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AN EARLY HISTORY OF ALEXANDER CRUM BROWN'S GRAPHICAL FORMULAS

> The exact sciences are a set of formulae which have a bearing on experience. ... an object is transformed into a tool by a purposive effort ...
>
> Michael Polanyi, *Personal Knowledge*

Chemical structure and atomism were lively topics for chemists in the 1860s. Yet the central achievement of intercalated theoretical, laboratory, and didactic practices of chemistry in that decade was neither structure theory nor a triumph of atomism. Instead, a project that was crucial to the subsequent success of chemical structure and atomism made a large step in its ongoing development. This was the stabilization and production of chemical knowledge on the page. After 1861 the core of this project came to involve the graphical formulas of Alexander Crum Brown, which became "Frankland's notation," which became modern structural notation. This account of the early trajectory of Crum Brown's graphical formulas focuses on how those formulas became paper tools.

VISUALIZING CHEMISTRY

An impulse to visualize chemical knowledge was manifested during the chemical revolution (if not well before in Etienne François Geoffroy's *table des rapports,* or even earlier in alchemical symbology).[1] Jean Henri Hassenfratz and Pierre August Adet fashioned a symbolic counterpart to the new nomenclature of Guyton, Lavoisier, Berthollet, and Fourcroy in 1787.[2] Reminiscent of alchemical symbols, Hassenfratz and Adet's system was never widely used. However, Lavoisier, Berthollet, and Fourcroy placed an imprimatur on the visualization of chemical knowledge by writing of those symbols that they had "the advantage of painting to the sight, not words, but facts, and giving just ideas of the combinations which they represent."[3] John Dalton extended the project of visualizing chemistry by inaugurating a structural practice of chemistry with his atomic system, which employed different circles to represent the atoms of various chemical elements.[4] Dalton's system may have enjoyed somewhat wider use than that of Hassenfratz and Adet, but it was nudged aside by a more aptly skeptical yet flexible vehicle for chemical atomism, Berzelian notation, particularly after 1830.[5] By the 1850s type theory employed a new notational scheme that expanded upon Berzelian formulas, which set the stage for many different graphical (or structural) models at the end of that decade.[6]

U. Klein (ed.), Tools and Modes of Representation in the Laboratory Sciences, 35–46.

At mid-century as typographical possibilities advanced in tandem with the increasing use of visual tools in chemistry, Dalton's larger commitment to chemical structure was revitalized. It was the Scottish chemist—then a young medical student—Alexander Crum Brown who gave lasting form to chemical structure with the "graphical formulae" introduced in his 1861 University of Edinburgh medical thesis.[7] Crum Brown's thesis has not gone unnoticed in the history of chemistry, but in order to better understand the origin of paper tools that remain central to chemistry, it merits renewed attention.

ALEXANDER CRUM BROWN'S 1861 M.D. THESIS

Although the entire thesis is a fascinating window on nineteenth-century chemistry, I will focus upon Crum Brown's introduction and use of a new graphical tool for molecular hypothesizing.[8] Crum Brown elaborated at some length on types and radicals, and paid particular attention to the concept of atomicity (or valence). Midway in the thesis, he addressed multiple and mixed types, and he condensed Charles Gerhardt's four types to "the simplest type viz. the multiple type of hydrogen." This was the crux of Crum Brown's move from types to structure, in which he effectively transformed the concept of the chemical type into what Edward Frankland was soon to call the chemical bond. Crum Brown employed two Daltonian hydrogen atoms, connected by a line of force. He wrote, "For if we consider two monatomic atoms in the single hydrogen type to be connected together by one line of force ..."[9]

