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Education

A FAST SOLUTION TO THE PROBLEM OF BALANCING REDOX EQUATIONS
NUMBERS INTRODUCING FORMAL BALANCE

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There are quite a number of methods for balancing chemical equations. A variant of the oxydation number method is proposed for fast and easy balancing of complex redox equations. The principal aid are formal balance numbers (FBN). These have been introduced as an alternative to the conventional/traditional values of the oxydation numbers. The values of the FBNs are chosen in such a way, to ensure that only two elements change their state, in which case the original oxydation number technique for balancing equations may be employed. The method is probably the fastest of all possible methods that rely on 'chalk and blackboard'.

Keywords: chemical equation balancing; graduate education research; teaching/learning aids

LITERATURE SURVEY

The problem of balancing redox chemical equations has been treated many times, throughout the literature. A short literature check shows that a principal source of papers in the last 20 years is the Journal of Chemical Education (JCE) [1–22] although information may be found elsewhere too [23, 24].

In the first cited reference, attention was paid by Carrano [1] to "an atypical redox equation" which is solved by separating it into half-reactions. Then, on several occasions, Kolb [2, 3, 4] has discussed various examples of oxidation-reduction reactions as well as various methods to balance the corresponding equations (the oxydation number method, the ion-electron method, the algebraic method and the inspection method were explicitly mentioned). Kennedy [5] introduced a calculator as an aid, and Blakley [6] discussed a general method that is quick, simple and has unexpected applications (both methods are, in fact, based on the matrix method of balancing equations). Swinehart [7] breaks up the complex equation into a group of equations. Harjadi [8] works out the same example as Blakley [6] and Swinehart [7], his method being a mixture of the inspection method [4] and another, called by the author "the pingpong method". Garcia's method [9] is similar to that of Swinehart [7] and Carrano [1], as he divides the chemical reactions into two half-reactions, which are then balanced independently. Filgueiras [10] discusses the meaning of balancing a chemical equation, not offering any improvement of the methods used for balancing. Stout [11] offers the reader three rather involved redox equations for balancing, the third one being a real challenge (however, no mention is made of the method used for balancing).

Soon after the Stouts paper was published, lots of comments emerged [12–21]. Nelson [12] points to a solution (actually derived by his student) that is, in fact, a variant of the algebraic method. Tóth [13], and Ludwig [14] point to the usefulness of the use of unconventional oxidation numbers, while Woolf [15] criticises this concept. Herndon [16] gives a critical review on balancing equations. Tóth [17] and Guo [18] present some new ideas about the inspection method. Brief contributions were given by Hoor [19], Glaister [20] and also by Smith and Missen [21] (the last authors have employed the Mathematica programming package in balancing chemical equations). It seems that this was really enough for the Editor of JCE, who, in conclusion, declared moratorium on balancing equations [22].

Let us mention, in passing, that Afanas'ev [23, 24] points to several well known methods. His papers, actually, appeared shortly after the original papers [7, 8] were published in JCE.

As pointed by Kolb [3] no method could be given absolute advantage. In fact, in most cases more than one method may be successfully applied. Very often, however, the oxidation number method [2] is the one that is preferred, for it is both logical and easy to use in a number of different situations. Of course, this method has its limitations: as the number of elements that change their oxidation state increases, this method becomes less applicable, and in the case of very complex redox reactions, it is of no use at all.

One should also note that sometimes there is some ambiguity, as to what values should be assigned to the oxidation numbers. For instance, following the sequence NF_3, NCl_3, NBr_3, NI_3 it is questionable whether one should assign different values (+3 and –3) to the oxidation number of N throughout the series or should adopt a single value instead? If different values are to be chosen, then which one is more appropriate for the oxidation number of N in NCl_3? Furthermore, is the oxidation number of oxygen –2 or 0, in HOF? If 0 is assigned (which is correct when electronegativity is considered), wouldn't it suggest that the structure is perhaps HF:O?

