Ask the Historian

The Origin of the Term "Allotrope"

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Question

What is the origin of the term "allotrope"?

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Answer

The term *allotrope* or *allotropic* was introduced by Berzelius in 1841 in the course of a review of the work of the German physicist, Moritz Frankenheim, on the thermal transitions between both the red and yellow forms of HgI_2 and the monoclinic and rhombic forms of sulfur (1). Frankenheim had described these transformations as examples of *isomerism*, a term that had been introduced several years earlier by Berzelius to describe substances having identical compositions but differing properties (2). Soon after, Berzelius had further distinguished between two possible causes of isomerism: *metamerism* or a difference in the arrangment of the component atoms, such as that found in ethyl formate versus methyl acetate; and *polymerism* or a difference in absolute composition, such as that found in ethene versus butene (3). However, he now pointed out that neither of these could be used to explain the difference between two forms of the same element, such as monoclinic and rhombic sulfur or graphite and diamond. This was because Berzelius, in common with most chemists of this period, believed that the pure elements were inherently monoatomic. As a consequence, they had no molecular structures to vary and any differences had to instead reside in an inherent variation in the nature of the atoms themselves. It was in order to call attention to this intrinsic difference that Berzelius proposed the new term allotrope as yet a third possible cause of isomerism.

Interestingly, most modern books incorrectly define this word to mean "other form," a definition that actually corresponds to the word *allomorph* (4). In fact, the Greek word *tropos* means "to turn," as in the biological term *tropism*, and the term allotrope literally means "other turn" or, more figuratively, "other behavior."

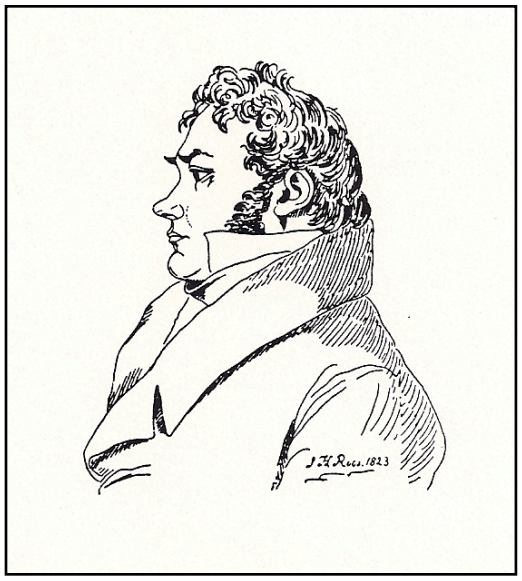

Figure 1. Jöns Jacob Berzelius (1779-1848).

As defined by Berzelius, allotropism served not only to rationalize the isomerism of the pure elements, it was also a third potential cause of isomerism among compounds and, in keeping with this, he proposed that the two forms of FeS_2 found in the minerals pyrites and marcasite might be the result of one containing monoclinic sulfur atoms and the other rhombic sulfur atoms. Two years later, based on the discovery of the red and white allotropes of phosphorus, he further suggested that the various forms of phosphoric acid might have a similar cause (5).

With the rise of organic chemistry in the 1840s and 1850s, Berzelius' original definitions became muddled. Polymerism was given coequal status with isomerism as a separate and distinct phenomenon, isomerism was conflated with metamerism, and allotropy was shunted into inorganic chemistry. Berzelius had offered no opinion

as to the cause of allotropy. Later speculations, largely in connection with early attempts to explain the nature of ozone, included the suggestions that it corresponded to atoms in different states of electrification, to atoms having different energy contents, or to a difference in the arrangement of hypothetical subatomic particles (6). By the 1870s the term had become so vague that it was made the brunt of Stanley Jevons' famous quip concerning those (7):

... curious states, which chemists conveniently dispose of by calling them allotropic, a term freely used when they are puzzled to know what has happened.