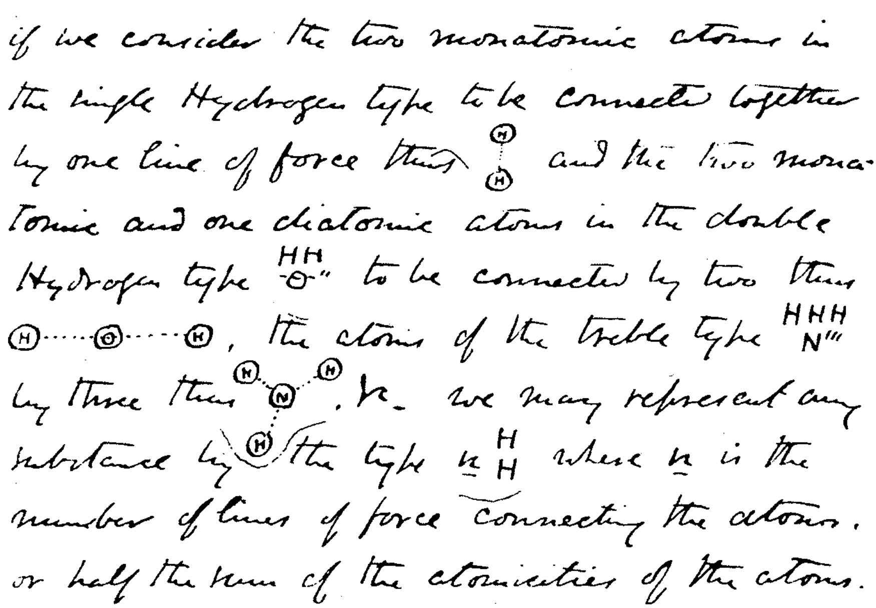
if we consider the two monatomic atoms in the single Hydrogen type to be connected together by one line of force thus H–H and the two monatomic and one diatomic atoms in the double Hydrogen type $\overset{HH}{\Theta''}$ to be connected by two thus H···O···H, the atoms of the treble type $\overset{HHH}{N'''}$ by three thus, &c. we may represent any substance by the type $n\frac{H}{H}$ where n is the number of lines of force connecting the atoms, or half the sum of the atomicities of the atoms.

Fig. 1. Crum Brown's first use of graphical formulas (Thesis, 30).

Fig. 1 reproduces Crum Brown's introduction of graphical formulas in his own hand, in which he explained the first graphical formulas for molecular hydrogen, water, and ammonia. Having demonstrated the method with the simplest molecules, Crum Brown then moved to the more complex formula for ethanol. He drew a (to us) familiar formula, in Fig. 2,

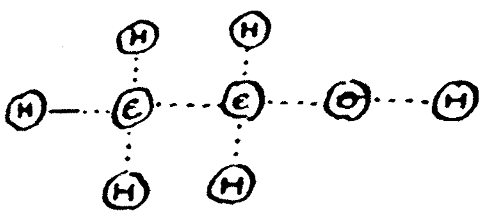

Fig. 2. Graphical formula for alcohol (Thesis, 31).

which was placed next to a corresponding formula for the same substance, in Fig. 3.

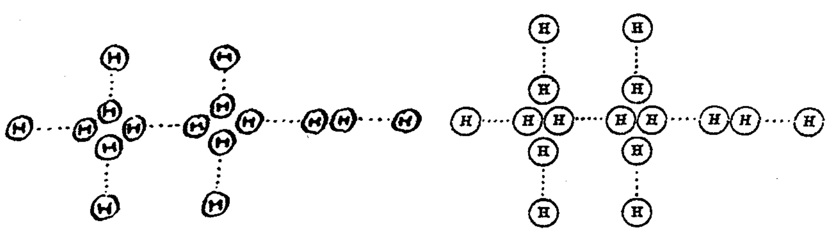

Fig. 3. Formula for alcohol ($8\frac{H}{H}$ type). (Left: Crum Brown's 1861 thesis, 31; right: 1879 published version of this thesis, 17.)

