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The Birth of Stoichiometry

A three-volume work appeared in Silesia in 1792–3 with the title "Anfangsgründe der Stöchyometrie oder Messkunst chymischer Elemente." It attracted no notice and certainly few bothered to read it. The copy in the library at Budapest still had its pages uncut when it first came into this writer's hands.

Despite this indifference the book proved to be extremely important in the development of chemistry; however, this effect came long after its publication date. It contains the rudiments of chemical calculations, i. e., of stoichiometry, a term coined by the author of the book. Perhaps this word itself contributed to the coldness of the reception accorded the work.

Jeremias Benjamin Richter (Fig. 1) was born just 200 years ago, on March 10, 1762, at Hirschberg in Silesia. He decided on a military career and served in the engineering corps of the Prussian army for seven years. He had to leave the army because of a breach of discipline; the details are not known. However, it has been said that his heart was not in the army but in chemistry, in which he had trained himself by reading such textbooks as were within his means. In 1785 he entered the University of Königsberg and studied philosophy and mathematics. Immanuel Kant was then teaching there and the great philosopher made a deep impression on the young Richter. He was especially influenced by the Kantian statement that any discipline among the natural sciences is a true science only to the extent it contains mathematics. Richter decided to make chemistry a true science in this sense, in other words to impart a mathematical character to chemistry which was then a purely empirical field. This idea appears clearly in the title of his doctoral dissertation: "De usu matheseos in Chemia" (1789). After obtaining his degree, he remained at the University of Königsberg for a time as Privatdozent. However, his income was inadequate and he augmented his earnings by doing land surveying on a near-by estate. He fitted up a small laboratory where he carried out his chemical experiments, and it was here that he wrote his book.

In 1795 he became a mine inspector and assayer in Silesia; it was not much of a position. His annual salary was only 300 thalers; he and his assistant shared a drafty clammy room where his clothes and books rotted and his instruments rusted. He always nourished the hope of securing a chair at a university or at least a secondary school, but in vain. He earned money for books and chemical supplies by constructing aerometers, and in fact the arbitrary scale he introduced lasted for a long time as the "Richter" scale. His financial condition was somewhat bettered in 1798 when he took a position in the Royal Porcelain Works at Berlin as "second arcanist" with an annual salary of 700 thalers. He worked principally in the pigment laboratory. He never married; he lived by himself; and he worked incessantly, day and night, as though he had a presentiment that he had not long to live. He died at 45 of tuberculosis, on May 4, 1807. During his lifetime he received no recognition; the honors which his ideas brought were purely posthumous.

Figure 1. Jeremias Benjamin Richter (1762–1807).

The objective and content of his book are best summed up in Richter's own words:

> Mathematics includes in its sphere all those sciences where there are only magnitudes and consequently a science lies more or less in the field of measuring according to the more or fewer magnitudes it contains to be measured. Because of this truism I frequently was led during chemical experiments to consider the problem whether and to what extent chemistry is really a branch of applied mathematics; it arose especially in the familiar finding that two neutral salts, on reacting with each other, again produce neutral compounds. The direct conclusion which I drew from this fact could be no other than that there must be definite weight relationships between the components of the neutral salts. From that time on I cogitated as to how these relationships could be discovered, partly by precise trials, and partly by combining chemical analysis with mathematical analysis . . . .
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> Since the mathematical part of chemistry deals mostly with materials that are indestructible substances or elements and teaches how the relative proportions between them are determined, I was not able to find a shorter or more fitting name for this discipline than the word stoichiometry from στοιχειον, which in the Greek language denotes something which cannot be further subdivided, and μετρειν, which means finding proportions of magnitude (*1*).

The essential content of the three volumes can be summed up rather freely as follows. Compounds have a constant composition. If one and the same amount of an acid is neutralized by different amounts of two bases, the neutralization of these amounts of these bases requires like amounts of any acid. It follows that when two salts react with each other, and if the quantity relation of their components is known, the quantity relation of the components in the reaction products can also be calculated. These facts however were expressed by Richter in a much more laborious, and complicated, and drawn-out fashion. The modern reader senses how difficult it was for Richter to find expressions for these relations and proportions which are so familiar to us. As was stated above, Richter really recognized that certain quantities of compounds are equivalent, and by means of these equivalent weights it is possible to treat chemical changes mathematically and to calculate the composition of the products. He, in fact, determined these equivalent quantities experimentally, and designated them as "Massenzahlen."

