Problems
Задачи

BALANCING OF OXIDATION-REDUCTION (REDOX) REACTIONS WITH HIGHER BORANES PARTICIPATION: OXIDATION NUMBER METHOD OR MATERIAL BALANCE METHOD?

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Abstract. As a result of the complex structure of the higher boranes, the balancing of redox reactions with their participation by the oxidation number method is connected with the acceptance of non-integer values of the oxidation numbers of the boron atoms which is in contradiction with some IUPAC recommendations. An alternative method is the material balance method (algebraic method) based on the natural law of mass conservation in chemical reactions. Its modified form permits easy and fast balancing of redox reactions without any restrictions.

Keywords: higher boranes; redox reactions; oxidation number method; material balance method

Oxidation number method

It is known that the oxidation number method is an extensively used technique for balancing of redox reactions. It is connected with the determination of the oxidation number (state) of the oxidizer and reducer. The terms oxidation state and oxidation number are interchangeable (Karen et al., 2014). There are several definitions of the oxidation number (Silverstein, 2011; Loock, 2011). An IUPAC Technical Report (Karen et al., 2014) and IUPAC Recommendations (Karen et al., 2016) were published recently in order to provide an unambiguous and comprehensive definition of the oxidation state. A definition that could be applied for the determination of the oxidation numbers of boron atoms in boranes is:

> [B]ond electrons are moved onto the more negative bond partner identified by ionic approximation, and atom charges are evaluated giving the oxidation state (Karen et al., 2014).

According to the Allred – Rochow scale, the electronegativity of boron is 2.0 and those of hydrogen is 2.2. Therefore, according to the Karen's definition the hydrogen atoms will have a negative oxidation number (–I). Then the boron atoms will have positive non-integer oxidation number to keep the electroneutrality of the borane molecules. Hence, in B_4H_{10}, B_6H_{10} and B_5H_{11} the oxidation numbers of the boron atoms will be (5/2)+, (5/3)+ and ((11/5)+, respectively. Since the oxidation numbers of the boron atoms are non-integer, to balance successfully redox reactions with higher boranes participation the following IUPAC recommendations listed in The Nomenclature of Inorganic Chemistry 2005 (The Red Book) have to be ignored: (i) Roman numerals are used in formulae as right superscript to designate to formal oxidation state (IR-2.8.2); (ii) The oxidation number designates the oxidation state (Connelly et al., 2005).

The oxidation number may be positive, negative or zero (represented by the numeral 0). The oxidation number is always non-negative unless the minus sign is explicitly used (the positive sign is never used). Non-integer oxidation numbers are not used for nomenclature purposes (IR-5.4.2.2).

Examples for balancing of redox reactions with participation of B_4H_{10}, B_6H_{10} and B_5H_{11} will be shown below. The procedure is described in details. For the reaction

$$B_4H_{10} + KMnO_4 \rightarrow MnO_2 + KBO_2 + KOH + H_2O$$

the oxidation numbers of oxidizer and reducer are given at the corresponding atoms

$$\overset{2.5+}{B}{}_4\overset{1-}{H}{}_{10} + K\overset{7+}{Mn}O_4 \rightarrow \overset{4+}{Mn}O_2 + K\overset{3+}{B}O_2 + KO\overset{1+}{H} + \overset{1+}{H}{}_2O$$

Both the boron atoms and hydrogen atoms are reducers. The boron atoms change their oxidation number from 2.5 to 3. Every of the four boron atoms loses 0.5 electron (total 2 electrons). The hydrogen atoms change their oxidation number from 1– to 1+. Every hydrogen atom loses 2 electrons and ten hydrogen atoms lose 20 electrons. The scheme of the electronic balance is

$$\left.\begin{array}{l} 4\overset{2,5+}{B} - 2e \rightarrow 4\overset{3+}{B} \\ 10\overset{1-}{H} - 20e \rightarrow 10\overset{1+}{H} \end{array}\right\} 22\times 3$$
$$\left.\overset{7+}{Mn} + 3e \rightarrow \overset{4+}{Mn}\right\} 3\times 22$$

