficients can be determined in this manner.

The sets of stoiciometric coefficients can be determined easier and faster if the unknown coefficients *a* and *b* are given to the reactants Li and HN_3 and the coefficients of the products on the right side are derived from those on the left side. Then, the coefficients before LiN_3, NH_3 and N_2 will be *a*, *b*/3 and $\frac{3b-3a-b/3}{2} = \frac{8b-9a}{6}$, respectively. So, the equation can be represented as

$$a\mathrm{Li} + b\mathrm{HN_3} \rightarrow a\mathrm{LiN_3} + \frac{b}{3}\mathrm{NH_3} + \frac{8b-9a}{6}\mathrm{N_2}$$

Since the unknown coefficients are two and the chemical equation depends on two degrees of freedom (two independent parameters), it is clear that *a* and *b* are independent parameters and the equation can be balanced giving arbitrary values of *a* and *b* keeping the limiting condition $8b > 9a$. Thus, infinite sets of non multiple coefficients can be obtained again. Hence, if $a = 1$ and $b = 2$, the balanced equation is

$$\mathrm{Li} + 2\mathrm{HN_3} \rightarrow \mathrm{LiN_3} + \frac{2}{3}\mathrm{NH_3} + \frac{7}{6}\mathrm{N_2}$$

or in integers,

$$6\mathrm{Li} + 12\mathrm{HN_3} \rightarrow 6\mathrm{LiN_3} + 4\mathrm{NH_3} + 7\mathrm{N_2};$$

if $a = 1$ and $b = 3$,

$$\mathrm{Li} + 3\mathrm{HN_3} \rightarrow \mathrm{LiN_3} + \mathrm{NH_3} + \frac{5}{2}\mathrm{N_2}$$

or

$$2\mathrm{Li} + 6\mathrm{HN_3} \rightarrow 2\mathrm{LiN_3} + 2\mathrm{NH_3} + 5\mathrm{N_2}$$

and if $a = 2$ and $b = 3$,

$$2\mathrm{Li} + 3\mathrm{HN_3} \rightarrow 2\mathrm{LiN_3} + \mathrm{NH_3} + \mathrm{N_2}.$$

This equation can be balanced by oxidation number method, too. The scheme of the electronic balance (rather complex) is

$$\overset{0}{\mathrm{Li}} + \overset{1-}{\mathrm{HN_3}} \rightarrow \overset{1+}{\mathrm{Li}}\mathrm{N_3} + \overset{3-}{\mathrm{N}}\mathrm{H_3} + \overset{0}{\mathrm{N_2}}$$

$$\left.\begin{array}{l}\left.\begin{array}{l}\mathrm{Li^0} - 1e^- \rightarrow \mathrm{Li^+} \\ \mathrm{N_3^-} - 1e^- \rightarrow 3\mathrm{N^0}\end{array}\right\}2 \\ \mathrm{N_3^-} + 8e^- \rightarrow 3\mathrm{N^{3-}}\}8\end{array}\right|\begin{array}{l}\times 4 \\ \\ \times 1\end{array}$$

Therefore, 4 molecules of HN_3 will react with 4 Li's forming a salt (LiN_3). Another 4 molecules HN_3 take part in the formation of 6 molecules N_2 and one molecule HN_3 takes part in the formation of 3 molecules NH_3 (total 9 HN_3). The balanced equation is

$$4\mathrm{Li} + 9\mathrm{HN_3} \rightarrow 4\mathrm{LiN_3} + 3\mathrm{NH_3} + 6\mathrm{N_2}$$

Thus, the method permits to obtain only one of the possible sets of coefficients. This is due to the fact that the oxidation number method introduces a restriction in addition to element conservation [13].

The proposed modification is even more attractive when the chemical equation involves more chemical elements and compounds. The equation

$$K_2Cr_2O_7 + H_2S + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + S + H_2O$$

involves five chemical elements and seven compounds. The original material balance method requires solution of a system of five algebraic equations. Using the modified method, the balancing can be realized easily if the reactants $K_2Cr_2O_7$, H_2S and H_2SO_4 are given coefficients a, b and c. Then, the coefficients of the products $Cr_2(SO_4)_3$, K_2SO_4, S and H_2O, derived from those of the reactants, will be a, a, $(b+c-4a)$ and $(b+c)$, respectively, and the equation can be represented as

$$aK_2Cr_2O_7 + bH_2S + cH_2SO_4 \rightarrow aCr_2(SO_4)_3 + aK_2SO_4 + (b+c\text{-}4a)\ S + (b+c)H_2O$$

Since the unknown coefficients are three and there are two independent parameters, one algebraic equation, balancing the oxygen atoms on both sides, permits to balance the redox equation, i.e.

$$O:=\ 7a + 4c = 12a + 4a + b + c$$

Then,

$$a = \frac{3c-b}{9}$$

Giving the parameters b and c various values and keeping the limiting condition $3c > b$, infinite sets of not multiple coefficients can be determined. Two of them are given below:

if $b = 1$ and $c = 1$,

$$a = \frac{2}{9} \text{ and } b + c - 4a = \frac{10}{9}\ .$$

Then,

$$\frac{2}{9}K_2Cr_2O_7 + H_2S + H_2SO_4 \rightarrow \frac{2}{9}Cr_2(SO_4)_3 + \frac{2}{9}K_2SO_4 + \frac{10}{9}S + 2H_2O$$

or

$$2K_2Cr_2O_7 + 9H_2S + 9H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 2K_2SO_4 + 10S + 18H_2O$$

if $b = 1$ and $c = 2$,

$$a = \frac{5}{9} \text{ and } b + c - 4a = \frac{7}{9}\ .$$

Then,

$$\frac{5}{9}K_2Cr_2O_7 + H_2S + 2H_2SO_4 \rightarrow \frac{5}{9}Cr_2(SO_4)_3 + \frac{5}{9}K_2SO_4 + \frac{7}{9}S + 3H_2O$$

or

$$5K_2Cr_2O_7 + 9H_2S + 18H_2SO_4 \rightarrow 5Cr_2(SO_4)_3 + 5K_2SO_4 + 7S + 27H_2O$$

