letters

Stoichiometry and Chemical Reactions

To the Editor:

In a recent article (*1*) Carlos A. L. Filgueiras described the fruitful discussions he had with students on an interesting problem on balancing chemical reactions. The paper appears to indicate that some satisfactory solution was arrived at to understand how a number of balanced chemical reactions could arise in balancing chemical reactions. In various other contexts (*2, 3*) this problem has been discussed in different apparently unrelated garbs.

In our opinion, the basic problem is simple, which when not recognized could give rise to various ad hoc solutions. We pose the problem as follows.

Given the reactants and products, can there exist different ways of balancing a chemical reaction?

Because we know that a given reaction (reactants and products in a given thermodynamic state of temperature and pressure) must satisfy stoichiometry, it can have no more than one balanced equation. Therefore, we will be left with the problem of identifying which of the infinite balanced equations that are possible is the correct equation representing the reaction.

Thus, for example, our problem would be to identify which of the following equations is the correct one representing the reaction between ClO_3^-, ClO_2, Cl^-, Cl_2, H^+, and H_2O.

$$2ClO_3^- + 2\ Cl^- + 4\ H^+ = 2\ ClO_2 + Cl_2 + 2\ H_2O \qquad (1)$$

$$4\ ClO_3^- + 12\ Cl^- + 16\ H^+ = 2\ ClO2 + 7\ Cl_2 + 8\ H_2O \qquad (2)$$

$$8\ ClO_3^- + 16\ Cl^- + 24\ H^+ = 6\ ClO_2 + 9\ Cl_2 + 12\ H_2O \qquad (3)$$

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

Consider along with the above equations, the following reaction.

$$ClO_3^- + 5\ Cl^- + 6\ H^+ = 3\ Cl_2 + 3\ H_2O \qquad (5)$$

Equations 2, 3, and 4 represent combinations of the independent chemical reactions 1 and 5 in various ratios, and, therefore, are not simple chemical reactions but combinations of chemical reactions. We can, therefore, get an infinite number of balanced equations by combining in various ratios two or more balanced reactions. But out of the infinite number of balanced equations only one qualifies to be a reaction.

Thus, when two or more equations involving the same reactants and products are given, we immediately infer that the equation is a combination of independent reactions and does not represent a single chemical reaction.

However, a problem arises when only one such equation is given and its thermodynamic properties such as ΔG^0, E^0 etc., are discussed. In such cases, we can try to find out the two half-cell reactions that give rise to the given reaction. Thus,in the example under discussion, chlorine in the oxidation states 5, and −1, react to give 4 and zero. When half-cell reactions involving these states is written we immediately get the reaction involving the four species. If the given equation is different from this one, it is deemed to be a combination of more than one reaction.

That a given reaction is a combination of other independent equations does not amount to finding out the mechanism of the process, as was given by Carlos A. L. Filgueiras. Mechanism of a given reaction cannot be obtained from considerations of stoichiometry. A given reaction can follow different paths (mechanisms) depending on the conditions of experiment (e.g., presence of catalysts); whereas, it cannot have different stoichiometries.

Literature Cited

1. Filgueiras, C.A.L. *J. Chem. Educ.* **1992,** *69,* 276–277.
2. Jeremy, R.; Richmond, T. G. *J. Chem. Educ.* **1992,** *69,* 114–115.
3. Gil, V. M. S. *J. Chem. Educ.* **1989**, *66*, 324.

P. Radhakrishnamurty
Central Electrochemical Research Institute
Karaikudi 623 006, India

To the Editor:

The letter by P. Radhakrishnamurty concerning my paper [*J. Chem. Educ.* **1989,** *69* (4), 276] seems to imply that I might hold the belief that reaction mechanisms can be determined from stoichiometry. This is so far from the truth that it reverses the whole meaning of the paper, which was written to show, among other things, how the mere writing up of balanced equations may be unrelated to the actual reaction which takes place.

The second half of the article clearly addresses the misconceptions many people have regarding the words "equation" and "reaction". What happens when chlorate and chloride ions interact in acidic medium makes an excellent case for classroom discussion of those terms, as well as that of the reaction mechanism. As I stated in my paper, "It is not enough to know how to add several half reactions. Knowing the actual mechanisms is necessary in determining what the main chemical process is and what side reactions occur, if any."

Carlos A. L. Filgueiras
Departamento de Quimica—ICEX—UFMG
31.270 Belo Horizonte, MG, Brasil

Improving Laboratory Technique When Titrating Silver Ion with Ethylenediammine

To the Editor:

The article by H. Meyer [*J. Chem. Educ.* **1992,** *69,* 499] is a valuable contribution of laboratory technique. However, the interpretation of the titration of silver ion with ethylenediammine is flawed. The molar ratio of en/silver ion of 1.15 surely indicates the formation of polynuclear complexes [Cotton, F.A.; Wilkinson, G., *Advanced Inorganic Chemistry*, 3rd ed.; 1972; pp 1047, 1048]. If mononuclear complexes of en and silver ion are formed, it would be at a much lower concentration of silver ion. Monoethanolamine should work well as an alternative to ammonia with less chance of forming polynuclear complexes. It would be better technique to use a number of points past the end point to verify the coordination number and stability constants of the complexes of silver ion formed in solution.

Dean C. Luehrs
Michigan Technological University
Houghton, Michigan

Empirical Formulas

To the Editor:

The article by E. Weltin on "Empirical Formulas from Atom Ratios" [*J. Chem. Educ.* **1993,** *70*, 280] reminds this old-timer of another method: Use a slide rule to divide the number of moles of carbon by the number of moles of hydrogen, and look up and down the C and D (and CF and DF) scales for pairs of integers which give the same ratio.

Alex R. Nisbet
Ouachita Baptist University
Arkadelphia, AR 71923