By the way, in the case of HOF Lee [25] uses –2 for O and +1 for F. According to this author, HOF is the only compound where the oxidation number of F is +1. (One may suspect that the choice was done for consistency with the oxidation numbers of Cl, Br and I in HOCl, HOBr and HI.)

What values should be assigned to the oxidation numbers of Cr and O in CrO_5, particularly if one knows nothing about the structure of the compound (as is often the case)? Isn't it logical to assign –2 to the oxygens and +10 to the chromium?

Bearing the above in mind, for many years whenever I had to balance some more involved chemical equation, I used a modification of the oxidation number method which is really a very efficient one. In fact, the *technique* that lies behind the balancing of redox equations in this variant of the oxidation number method is exactly the same as in the original oxidation number method. Some authors [13, 14] have already came across with ideas that are at the origin of the presently proposed method (they used, as they say, *unconventional oxidation numbers*), following the idea of Swinehart [26] according to whom only two rules are important:

- The sum of the oxidation numbers of the elements in any chemical species should be equal to the charge of that species.
- The sum of the changes in oxidation number in a balanced equation should be zero.

However, in order to gain the maximum advantage of this variant, it may seem necessary to relax the meaning of the phrase *oxidation number*. Being conservative, people are usually reluctant to such radical changes of the basic concepts. The result is – an efficient method is practically being forgotten for decades!

THE FORMAL BALANCE NUMBERS (FBN)

For this reason and in order to prevent any confusion, I will hereafter introduce the term formal balance number (FBN). What is this and why is it important? The brief explanation that follows is not completely precise, but it helps to explain the basic idea. The full significance of FBN will hopefully be understood by the end of the paper.

Formal balance numbers are an aid that may grossly facilitate the problem of balancing complex redox equations. They may be chosen as being equal to the traditional values of oxidation numbers, but not necessarily. An inspection of the redox equation may suggest the optimal values that are to be assigned to formal balance numbers. In most cases, these optimal values ensure that only two elements will "change their state" (i.e. the values of the formal balance numbers), allowing the use of the oxidation number technique for balancing equations, in its simplest form. Just like for oxidation numbers, the algebraic sum of the formal *balance numbers in a molecule/neutral unit is 0, while in an ion it is equal to its charge (the sum rule).*

Whenever in a given redox equation there is a pair of elements, one of which has increased and the other one decreased its oxidation number, the formal balance numbers are defined as being equal to the oxidation numbers of the elements in question. In this case, balancing the equation will be exactly the same as with the traditional/original oxidation number method. This is trivial.

When more than two elements change their oxidation state, a careful choice has to be made for the FBNs to be most effective in equation balancing. Usually, the FBN value for some element that *do change* its oxidation state *is fixed* (i.e. it is treated as a *constant* for that particular equation) to the value of the oxidation number of that element on the right-hand side of the equation. The choice may not be unique, as will be demonstrated by several examples below.

EXAMPLES

Example 1:

$$FeS_2 + O_2 \rightarrow SO_2 + Fe_2O_3$$

In terms of the oxidation numbers, one may write:

$$Fe^{+2} - 1e \rightarrow Fe^{+3}$$

$$S_2^{-1} - 10e \rightarrow 2S^{+4}$$

$$O_2^{0} + 4e \rightarrow 2O^{-2}$$

and the equation may easily be balanced, since both elements that are oxidized (Fe and S) are linked in FeS_2 unit. There is a transfer of –11e for the FeS_2 unit and +4e for the O_2 unit, and the balanced equation takes the form:

$$4FeS_2 + 11O_2 \rightarrow 8SO_2 + 2Fe_2O_3$$

Now let us show an alternative approach, employing FBNs. For oxygen these may be picked as being equal to the oxidation numbers (0 and –2, on the left and right-hand side of the equation, respectively). One **may postulate** that in the above reaction the FBNs for sulphur are **constant** and equal to +4 (the oxidation number of S in SO_2). In that case only Fe and O "change their state". From the sum rule, one gets:

$$Fe^{-8} - 11e \rightarrow Fe^{+3}$$

$$O_2^{0} + 4e \rightarrow 2O^{-2}$$

and the coefficients 4 and 11 are obtained immediately.