The skeletal equation

$$Na_2S_3 + KMnO_4 + H_2SO_4 \rightarrow Na_2SO_4 + K_2SO_4 + MnSO_4 + S + H_2O$$

involves six chemical elements and eight compounds. It can be balanced without difficulty, if the coefficients of the reactants Na_2S_3, $KMnO_4$ and H_2SO_4 are *a*, *b* and *c*, respectively. Then, the coefficients of the products Na_2SO_4, K_2SO_4, $MnSO_4$, S and H_2O, derived from those of the reactants, will be *a*, *b*/2, *b*, $\frac{4a+2c-3b}{2}$ and *c* and the equation can be represented as

$$aNa_2S_3 + bKMnO_4 + cH_2SO_4 \rightarrow aNa_2SO_4 + \frac{b}{2}K_2SO_4 + bMnSO_4 + \frac{4a+2c-3b}{2}S + cH_2O$$

The coefficient of S was obtained balancing the sulphur atoms on both sides of the equation, i.e.

$$3a + c - a - \frac{b}{2} - b = \frac{4a+2c-3b}{2}.$$

Then, only one equation balancing the oxygen atoms can be written down, namely

$$O: \quad 4b + 4c = 4a + 4\frac{b}{2} + 4b + c.$$

The solution gives

$$3c = 4a + 2b \text{ or } c = \frac{4a+2b}{3}.$$

A limiting condition permitting to obtain positive coefficients is $4a + 2c > 3b$. If coefficients *a* and *b* are given various values (keeping the limiting condition), the equation can be balanced with infinite sets of non multiple coefficients. Three of them are given below:

if $a = 1$ and $b = 1$,

$$c = \frac{4+2}{3} = 2.$$

The coefficient of sulfur atoms becomes $\frac{4+4-3}{2} = \frac{5}{2}$. Then,

$$Na_2S_3 + KMnO_4 + 2H_2SO_4 \rightarrow Na_2SO_4 + \frac{1}{2}K_2SO_4 + MnSO_4 + \frac{5}{2}S + 2H_2O$$

or

$$2Na_2S_3 + 2KMnO_4 + 4H_2SO_4 \rightarrow 2Na_2SO_4 + K_2SO_4 + 2MnSO_4 + 5S + 4H_2O$$

if $a = 2$ and $b = 1$,

$$c = \frac{10}{3}.$$

The coefficient of sulphur atoms becomes $\frac{8+2(10/3)-3}{2}=\frac{35}{6}$. In this case the balanced equation can be represented as

$$2Na_2S_3 + KMnO_4 + \frac{10}{3}H_2SO_4 \rightarrow 2Na_2SO_4 + \frac{1}{2}K_2SO_4 + MnSO_4 + \frac{35}{6}S + \frac{10}{3}H_2O$$

or

$$12Na_2S_3 + 6KMnO_4 + 20H_2SO_4 \rightarrow 12Na_2SO_4 + 3K_2SO_4 + 6MnSO_4 + 35S + 20H_2O$$

Another set of coefficients can be obtained if $a = 3$ an $b = 2$. Then $c = \frac{16}{3}$ and the coefficient of sulphur atoms becomes $\frac{12+2(16/3)-6}{2}=\frac{25}{3}$. The balanced equation is

$$3Na_2S_3 + 2KMnO_4 + \frac{16}{3}H_2SO_4 \rightarrow 3Na_2SO_4 + K_2SO_4 + 2MnSO_4 + \frac{25}{3}S + \frac{16}{3}H_2O$$

or

$$9Na_2S_3 + 6KMnO_4 + 16H_2SO_4 \rightarrow 9Na_2SO_4 + 3K_2SO_4 + 6MnSO_4 + 25S + 16H_2O$$

Other sets of coefficients can be obtained in similar way. If the classical material balance method is applied, a system of six algebraic equations balancing the six chemical elements involved in the equation must be solved. Solution of such a system is really laborious and requires definite mathematical skills. This may embarrass some students and even teachers. Hence, the proposed modification is appropriate to be used in chemical class and laboratory. However, there is limited number of very complex redox equations that cannot be balanced by the proposed modification, because of too much limiting conditions. They often depend on more than two degrees of freedom. Then, the unique method for balancing such equations, regardless of its complexity, is the material balance technique in its full form [17].

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МОДИФИКАЦИЯ НА МЕТОДА НА МАТЕРИАЛНИЯ БАЛАНС ЗА ИЗРАВНЯВАНЕ НА РЕДОКС УРАВНЕНИЯ С ДВЕ СТЕПЕНИ НА СВОБОДА

Резюме. Предложена е модифицирана форма на метода на материалния баланс за изравняване на редокс уравнения, притежаващи две степени на свобода, с различни набори от непропорционални стехиометрични коефициенти. Подходът дава възможност да бъде намален значително броя на уравненията, даващи баланса на атомите на всеки елемент в лявата и дясна част на химичното уравнение и позволява наборите от стехиометрични коефициенти да бъдат намерени лесно и бързо.

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