The balanced reaction is

$$3B_4H_{10} + 22KMnO_4 \rightarrow 22MnO_2 + 12KBO_2 + 10KOH + 10H_2O$$

The balancing of redox reactions with other higher boranes participation can be carried out by the same manner. For the reaction

$$B_6H_{10} + K_2Cr_2O_7 + H_2SO_4 \text{ ® } K_2SO_4 + Cr_2(SO_4)_3 + H_3BO_3 + H_2O$$

the scheme of the electronic balance is

$$\left.\begin{array}{l} 6\overset{(5/3)+}{\mathrm{B}} - 6(4/3)e \rightarrow 6\overset{3+}{\mathrm{B}} \\ 10\overset{1-}{\mathrm{H}} - 20e \rightarrow 10\overset{1+}{\mathrm{H}} \end{array}\right\} 28\times3$$

$$2\overset{6+}{\mathrm{Cr}} + 2\times3e \rightarrow 2\overset{3+}{\mathrm{Cr}} \Big\} 6\times14$$

The balanced reaction is

$$3B_6H_{10} + 14K_2Cr_2O_7 + 56H_2SO_4 \text{ ® } 14K_2SO_4 + 14Cr_2(SO_4)_3 + 18H_3BO_3 + 44H_2O$$

For the reaction

$$B_5H_{11} + K_2Cr_2O_7 + H_2SO_4 \text{ ® } K_2SO_4 + Cr_2(SO_4)_3 + H_3BO_3 + H_2O$$

the scheme of the electronic balance is

$$\left.\begin{array}{l} 5\overset{(1\,1/5)+}{\mathrm{B}} - 5(4/5)e \rightarrow 5\overset{3+}{\mathrm{B}} \\ 11\overset{1-}{\mathrm{H}} - 22e \rightarrow 11\overset{1+}{\mathrm{H}} \end{array}\right\} 26\times3$$

$$2\overset{6+}{\mathrm{Cr}} + 2\times3e \rightarrow 2\overset{3+}{\mathrm{Cr}} \Big\} 6\times13$$

The balanced reaction is

$$3B_5H_{11} + 13K_2Cr_2O_7 + 52H_2SO_4 \text{ ® } 13K_2SO_4 + 13Cr_2(SO_4)_3 + 15H_3BO_3 + 46H_2O$$

These examples show that the balancing is possible if is accepted that the boron atoms oxidation number is non-integer and as a result the boron atoms lose non-integer number of electrons. This is due to the very complex structure of the higher boranes including electron-deficient bonds (three-center two-electron B–B–B and B–H–B bonds) as well as two-center two-electron B–B and B–H bonds. In C_4H_{10} there are four B–H–B bonds, one B–B bond and six B–H bonds. The electrons used in the four B–H–B bonds are 8 (4´2); the electrons used in one B–B bond are 2; the electrons used in six B–H bonds are 12 (6´2). The total number of the used electrons is 22 (12 from four boron atoms (4´3) and 10 electrons from 10 hydrogen atoms). In C_6H_{10} there are four B–H–B bonds, two B–B–B bonds, two B–B bonds and six terminal B–H bonds. The electrons used in four B–H–B bonds are 8 (4´2); the electrons used in two B–B–B bonds are 4 (2´2); the electrons used in two B–B bonds are 4 (2´2); the electrons used in six B–H bonds are 12 (6´2). The total number of the used electrons is 28 (18 from six boron atoms (6´3) and 10 electrons from 10 hydrogen atoms). In C_5H_{11} there are three B–H–B bonds, two B–B–B bonds and eight terminal B–H bonds. The electrons used in three B–H–B bonds are 6 (3´2); the electrons used in two B–B–B bonds are 4 (2´2); the electrons used in eight B–H bonds are 16 (8´2). The total number of the used electrons is 26 (15 from five boron atoms (5´3) and 11 electrons from 11 hydrogen atoms).