One may also fix the FBNs of Fe to +3, in which case those of S vary from –1.5 to +4:

$$S_2^{-1.5} - 11e \rightarrow 2S^{+4}$$

$$O_2^{0} + 4e \rightarrow 2O^{-2}$$

giving the same result, of course.

Example 2:

$$Fe(CNS)_3 + Cl_2 + H_2O \rightarrow HCl + H_2SO_4 + FeCl_3 + CO_2 + N_2$$

In terms of oxidation numbers, three elements (N, S and Cl) are involved in the redox process. It is much easier to use FBNs, which may be chosen in the following way: the FBNs of Fe, H and O may be fixed as the values of the corresponding oxidation numbers. The FBNs of Cl are 0 and –1, respectively (again, they are equal to the values of oxidation numbers). To have a **single element** that increases its FBN (which is analogous to oxidation), one may fix the FBN values of N to 0 and that of S to +6 (the true values of the oxidation numbers of these elements on the right-hand side of the equation). Then, using the sum rule:

$$C_3^{-7} - 33e \rightarrow 3C^{+4}$$

$$Cl_2^{0} + 2e \rightarrow 2Cl^{-1}$$

and the balanced equation is:

$$2Fe(CNS)_3 + 33Cl_2 + 36H_2O \rightarrow 60HCl + 6H_2SO_4 + 2FeCl_3 + 6CO_2 + 3N_2$$

Example 3:

$$Ag_3AsO_4 + Zn + H_2SO_4 \rightarrow AsH_3 + Ag + ZnSO_4 + H_2O$$

The equation is taken from Kolb [2]. In terms of oxidation numbers, Ag and As are reduced and Zn is oxidized. Alternatively, one may fix the FBN for Ag to 0 (the oxidation number for Ag on the right-hand side). The FBNs for Zn, H, O and S are equal to the conventional oxidation numbers. The FBNs for As are obtained by the sum rule:

$$As^{+8} + 11e \rightarrow As^{-3}$$

$$Zn^{0} - 2e \rightarrow Zn^{2+}$$

and the balanced equation takes the form:

$$2Ag_3AsO_4 + 11Zn + 11H_2SO_4 \rightarrow 2AsH_3 + 6Ag + + 11ZnSO_4 + 8H_2O$$

Example 4:

$$P_4 + P_2I_4 + H_2O \rightarrow PH_4I + H_3PO_4$$

This equation is the already mentioned "atypical redox equation" [1]. We will show one way to apply the FBN method. The FBNs for H and O are fixed to their oxidation number values (+1 and –2, respectively), and the FBN value for I is fixed to 0! In that case, the FBN of phosphorus on the left-hand side is also 0, but it is –4 in PH_4I and +5 in H_3PO_4. Now, one writes:

$$P^{0} + 4e \rightarrow P^{-4}$$

$$P^{0} - 5e \rightarrow P^{+5}$$

It is clear from the above, that the coefficients in front of PH_4I and H_3PO_4 should be in a ratio 5 : 4. In the first step of balancing, one may write:

$$aP_4 + bP_2I_4 + cH_2O \rightarrow 5PH_4I + 4H_3PO_4$$

and the reaction is balanced with a = 13/8 ; b = 5/4 and c = 16. In order to have all coefficients in integer form, the equation is to be multiplied by 8, i.e.:

$$13P_4 + 10P_2I_4 + 128H_2O \rightarrow 40PH_4I + 32H_3PO_4$$

Example 5:

$$Pb(N_3)_2 + Cr(MnO_4)_2 \rightarrow Cr_2O_3 + MnO_2 + + Pb_3O_4 + NO$$

This equation is, again, taken from Kolb [2]. It is questionable whether the process described by it is feasible, because the very existence of chromium(II) permanganate is highly improbable, if not impossible. Anyway, it may be balanced easily. The FBN value for N is fixed to +2, and that of Mn to +4 (these are, as in the previous examples above, the oxidation numbers of the corresponding elements on the right-hand side of the equation). In that case, only lead and chromium change their FBN values:

$$3Pb^{-12} - 44e \rightarrow Pb_3^{+8/3}$$

$$2Cr^{+8} + 10e \rightarrow Cr_2^{+3}$$

and the balanced equation is:

$$15Pb(N_3)_2 + 44Cr(MnO_4)_2 \rightarrow 22Cr_2O_3 + 88MnO_2 + + 5Pb_3O_4 + 90NO$$

