Balancing a Chemical Equation

What Does It Mean?

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Recently, I gave my general chemistry students a series of chemical equations to balance. Several of these concerned redox reactions. One in particular referred to the production of chlorine IV oxide and chlorine gas from chlorate and chloride ions in acidic medium.

$$ClO_3^- + Cl^- + 2H^+ \rightarrow ClO_2 + 1/2Cl_2 + H_2O$$

This reaction is described in many texts as a suitable way to obtain the highly reactive yellow–green gas ClO_2 (mp = –59 °C; bp = 11 °C).[1]

ClO_2 is an important bleaching agent with many industrial applications such as the bleaching of wood pulp. Due to the great reactivity of ClO_2 it is produced industrially in situ from chlorate, as $NaClO_3$ or $KClO_3$, and from a reducing agent in acidic medium, for example, SO_2 in an acid, such as H_2SO_4 or HCl, or SO_2 in moist oxalic acid.[2]

A student readily reported the correct balanced equation as given above. He had arrived at his coefficients by the method of changing the oxidation number. The same result could be better described using two half reactions that show the transfer of only one electron.

$$ClO_3^- + e^- + 2H^+ \rightarrow ClO_2 + H_2O \qquad E^o = +1.15\ V$$

$$Cl^- \rightarrow 1/2Cl_2 + H_2O + e^- \qquad E^o = -1.36\ V$$

$$ClO_3^- + Cl^- + 2H^+ \rightarrow ClO_2 + 1/2Cl_2 + H_2O \qquad \Delta E^o = -0.21\ V$$

The reaction is not spontaneous because the emf values for the two half reactions give $\Delta E^o = -0.21$ V, which corresponds to a positive ΔG^o value.

What came next was very interesting. Other students claimed to have arrived at different coefficients for the overall reaction. They claimed that their numbers were equally correct, meaning that quite different stoichiometries were possible. Some examples are given below, including eq 1 above, multiplied by a factor of 8.

$$8ClO_3^- + 8Cl^- + 16H^+ \rightarrow 8ClO_2 + 4Cl_2 + 8H_2O \qquad (1)$$

$$8ClO_3^- + 16Cl^- + 24H^+ \rightarrow 6ClO_2 + 9Cl_2 + 12H_2O \qquad (2)$$

$$8ClO_3^- + 24Cl^- + 32H^+ \rightarrow 4ClO_2 + 14Cl_2 + 16H_2O \qquad (3)$$

$$8ClO_3^- + 32Cl^- + 40H^+ \rightarrow 2ClO_2 + 19Cl_2 + 20H_2O \qquad (4)$$

Needless to say, the students were puzzled by this seeming paradox. Furthermore, they noticed that the coefficients changed regularly in the sequence above. Thus, they were able to envisage the possibility that no ClO_2 would be produced.

$$8ClO_3^- + 40Cl^- + 48H^+ \rightarrow 24Cl_2 + 24H_2O \qquad (5)$$

Of course the equation can be balanced algebraically. This is straightforward, and gives the following general expression.

$$aClO_3^- + bCl^- + (a + b)H^+ \rightarrow \frac{(5a - b)}{4}ClO_2 + \frac{(5b - a)}{8}Cl_2 + \frac{(a + b)}{2}H_2O$$

All the previous coefficients can be fitted into this arrangement because an infinite number of solutions can also be proposed.

It can also be shown that if both ClO_2 and Cl_2 are produced, then

$$\frac{a}{5} < b < 5a$$

However, if one of them is not formed, then

$$\frac{a}{5} \leq b \leq 5a$$

This leads to

$$b = 5a$$

when no ClO_2 appears on the right-hand side, as in eq 5. Conversely, it leads to

$$b = \frac{a}{5}$$

when there is no Cl_2, as in eq 6.

$$5ClO_3^- + Cl^- + 6H^+ \rightarrow 6ClO_2 + 3H_2O \qquad (6)$$

The reader can readily show that eq 6 is rather unlikely to occur, by considering the corresponding half reactions and by using their emf's (from footnote 3, for example) to determine ΔE^o for the overall reaction.

The whole situation raised a very pertinent question that both texts and instructors frequently fail to emphasize.

> What is the meaning of a chemical equation?

In other words

> To what extent does a chemical equation truthfully describe an actual reaction both qualitatively and quantitatively?

All this led to very fruitful discussions with the students. They wanted to know how exact a science chemistry is, after all.

Of course we are dealing with a special type of redox reaction. If chlorate can be reduced to chlorine IV oxide, it can also be reduced further to chlorine gas, and intermediate species can intervene in the process. Thus, there are two possiblle sources of chlorine gas: chlorate and chloride.