It is seen by the schemes of the electronic balance that the number of electrons lost by the reducers (boron and hydrogen atoms) coincide with the total number of electrons taking part in the covalent bonds in the boranes (B–H–B, B–B–B, B–B or B–H).

Material balance method (algebraic method)

When, by nomenclature or formal reasons, the method of oxidation number is not suitable, the alternative is the material balance method or algebraic method. It is far more general in comparison with the other methods because is based on the law of conservation of mass firstly established by Lavoisier in 1789 (Jensen, 2009). It states that the total mass of the compounds remains constant during a chemical reaction. Therefore, the balanced reaction must obey the law of mass conservation by having the same number of atoms on each side of the reaction. When this method is used, the stoichiometric coefficients must be represented as variables. Linear algebraic equations giving the balance of each element atoms have to be constructed. They can be solved using the methods available for solution of linear algebraic equations. Frequently, the conservation of atoms is expressed by a conservation matrix with a raw for each element and a column for each compound. The construction of a conservation matrix representing the system of linear algebraic equations was shown in several papers (Campanario, 1995; Petkova et al., 2010; Padmaja et al., 2017; Wang et al., 2017). Although the method is useful (Jensen, 2009), it is the less frequently used technique in chemistry. The major criticisms are that it is "mathematics, not chemistry" and that the solution of a set of linear algebraic equations (sometimes large number) is laborious (Kolb, 1979; Olson, 1997). To simplify the method making it more attractive for the chemists, a modification of the material balance technique permitting to reduce significantly the number of the algebraic equations was proposed earlier (Petkova et al., 2011). The simplification can be realized if not all but a part of the stoichiometric coefficients (most often 2 or 3) are presented as unknown quantities and all the rest stoichiometric coefficients are derived from them keeping the condition of atom conservation. In this manner the conservation of the most elements is reached in advance and it is necessary to construct a small number of algebraic equations. Their solution is quite easy and construction of matrix or use of computer program is not necessary. A comparative study of the modified form of the material balance technique and the oxidation number method was carried out, too (Dukov & Atanassova, 2011; Dukov, 2014).

The application of the material balance method in its modified form for balancing redox reactions with participation of B_4H_{10}, B_6H_{10} and B_5H_{11} is shown below.

If in the reaction

$$B_4H_{10} + KMnO_4 \rightarrow MnO_2 + KBO_2 + KOH + H_2O$$

to B_4H_{10} and $KMnO_4$ are ascribed the unknown stoichiometric coefficients *a* and *b*, the coefficients of MnO_2, KBO_2, KOH and H_2O can be obtained from *a* and *b* by keeping the material balance of the atoms of every element on the left and right side of the reaction. It is quite easy to be established that they will be as follows: b for MnO_2 (from the balance of manganese atoms); $4a$ for KBO_2 (from the balance of boron atoms); $(b - 4a)$ for KOH (from the balance of potassium atoms); $(10a - (b - 4a)/2 = (14a - b)/2$ for H_2O (from the balance of hydrogen atoms). In this case the necessary conditions are $b > 4a$ and $14a > b$ because the stoichiometric coefficients must be positive. Then the reaction with all coefficients is

$$aB_4H_{10} + bKMnO_4 \rightarrow bMnO_2 + 4aKBO_2 + (b - 4a)KOH + \frac{14a-b}{2}H_2O.$$

Since the conservation of the boron, potassium, manganese and hydrogen atoms is reached in advance, only one algebraic equation giving the conservation of the oxygen atoms have to be constructed viz. $4b = 2b + 8a + b - 4a + \frac{14a-b}{2}$. The solution of the equation gives $3b = 22a$. So, $b = \frac{22}{3}a$. If $a = 1$, $b = \frac{22}{3}$. The other coefficients are: $4a = 4$; $b - 4a = \frac{22}{3} - 4 = \frac{10}{3}$ and $\frac{14a-b}{2} = \frac{14-\frac{22}{3}}{2} = \frac{10}{3}$.