He determined the quantities of alkalis and earths which combine with 1000 parts by weight of the various acids. An example will illustrate (the old names are here given in their modern equivalents): 2400 grains of $CaCO_3$ yield 1342 grains of CaO, i.e., $CaCO_3:CaO = 1000:559$; the saturation of 5760 grains of HCl requires 2393 grains of $CaCO_3$, and the evaporation residue after ignition weighs 2544 grains. Therefore, $HCl:CaCO_3 = 5760:2393$, but since $CaO = CaCO_3 \times 559/1000$, it follows that $HCl:CaO = 5760:2393 \times 559/1000 = 5760:1337$. These 1337 grains have been formed in the resulting salt from the oxide. If this amount is subtracted from the weight of the salt, there remains $2544 - 1337 = 1207$ for the acid. Accordingly, in the case of $CaCl_2$, the relation between the acid and the base must be $1207:1337 = 1000:1107$. By this procedure he found, for example, that on the basis of 1000 units of hydrochloric acid, the equivalent of alumina is 734, of magnesia 858, of lime 1107, etc. He also determined in this manner the equivalent weights corresponding to 1000 parts of other acids. Had he referred all of these values to a single compound, a real stoichiometric table of equivalents would have emerged. However, he did not do this, even though such conversions were not outside his experience since actually he had made similar recalculations in his reaction equations. Richter had in fact developed a notation by which he could represent chemical reactions and their quantity relationships.

The upper equation in Figure 2 shows the reaction

$$BaCl_2 + MgSO_4 = BaSO_4 + MgCl_2$$

The heading "3099 Schwererden Salz 1000" signifies that the proportion oxide:acid in this salt equals 3099:1000. While 1000 parts of hydrochloric acid saturate (neutralize) 858 parts of magnesia, 1000 parts of sulfuric acid neutralize 616 parts of magnesia, and consequently the neutralization of 858 parts of magnesia requires 1394 parts of sulfuric acid. This proportion is shown in the lower line of the diagram. The oblique lines represent the reaction products, whose composition is then given at both ends. In other words, 1858 parts of Magnesien-Salz ($MgCl_2$) consist of 1000 parts of acid and 858 parts of the earth (MgO), and 4493 parts of Schwerspath ($BaSO_4$) consist of 3099 parts of the earth (BaO) and 1394 parts of the acid (SO_3) (*2*). In the latter instance, the correct figures are 2951 BaO and 1542 SO_3.

Nonetheless, Richter's book and his ingenious and original ideas met with little success during his lifetime. It is of interest to inquire into the causes for this disappointing lack of appreciation and acceptance.

The first cause lay in the involved complicated manner in which Richter expressed his ideas. Secondly, Volume 1 frightened many readers from continuing. It was Richter's intention in this volume to instruct the chemists in mathematics, a field in which, in general, they were not at home. He must have had an extremely poor opinion of the mathematical ability of his fellow chemists since he began as follows:

> When a number or a magnitude is to be added or summed with another, one writes before it the sign +, which is called plus; if on the other hand it is to be taken from or subtracted, then it should be preceded by the sign −, which is known as minus. For instance, +19 + 424 is the same as 19 and 424 or 424 and 19, *i.e.* 443 . . . (*3*).

He then proceeds rather rapidly to equations of the second order. Then comes the discussion of the so-called "pure stoichiometry" which is initially treated in condensed form in two pages (*4*). This brief treatment is followed by all sorts of theoretical problems dealing with density, affinity, and masses of compounds, and the results demonstrated with the aid of endlessly long mathematical equations. The present writer skimmed through these pages but he confesses that he did not grasp much of what Richter presented there. The determination of the Masszahlen, *i.e.*, the equivalent weights, is given in Volumes 2 and 3, where the so-called "applied stoichiometry" is discussed.

A further error of Richter was that he based his numerical values on very incorrect analyses of salts. The composition of various salts had been determined with greater accuracy by earlier workers. For instance, the analyses of salts published by C. F. Wenzel (1740–1793) in 1777 were much more accurate (*5*).