The overall reaction is simply the sum of several steps; It does not tell what is actually occurring. Thus, by choosing different steps we can arrive at each of the final results given by eqs 2–5.

As an example, let us look at eq 2 (E^o values fromfootnote 1 and 3):

[1]Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1970; pp 989–992.
[2]Cotton, F. A.; Wilkinson, G. *Basic Inorganic Chemistry*; Wiley: New York, 1976; p 326.
[3]Douglas, B.; McDaniel, D. H.; Alexander, J. J. *Concepts and Models of Inorganic Chemistry*; Wiley: New York, 1983; p 504.

$$3ClO_3^- + 3e^- + 6H^+ \rightarrow 3ClO_2 + 3H_2O \qquad E^\circ = +1.15\ V$$

$$ClO_3^- + 5e^- + 6H^+ \rightarrow 1/2Cl_2 + 3H_2O \qquad E^\circ = +1.47\ V$$

$$8Cl^- \rightarrow 4Cl_2 + 8e^- \qquad E^\circ = -1.36\ V$$

$$4ClO_3^- + 8Cl^- + 12H^+ \rightarrow 3ClO_2 + 9/2Cl_2 + 6H_2O \qquad \Delta E^\circ = -0.01V$$

or

$$8ClO_3^- + 16Cl^- + 24H^+ \rightarrow 6ClO_2 + 9Cl_2 + 12H_2O$$

This last result is obviously identical to eq 2.

Alternatively, the following pathway can also be written.

$$3ClO_3^- + 3e^- + 6H^+ \rightarrow 3ClO_2 + 3H_2O \qquad E^\circ = +1.15\ V$$

$$ClO_3^- + 2e^- + 3H^+ \rightarrow HClO_2 + H_2O \qquad E^\circ = +1.21\ V$$

$$HClO_2 + 3e^- + 3H^+ \rightarrow 1/2Cl_2 + 2H_2O \qquad E^\circ = +1.64\ V$$

$$8Cl^- \rightarrow 4Cl_2 + 8e^- \qquad E^\circ = -1.36\ V$$

$$4ClO_3^- + 8Cl^- + 12H^+ \rightarrow 3ClO_2 + 9/2Cl_2 + 6H_2O \qquad \Delta E^\circ = -0.01\ V$$

The latter result is also obviously equivalent to eq 2.

Similar schemes can be devised for eqs 3 and 4, with alternative pathways as well. The values of ΔE° for the reactions of these two equations and for eq 5 are listed below.

eq 3: $\Delta E^\circ = +0.06\ V$

eq 4: $\Delta E^\circ = +0.09\ V$

eq 5: $\Delta E^\circ = +0.11\ V$

The ΔE° values show that the reaction of eq 5 is more favorable in terms of ΔG°.

These reactions also depend upon the availability of H^+. The H^+/Cl^- ratio increases from 1.2, for the reaction of eq 5, to 2.0, for the reaction of eq 1. Since this ratio varies during the course of the reaction, several different reactions are actually likely to occur. This shows that we actually have a complex process of competing reactions.The reactions written above represent only a few.

This seeming anomaly arises from a common misconception held by beginning students in which they equate chemical equations with actual reactions. In fact, the former equations represent only a partial shorthand for the latter.

A chemical equation is expected to describe what occurs as accurately as possible—qualitatively as well as quantitatively. If a reaction yields only one set of products, this will become much easier. On the other hand, if side reactions can also occur with the main process, and if this leads to more than one set of products, the search for the mechanism (or mechanisms) may be much more difficult.

This is also the case if the same set of products can be obtained in different proportions. Here too a precise statement is needed concerning the conditions under which the reaction is to be carried out. For example, the concentrations of the reagents are of paramount importance. Most students know that concentrated HNO_3 reacts with copper to give reddish NO_2 gas, whereas the dilute acid will produce colorless NO. Thus, it is not enough to speak of the reaction between HNO_3 and copper; it becomes necessary to specify the conditions.

The considerations above are important when dealing with the reaction described in this paper. The main chemical phenomenon under discussion is the production of chlorine dioxide from a mixture of chlorate and chloride in acidic medium. Besides the main course of the reaction, side reactions are also possible.

The seeming paradox arises when one considers that all reactions have the same probability of occurring, which is obviously not possible. Thus, to understand the problem, it is not enough to know how to add several half reactions. Knowing the actual mechanism is necessary in determining what the main chemical process is and what side reactions occur, if any.

Conclusion

I believe this discussion should be brought to the attention of chemistry instructors because it offers such a wealth of topics that are relevant to chemical education. As a final note, students and their teachers are asked to look for additional examples of reactions that fall into this category, in which one of the products is formed from one reactant, and the other product can be originated by either reactant.