The formula (in two versions) in Fig. 3 is a crucial display; it gives visual form to the transformation of type theoretical notation into graphical notation. Crum Brown wrote that any substance could be represented by the type $n\frac{\mathrm{H}}{\mathrm{H}}$ (see Fig. 1). Thus the five carbon-hydrogen "lines of force," the carbon-carbon line, the oxygen-carbon line, and the oxygen-hydrogen line of the alcohol formula in Fig. 2 gave fully graphical form to the $8\frac{\mathrm{H}}{\mathrm{H}}$ type representation of alcohol in Fig. 3. The $8\frac{\mathrm{H}}{\mathrm{H}}$ type hybrid graphical formula is therefore less a representation of ethanol than a bridging formula that relates type theoretical concepts and formulas with Crum Brown's notion of atomic forces and their representation with his new formulas. In keeping with its function as a transitional formula, Crum Brown never employed its like again.

There is more to Fig. 3 than meets the eye, although precisely what it presents to the eye is important. Alan Rocke has suggested that the sudden bloom of structural models in the late 1850s may derive from a speculation made by Auguste Laurent about the divisibility of atoms, which was elaborated by Adolph Wurtz, August Kekulé, and others into a supposition that the origin of atomicity, and thus of molecular structure itself, derives from the grouping of smaller, monovalent atoms into polyvalent chemical atoms. This historiographically rich insight supports Rocke's "warranted assumption" that the formula in Fig. 3 is Crum Brown's graphical speculation on a subatomic origin of valence derived from Wurtz and Kekulé.[10] I regard it from a different point of view. My interpretation applies to the role the formula plays in Crum Brown's graphical argument—as a bridging device from older theory and graphical formalism to newer—in contrast to its being a theoretical statement about the ontology of atomicity, about which Crum Brown said nothing further in the thesis. Rocke's interpretation of this formula and mine are not, however, mutually exclusive, and both lead to a caveat: one must take care when viewing any nineteenth-century drawing with twenty-first-century eyes. In the printed version of this formula, in the published thesis (right, in Fig. 3), the neatly printed nuclear clusters of two and four closely spaced Daltonian hydrogen atoms more readily suggest—at least to the modern eye—a possibility of sub-atomic structure than does the original formula in the 1861 thesis, in which the hydrogen molecules (or types) seem to claim greater visual primacy. Although sub-atomic speculation could well have nudged the theoretically informed Crum Brown toward the conception of the formula in Fig. 3, I want to emphasize that such theoretical speculation is less significant than the role the formula plays in the visual argument, and thus in the development of a chemical practice of structural hypothesizing.

Eliding Crum Brown's discussion of even and odd number atomicities, the final topic he addressed in his thesis was "those phenomena which we have collectively designated polar." Crum Brown cited Kekulé's remarks in the latter's *Lehrbuch* on the differing behavior of the two "typical" hydrogen atoms of monobasic glycolic and lactic acid. Crum Brown addressed Kekulé's explanation that one hydrogen lies near one oxygen atom, while the other lies near two oxygen atoms, which accounts for their differing chemical behavior. Crum Brown raised a dual objection: "We have no means of knowing that one of the typical H atoms is nearer the O of the radical than the other," and "We have no reason to suppose that such greater nearness would render that atom more basic than the other."[11]

In Kekulé's formulas (Fig. 4), atomicity, or valence, was represented by circular, two-, and four-lobed figures for, respectively, mono-, di-, and tetravalent hydrogen, oxygen, and carbon. Vertical superposition indicated a relation of chemical bonding. Crum Brown constructed formulas using Kekulé's "sausage" models to depict glycol, and glycolic and oxalic acid.