Example 6:

$$CuSCN + KIO_3 + HCl \rightarrow CuSO_4 + KCl + HCN + + ICl + H_2O$$

This is one of the challenges offered by Stout [11]. The FBNs of I are equal to the values of the oxidation numbers of iodine (+5 and +1, respectively). According to what was a common practice so far, it is perhaps most convenient to fix the FBN values of S, C, and N to +6, +2 and –3. The FBNs of Cu and I change in the following way:

$$Cu^{-5} - 7e \rightarrow Cu^{+2}$$

$$I^{+5} + 4e \rightarrow I^{+1}$$

and result in:

$$4CuSCN + 7KIO_3 + 14HCl \rightarrow 4CuSO_4 + 7KCl + + 4HCN + 7ICl + 5H_2O$$

Example 7:

$$[Cr(N_2H_4CO)_6]_4[Cr(CN)_6]_3 + KMnO_4 + H_2SO_4 \rightarrow$$

$$K_2Cr_2O_7 + MnSO_4 + CO_2 + KNO_3 + K_2SO_4 + H_2O$$

This is the final example and it is also taken from Stout [11]. The author stated that several hours were needed to balance the equation, and another hour to check the result. Employing FBNs, it took between 5 and 10 minutes to balance the equation and about 1 minute to check the result (actually, to count the atoms on both sides). To have a better control over the process of balancing, let us first rewrite the equation as:

$$Cr_7C_{42}H_{96}N_{66}O_{24} + KMnO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + + MnSO_4 + CO_2 + KNO_3 + K_2SO_4 + H_2O$$

The FBN values of Mn are equal to +7 and +2 (the standard choice). The FBN values for N and C are fixed to +5 and +4, respectively. In terms of FBNs, chromium and manganese "change their state" in the following way:

$$2Cr_7^{-546/7} - 1176e \rightarrow 7Cr_2^{+6}$$

$$Mn^{+7} + 5e \rightarrow Mn^{+2}$$

and the coefficients are:

$$10[Cr(N_2H_4CO)_6]_4[Cr(CN)_6]_3 + 1176KMnO_4 + +1399H_2SO_4 \rightarrow 35K_2Cr_2O_7 + 1176MnSO_4 + + 420CO_2 + 660KNO_3 + +223K_2SO_4 + 1879H_2O$$

The above examples show that the method is highly efficient and time saving. In fact, this is the only method I know of, that is always fast enough, once you become familiar with it. Give it a try. The more you use it, the more you'll like it.

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Р е з и м е

ЕДЕН БРЗ НАЧИН ЗА ИЗРАМНУВАЊЕ НА РЕДОКС-РАВЕНКИ
ВОВЕДУВАЊЕ НА ФОРМАЛНИ БРОЕВИ ЗА ИЗРАМНУВАЊЕ

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Клучни зборови: хемиски равенки, израмнување; прилози кон високото образование по хемија; помош при учење/настава

Познат е голем број методи за израмнување хемиски равенки. Во трудов е предложена варијанта на методот на оксидациони броеви, која овозможува брзо и лесно израмнување на комплексни редокс-равенки. Клучно е воведувањето на поимот формални броеви за израмнување (formal balance numbers, FBN). Овие броеви се воведени како алтернатива за конвенционалните вредности на оксидационите броеви. Вредностите на FBN се избираат така што да овозможуваат промена на состојбата на само два елемента. Во таков случај може да се употреби оригиналниот метод на оксидациони броеви за израмнување на равенките. Предложениот метод е, веројатно, најбрзиот од сите што не вклучуваат употреба на сметачи.