The balanced reaction with integer coefficients is

$$3B_4H_{10} + 22KMnO_4 \rightarrow 22MnO_2 + 12KBO_2 + 10KOH + 10H_2O.$$

The balancing of the reaction

$$B_6H_{10} + K_2Cr_2O_7 + H_2SO_4 ® K_2SO_4 + Cr_2(SO_4)_3 + H_3BO_3 + H_2O$$

can be reached if coefficients a, b and c are ascribed to B_6H_{10}, $K_2Cr_2O_7$ and H_2SO_4, respectively. Then the coefficients of the compounds on the right side of the reaction can be determined from a, b and c. The coefficient of K_2SO_4 will be b (from the balance of potassium atoms); the coefficient of $Cr_2(SO_4)_3$ will be again b (from the balance of chromium atoms); the coefficient of H_3BO_3 will be $6a$ (from the balance of boron atoms) and the coefficients of H_2O will be $(10a + 2c - 18a)/2 = (c - 4a)$ (from the balance of hydrogen atoms). Since the coefficient must be positive, the condition is $c > 4a$. The reaction with all coefficients is

$$aB_6H_{10} + bK_2Cr_2O_7 + cH_2SO_4 ® bK_2SO_4 + bCr_2(SO_4)_3 + 6aH_3BO_3 + (c - 4a)H_2O$$

In this case two linear algebraic equations have to be constructed giving the conservation of the sulfur and oxygen atoms.

$$\text{S: } c = b + 3b = 4b$$
$$\text{O: } 7b + 4c = 4b + 12b + 18a + c - 4a = 16b + 14a + c$$

After transformation, the equation for the oxygen atoms is $14a = 3c - 9b$.

Since $c = 4b$, the solution of the equation for the oxygen atoms gives $a = \frac{3}{14}b$.
If $b = 1$, $a = \frac{3}{14}$, $c = 4$ and $c - 4a = 4 - 4\times\frac{3}{14} = \frac{44}{14}$. The condition $c > 4a$ is fulfilled. The balanced equation with integer coefficients is

$$3B_6H_{10} + 14K_2Cr_2O_7 + 56H_2SO_4 \text{ ® } 14K_2SO_4 + 14Cr_2(SO_4)_3 + 18H_3BO_3 + 44H_2O$$

The balancing of the reaction

$$B_5H_{11} + K_2Cr_2O_7 + H_2SO_4 \text{ ® } K_2SO_4 + Cr_2(SO_4)_3 + H_3BO_3 + H_2O$$

can be carried out in the same manner as those for the interaction between B_6H_{10} and $K_2Cr_2O_7$. The reaction with all coefficients is

$$aB_5H_{11} + bK_2Cr_2O_7 + cH_2SO_4 \text{ ® } bK_2SO_4 + bCr_2(SO_4)_3 + 5aH_3BO_3 + (c - 2a)H_2O$$

The solution of the algebraic equations for conservation of sulfur and oxygen atoms gives $a = \frac{3}{13}b$, $c = 4b$ and $c - 2a = 4b - 2\times\frac{3}{13}b = \frac{46}{13}b$. Assuming $b = 1$, the balanced reaction with integer coefficients is

$$3B_5H_{11} + 13K_2Cr_2O_7 + 52H_2SO_4 \text{ ® } 13K_2SO_4 + 13Cr_2(SO_4)_3 + 15H_3BO_3 + 46H_2O\ .$$

Conclusion

The balancing redox reactions with higher boranes participation shows that the use of the oxidation number method requires to neglect some basic nomenclature rules. On the other hand, the use of the material balance method is based on the natural law of mass conservation. The proposed modification of the technique permits to reduce significantly the number of the linear algebraic equations. They can be solved quite easy without necessity to use matrices or the computer programs. So, the proposed approach permits fast and easy balancing of redox reactions without any restrictions. It has to be noted that the obtaining of non-integer stoichiometric coefficients is a result of linear algebraic equations solution and their transformation into integer-valued coefficients is a mathematical operation.

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