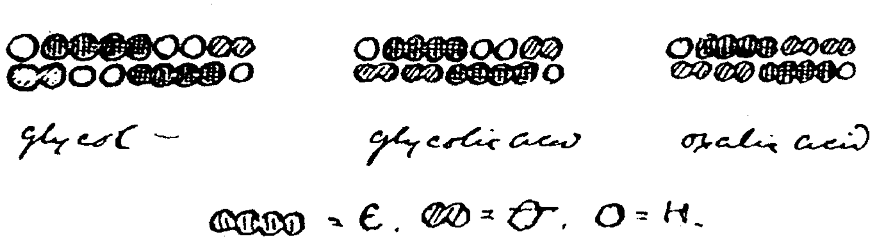

Fig. 4. Crum Brown's Kekulé formulas, glycol, glycolic acid, oxalic acid (Thesis, 41 and n. 41).

Crum Brown noted that "Kekulé's graphic method is a most artificial one," which "certainly does not represent the actual arrangement of the atoms."[12] This pejorative judgment served as both criticism and standard disclaimer of the day; it marked an ontological skepticism that was at the heart of chemical atomism.[13]

Of his own formulas for the same three substances, and for glycolic acid in particular,

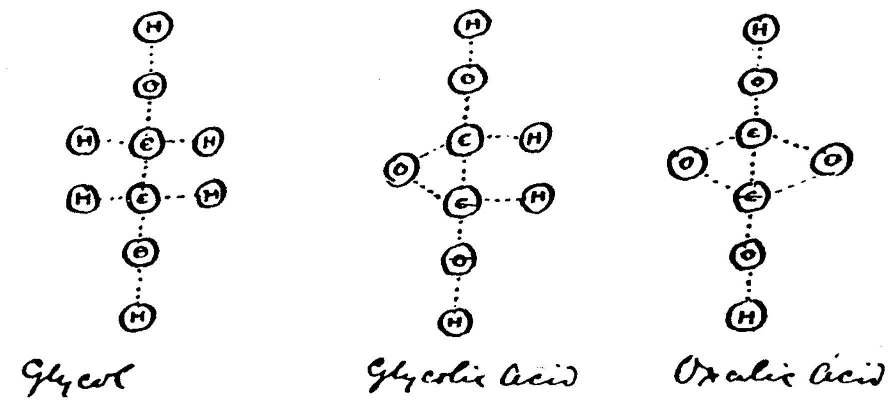

Fig. 5. Crum Brown's graphical formulas, glycol, glycolic acid, oxalic acid (Thesis, 42).

Crum Brown wrote,

> Of course I do not intend it to be supposed that this represents correctly, or even, more correctly than Kekulé's method does, the actual arrangement of the atoms, but it is, at least, as probable; and all that I wish to show is, that his is not the only possible arrangement.[14]

With the cyclic structure for glycolic acid, Crum Brown showed how a combined organic acid and alcohol might possess equivalent typical hydrogens.[15] Crum Brown suggested an experiment that would yield different results depending upon whether Kekulé's structural hypothesis for non-equivalent typical hydrogens or his own equivalent hydrogens hypothesis were correct.[16] Kekulé's formulas, we know now, more correctly reflect the structures of these three substances. What is salient, however, is how Crum Brown combined graphical conjecture with a proposal for synthetic investigation in the laboratory to resolve a chemical question.

Crum Brown said that he could not "see how the *neighborhood* of an atom of oxygen, fully saturated already, should influence the chemical relations of an atom of hydrogen not directly united to it." However, he concluded his thesis with a hypothesis about how "the peculiar properties of one atom may influence the chemical relations of another atom, in the same molecule, although the two are not *directly* combined." Crum Brown articulated a concept of polar forces at work in molecules, calling the forces positive and negative, although he did not mean it "to be understood that they are supposed to be of an electric nature." His remarkable concept of chemical influence seems advanced for its time, but the important point is that such theorizing could accomplish little without a graphical method by which

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http://www.springer.com/978-1-4020-0100-0

Tools and Modes of Representation in the Laboratory Sciences
Klein, U. (Ed.)
2001, XVI, 264 p., Hardcover
ISBN: 978-1-4020-0100-0