HAÜY'S CONTRIBUTION TO OUR KNOWLEDGE OF ISOMORPHISM

EDWARD H. KRAUS

University of Michigan

ALTHO the striking results of the first studies leading up to the establishment of the principle of isomorphism were not announced by Mitscherlich until 1819, only three years before Haüy's death, nevertheless, no historical account of the development and subsequent modifications of this important principle can be considered complete without referring in a comparatively large way to the earlier contributions of Abbé René-Just Haüy, in whose honor we have met. Probably next in importance for the advancement of crystallography to Haüy's discovery of the Law of the Rationality of Indices was the pronouncement by him that every solid substance with a definite chemical composition possesses a characteristic crystal form.

Haüy was early in life an ardent student of botany, and was impressed by the fact that there is a certain constancy to be observed in the forms of flowers and plants. This observation caused him to ponder extensively as to why there should not be a similar constancy among the minerals, which are so much simpler, chemically and geometrically. Thus, Haüy might have said: "How is it, that the same stone, the same salt, show themselves in cubes, in prisms, in needles, without the change of an atom in their composition; while the rose has always the same petals, the acorn the same curvature, the cedar the same height and the same development?" While this thought led primarily to the discovery of the Law of the Rationality of Indices, nevertheless, one cannot but feel that its influence undoubtedly extended further. It unquestionably played an important part, in connection with the constancy of angles, especially cleavage angles, in causing Haüy to make the pronouncement referred to above, which only a man of keen insight, unusual ability, and great intellectual boldness could have made.

It must be remembered that just at that time, namely, the last quarter of the eighteenth century, epoch-making discoveries in chemistry were being announced. Thus, in 1774, Priestly discovered oxygen, and, in 1783, Cavendish the compound nature of water. Lavoisier published his "Elements de Chimie" and "Reflexions sur le Phlogistique" in 1782 and 1783, respectively. To have dared to make such a generalization clearly indicates that Haüy was a close student of chemistry, and well acquainted with its recent advances.

As is well-known, immediately after discussing the results of his remarkable studies before the French Academy of Sciences in 1782 and the publication under the auspices of that Academy of his first book entitled "*Essai d'un Theorie sur la Structure des Cristaux*" in 1784, Haüy was universally recognized as having placed crystallography upon a sound and rational basis, and was accordingly heralded as the "father of crystallography." Haüy at once became the dominant figure of that period in crystallography.

His views on the relation of chemical composition to crystalline form were generally accepted, altho many facts were then known, which were not in accord with Haüy's pronouncement that "every chemical substance possesses a characteristic crystalline form, and that substances differing in chemical composition cannot occur in the same form." Thus, Romé de l'Isle knew, as early as 1772, that the sulfates of copper and iron crystallize together from a solution of both compounds. In 1784, Le Blanc showed that the chemical composition of these crystals varied, although the crystalline form remained the same. The observations of Beudant and von Fuchs, made a few years later, must also be mentioned. The former studied intensively the mixed crystallizations of the sulfates of zinc, iron, and copper, and obtained single crystals containing all three of these salts. These mixed crystals were obviously in direct opposition to Haüy's view.

To von Fuchs we owe the introduction of the term "vicarious constituents." He studied the composition of gehlenite in 1815 and observed the presence of iron, which he interpreted as replacing the calcium, and hence, not an essential but a "vicarious constituent." From further analytical data, it was soon evident that many minerals must be interpreted in this manner. In 1817 von Fuchs explained the similarity in the crystalline forms of the carbonates and the sulfates of calcium, strontium, and lead in this way.

One can readily see why Haüy could not be induced to change or modify his views, especially when we recall that by noting a marked difference in the size of the angles of specimens labelled sulfate of baryta, he concluded that they could not possibly have the same composition. Some were from Sicily, while the others were obtained from Derbyshire. Subsequent examination by Vauquelin showed clearly that those from Sicily consisted of sulfate of strontium, while the specimens from Derbyshire were sulfate of barium. The claim that two substances, chemically distinct and not crystallizing in the cubic system, could possess the same form, as indicated by the researches of Le Blanc, Beudant, and von Fuchs, was, hence, persistently opposed by Haüy. Small wonder then, that when the investigations of Beudant were submitted to the criticism of the French Academy of Sciences in 1819, they were discredited, judgment being passed by Haüy, Vauquelin, and Brochant. It was, however, postulated by this committee that one constitutent might determine the crystal form of a substance, even tho present in very small amounts, while the other constituents remained without influence in this respect.

