

The Symbolism of Chemical Equations

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Question

What is the origin of the equal sign and double arrow symbolism in balanced chemical equations?

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Answer

The earliest precursor of the modern chemical equation is the affinity diagram, first introduced in the late 18th century, and designed to highlight the various competing interparticle forces or affinities at work in a given chemical reaction. A typical example, taken from Antoine Fourcroy's textbook of 1789, is shown in figure 1 for the double decomposition reaction between calcium nitrate and potassium sulfate (1).

By the 1830s the hypothetical numerical affinity values used in these diagrams had been replaced by equivalent or atomic weight values, as shown in the example in figure 2, taken from the 1833 volume on *Chemical Diagrams* by Lee (2). Such diagrams continued to be used well into the 1860s, though the printed names for the various chemicals were gradually replaced by compositional formulas based on the atomic symbolism first introduced by Berzelius in 1814 (3).

The appearance of linear chemical equations and the accompanying use of the equal sign to separate the reactants from the products began in the late 1840s. They were, for example, introduced in the 1847 edition

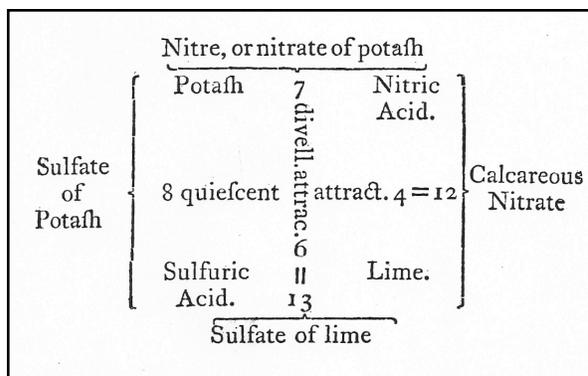


Figure 1. A typical 18th-century affinity diagram (1)

of George Fownes' introductory textbook, where they appear as a supplement to the more common affinity diagrams (4). It has been argued that this switch from diagrams to linear equations reflects a change in emphasis from the inequality of Newtonian forces of affinity to the conservation of Daltonian atomic and/or equivalent weights in chemical reactions (5).

Though the concept of chemical equilibrium was introduced by Berthollet as early as 1801 and was given a kinetic rationale by Guldberg and Waage as early as 1864, it was not until the end of the 19th century that this concept impacted on the symbolism used in the writing of chemical equations. In 1894 Ostwald suggested replacing the equal sign by a flattened "z" to indicate the presence of a reversible equilibrium (6), and in 1898 van't Hoff introduced the use of double arrows for the same purpose (7). A more elaborate symbolism was proposed by Marshall in 1902 which included the use of the currently favored double barb for equilibrium reactions (8).

Literature Cited

1. A. Fourcroy, *Elements of Natural History and Chemistry*, Vol. 1, Elliot and Kay: London, 1790, p. 65. This is a translation of the 3rd French edition of 1789. More elaborate examples of these diagrams may be found in T. Bergman, *A Dissertation on Elective Attractions*, Murray:

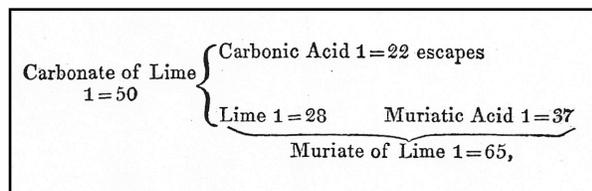


Figure 2. An early 19th-century reaction diagram using equivalent weights (2).

London, 1785. This is an English translation of the original Latin edition of 1775.

2. A. Lee, *Chemical Diagrams, Accompanied by a Concise Description of Each Decomposition*, Cox: London, 1833.

3. J. D. Steele, *A Fourteen Weeks Course in Chemistry*, Barnes: New York, NY, 1868. This was the most popular American high school text of the last quarter of the 19th century and contains more than a dozen reaction diagrams using the symbolism of Berzelius.

4. G. A. Fownes, *Manual of Elementary Chemistry, Theoretical and Practical*, 7th ed. Blanchard and Lee: Philadelphia, 1864. See the preface to the first edition of 1847, p. x. Dual use of both linear equations and affinity diagrams continued at least until the 10th edition of 1868.

5. A. Thackray, *Atoms and Powers. An Essay on Newtonian Matter-Theory and the Development of Chemistry*, Harvard: Cambridge, MA, 1970, p. 276.

6. W. Ostwald, *Die wissenschaftlichen Grundlagen der analytischen Chemie*, Engelmann: Leipzig, 1894, p. 54.

7. J. H. van't Hoff, *Lectures on Theoretical and Physical Chemistry*, Vol. 1, Arnold: London, 1898, p. 13.

8. H. Marshall, "Vorschlag, betreffend den Gebrauch modificierter Gleichheitszeichen in der chemischen Zeichensprache," *Z. physik. Chem.*, **1902**, *41*, 103-106.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

2009 Update

Since writing the original column I have discovered that van't Hoff had actually introduced the double-arrow symbolism for equilibrium reactions as early as 1884. See:

J. H. van't Hoff, *Etudes de dynamique chimique*, Muller: Amsterdam, 1884, p. 5.