Finally, Richter tried to find in chemistry more regularities that could be expressed mathematically than are actually there. He had a notion, which he constantly tried to prove, that the equivalent weights could be arranged in series which had to exhibit certain regularities. He shuffled these numbers and calculated them over and over until he thought that he had arrived at the proof that the mass series of the acids conform to true arithmetical progressions, whereas those of the bases follow geometrical progressions. He found no numbers corresponding to certain members of the progressions, and postulated, as Mendeleev did when setting up the periodic arrangement of the elements, that these gaps must belong to acids and oxides that were still unknown. However, Mendeleev's prophecies turned out to be correct, but Richter's predictions proved to be wrong. Who can say today whether Richter did not occasionally "correct" his experimental data to make them fit better into his imagined series; was this perhaps the real reason for his poor analytical results? Preconceived ideas to which a scientist clings too closely and which he insists on proving, have more than once served their originators poorly.

Nevertheless, the time came when the correct features of Richter's "Stochyometrie" began to have an effect. G. E. Fischer of Berlin did what Richter should have done and recalculated all of the latter's values to sulfuric acid 1000. This so-called Fischer table was included by Berthollet in his "Essai d'une statique chimique" (*6*). Dalton was acquainted with this text and was influenced by it. Berzelius had also read Richter's volumes and this work gave him the idea, even before he learned of Dalton's atomic theory, to make accurate measurements of the equivalent weights of compounds. He wrote (*7*) of Richter in the following terms:

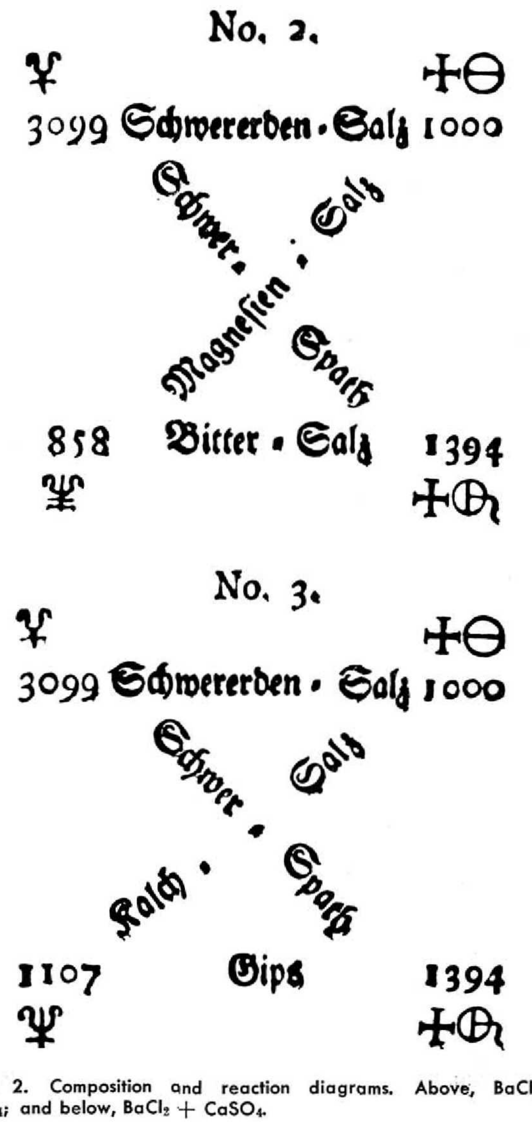

Figure 2. Composition and reaction diagrams. Above, $BaCl_2 + MgSO_4$; and below, $BaCl_2 + CaSO_4$.

Since I was planning to write a textbook of chemistry, I went through a number of not widely-read works, including also those written by Richter. I was astounded at how much light was shed there regarding the composition of salts and the mutual precipitation of metals, from which no advantage had been gleaned up to now.

Accordingly, Richter's ideas undoubtedly influenced Dalton and Berzelius, to whom we owe the atomic theory and the determination of atomic weights, through which the stoichiometric system of calculation was brought to its rightful status in chemistry.

Literature Cited

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(2) *Ibid.*, vol. 2, p. 59.
(3) *Ibid.*, vol. 1, p. 88.
(4) *Ibid.*, vol. 1, p. 124.
(5) Wenzel, C. E., "Lehre von der Verwandschaft der Körper," Dresden, **1777**.
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(7) Berzelius, J. J., "Lehrbuch der Chemie," Dresden-Leipzig, **1836**, vol. 24.