It was at this stage of our knowledge of the relationship between chemical composition and crystal form, that Mitscherlich published the results of his studies on the phosphates and arsenates of potassium and ammonium. His observations were apparently in direct opposition to the theory held by Haüy, for there could be no question about the difference in the chemical composition of the salts, and the crystals were to all intents and purposes identical in form. Further investigations were carried on by Mitscherlich, and two years later, namely in 1821, he characterized this phenomenon of analogous chemical substances crystallizing in forms which appeared to be identical as the principle of isomorphism. Undoubtedly Mitscherlich had at this time absolute identity of form in mind. The fact that Berzelius was greatly interested in Mitscherlich, and that the latter had studied for nearly two years in Berzelius's laboratory in Stockholm, aided materially in gaining wide recognition for this new principle.

As was to be expected from the course of events up to this date, Haüy did not look with favor upon Mitscherlich's work. Haüy still believed in his pronouncement that the chemical composition does exert a large influence upon the crystal form. His experience in applying this idea had been so successful, and his faith in it so great, that he could not believe that these observations invalidated his theory. It must not be forgotten in this connection, that it was Haüy who showed that the crystal development of the emerald agreed with that of beryl, and accordingly he predicted that an analysis of emerald must show the presence of the element beryllium. This was subsequently confirmed by Vauquelin. Many other illustrations of this character might be cited. Hence, we can fully appreciate Haüy's feelings when he wrote to Brochant that "if Mitscherlich's theory is correct, mineralogy would be the most wretched of the sciences."

Haüy died in 1822 believing firmly in his theory, and undoubtedly with a strong conviction that it would eventually be fully confirmed. However, with the establishment of the principle of dimorphism by Mitscherlich in 1823 it appeared as tho the evidence was overwhelmingly opposed to the theory of Haüy. Mitscherlich had observed that the element sulfur could occur in distinctly different crystal forms, depending upon the conditions of formation. Dimorphism also cleared up the mystery of calcite and aragonite, the true nature of which had been under discussion for many years. It also showed that Haüy's pronouncement could not be applied as universally as he had originally thought.

Further investigations, however, caused Mitscherlich to doubt the absolute agreement of angles or crystals of isomorphous substances. The construction and use of a reflecting goniometer of greater accuracy than had previously been employed showed unmistakably that slight but distinctive differences exist in the angles of isomorphous substances crystallizing in systems other than the cubic. These differences Mitscherlich was, however, inclined to attribute to variations caused by changes in temperature.

On account of the apparent contradiction in the views of Haüy and Mitscherlich regarding the relationship between chemical composition and crystal form, investigations in this field have been uncommonly numerous. It was recognized rather early that the original idea of absolute identity of form, expressed by Mitscherlich, must be modified, absolute identity giving way to striking similarity of form. Many studies involving careful crystallographic measurements show conclusively that compounds, which are very closely related chemically, yield crystals which may appear to be identical in form. However, when they are measured with a modern goniometer, it is observed that the angles between similar faces are not absolutely of the same value, there being small but nevertheless characteristic differences. Perhaps the most extensive and painstaking researches in this special field of chemical crystallography are those carried out by Tutton. Many isomorphous series of artificial compounds of unusual purity were studied. Some of these compounds were comparatively simple in composition, while others were very complex. As a result of these investigations, extending over many years, Tutton and others have definitely demonstrated that crystal angles are functions of the chemical composition, as Haüy had in the main postulated.

There can be no question whatever, but that the bold pronouncement by Haüy, at a time when modern chemistry was in its infancy, chemical compositions being expressed in percentages and by formulas, did much to stimulate research not only in mineralogy, but in chemistry as well. In those days these two subjects were more closely allied than they unfortunately are today. The many attempts, during a period of nearly a century, to reconcile the conflicting views of the early part of the nineteenth century have been fruitful of discoveries of great importance in bringing chemistry and mineralogy up to our present advanced stage of knowledge. The debt we owe to Haüy in this regard is indeed great.