But even as Jevons voiced his criticism the term was being imbued with new meaning, this time by the newly emerging field of physical chemistry. In 1877 the German physicist, Otto Lehmann, suggested that the term be used to designate all those variations of a given substance, whether element or compound, that were ultimately traceable to variations in the substance's intermolecular organization, whether these be due to changes in intermolecular structure or to changes in the degree of intermolecular association. This, in essence, subsumed all thermally induced changes in either the degree of aggregation (solid, liquid, gas) or in polymorphism. He further distinguished these underlying intermolecular causes of allotropism by the terms *physical isomerism* and *physical polymerism* in order to differentiate them from the older chemical or intramolecular isomerism and polymerism of the organic chemist, and also introduced the terms *enantiotropic* and *monotropic* to designate reversible and irreversible allotropic transformations (8, 9).

By the end of the 19th century this extended use of the term allotrope as a descriptor for phases of identical composition had become widespread in the literature dealing with the phase rule, where it persisted well into the 1940s (10-12). However, with the advent of X-ray crystal analysis in the early decades of the 20th century it became apparent that Lehmann's distinctions between physical versus chemical isomerism and physical versus chemical polymerism could no longer be maintained (13). Many solid polymorphs were in fact based on differences in the intramolecular structures of infinitely extended species rather than on differences in the intermolecular packing of discrete molecules and many changes of state actually involved concomitant changes in the degree of molecular polymerization or reversible changes in intramolecular structure.

As Lothar Meyer observed in 1888, with the acceptance of Avogadro's hypothesis and the idea that the elements can form polyatomic molecules when in the form of simple substances, it had become apparent that the underlying causes of traditional allotropy in the case of the elements and traditional isomerism and polymerism in the case of isocompositional compounds were one and the same, and that one must either abandon the traditional restricted usage of the term allotrope (elements only) or accept the extended usage found in the older phase literature (14). The first of these choices was advocated by Wilhelm Ostwald as early as 1912 with regard to the phenomenon of polymorphism, when he noted that there 15):

... is really no reason for making this distinction [between polymorphism and allotropism], and it is preferable to allow the second less common name to die out.

Regrettably, despite this sage advice, which many have since repeated (4), and the passage of more than 90 years, the restricted use of the term allotrope (for elements only) is still endorsed by IUPAC and is still being used in most chemistry textbooks (16).

Literature Cited

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3. J. Berzelius, "Isomerie, Unterscheidung von damit analogen Verhältnissen," *Jahres-Bericht*, **1833**, *12*, 63-67. Definition on p. 64.

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7. W. S. Jevons, *The Principles of Science*, Macmillan: London, 1874, p. 670.

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15. W. Ostwald, *Outlines of General Chemistry*, Macmillan: London, 1912, p. 104.

16. G. J. Leigh, Ed., *IUPAC: Nomenclature of Inorganic Chemistry*, Blackwell: Oxford, 1990, p. 31.

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

Update

In keeping with the above discussion, the British chemist, J. A. Wanklyn, in the article on isomerism written for the 1875 edition of Watt's *Dictionary of Chemistry*, noted that the term isomerism had acquired two meanings: isomerism in the general sense, which subsumed both polymerism and metamerism, and isomerism in the narrow sense, where it functioned as a synonym for metamerism alone. He also stated that, in the case of inorganic compounds, the term allotrope was generally used as a synonym for isomer (1).

Several chemists, such as Dalton and Faraday, anticipated the concept of isomerism before Berzelius but without assigning it a particular name. Thus, in his 1823 volume on the chemistry of animal fats and oils the French chemist, Michel Chevreul, wrote (2):

It is well known that there are substances that on analysis are found to contain the same elements combined in the same proportion, but that nevertheless display quite different properties. Therefore, to understand the cause of the difference these substances exhibit, we must look for a difference in the arrangement of either their elementary atoms or of their combined atoms or particles.

1. J. A. Wanklyn, "Isomerism," in H. Watt, Ed., A *Dictionary of Chemistry*, Vol. III, Longmans, Green & Co: London, 1875, pp. 415-423.

2. M. E. Chevreul, *A Chemical Study of Oils and Fats of Animal Origin*, Dijkstra-Tucker, Carbougnere 2009, p. 2. This is a modern English translation of M. E. Chevreul, *Recherches chimiques sur les corps gras d'origine animale*, Levrault: Paris, 1823. See also M. E. Chevereul, *Considerations générales sur l'analyse organique et sur ses applications,* Levrault: Paris, 1824, p. 32.