

Pythagoreanism and Theories

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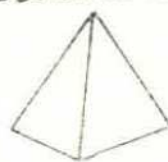
Geometry has long molded concepts in chemistry. We speak of spherically shaped s-orbitals, tetrahedral carbon atoms, trigonal planar boron fluoride molecules, octahedral ferricyanide ions, and face-centered cubic lattices of sodium chloride crystals. These present-day configurations have roots in the geometry of antiquity.

Pythagoras (fl. latter half —6th century) and his followers made up a religious brotherhood that believed in an arithmetically and geometrically organized universe, ruled by simple number ratios and revealed in perfect figures such as the sphere, circle, and cube. In Pythagorean cosmology, stars were small spheres attached to a large, hollow, rotating sphere and carried along by it. The spherical Earth remained stationary in this celestial sphere's center (8). This arrangement explained the apparent circular paths of stars, the position of the North Star, the fixed formation of the constellations, and the circumpolar motion of northern stars, because the large celestial sphere rotated uniformly and carried the fixed stars in precisely circular orbits.

Pythagoras himself is credited with discovering the relationship between string length and musical intervals. He showed that the sound made by two vibrating strings differs by an octave if one is twice the length of the other. Musical harmony was even compatible with the features of a cube, considered an especially beautiful figure having all solid angles identical and six identical faces, each being a perfect square with all sides and angles equal. The ratio of the cube's features—12 edges to 8 points to 6 faces—was also mathematically beautiful. The harmony of this ratio was also found in music. Three strings differing in lengths of 12 to 8 to 6 produced a harmonious chord when plucked (8). This Pythagorean view of a mathematically oriented world has influenced man's attempts to explain nature throughout the ages.

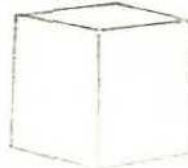
Plato (—428 to —347) was a mathematical idealist who saw much beauty in the numbers of the Pythagoreans. He adopted the four-element (fire, earth, air, water) theory of Empedocles (fl. about —450)—that objects in this world consist of varying proportions of two or more of those four elements—and related it to the regular solids. Plato's idealism meant that he believed this world is a reflection of ideal forms and so he tried to relate his idealism to objects of this world.

Tetrahedron



Fire

Cube



Earth

Octahedron



Air



Water

Figure 1. Regular polyhedra and corresponding Empedoclean elements

From among the five regular solids (Theaitetos, a contemporary of Plato, proved there could be only five), Plato selected four to represent the four Empedoclean elements—the tetrahedron for fire, octahedron for air, icosahedron for water, and the cube for earth (Figure 1). He argued that fire's penetrability and painful effects were a consequence of the tetrahedron's sharp angles. Earth's stability and solidity were ascribed to its cubic form, and the motion of water was related to the icosahedron. Air was represented by the octahedron because it was a figure more penetrating than the icosahedron but less penetrating than the tetrahedron (6).

In Plato's theory of matter, the elements were related to triangles:

In the first place, then, as is evident to all, fire and earth and water and air are bodies. And every sort of body possesses solidity, and every solid must necessarily be contained in planes; and every plane rectilinear figure is composed of triangles . . . (6).

The most beautiful triangular form was the right angle triangle, the basic unit from which the four figures of the elements could be constructed. Plato says single particles, which he calls the original elements or seeds

119635c Pythagoreanism and theories of the structure of matter. Feifer, Nathan (California State Univ., San Francisco, Calif.). *Chemistry* 1974, 47(3), 6-10 (Eng). The math. harmony and symmetry predicted by Pythagoras and postulated by Plato served as idealized forms for the geometry of matter, and these concepts served as simple models for the development of more complex and sophisticated theories. The polyhedra corresponding to the Empedoclean elements of fire, earth, air, and H₂O are shown as a basis for a discussion of modern crystallog.

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The tetrahedron, octahedron, cube, and icosahedron are the four regular solids.

of the Structure of Matter

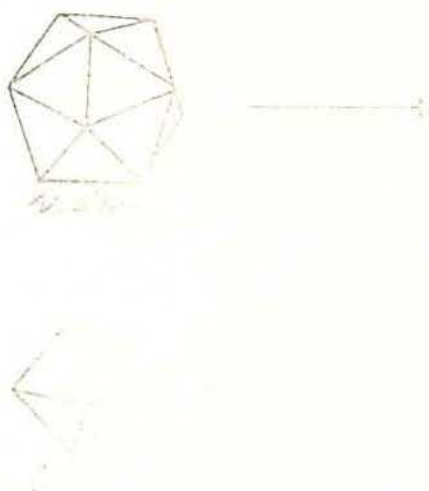
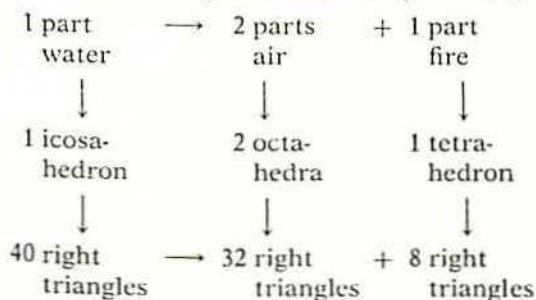


Figure 2. Water becomes two parts air and one part fire in Empedocles' system

of any of the four solids, are so small they cannot be seen by us. In aggregates, however, they can be seen. Changes occurred in nature when elements acted on each other. The role of motion is very important:

Earth, when meeting with fire and dissolved by its sharpness, whether the dissolution takes place in the fire itself or perhaps in some mass of air or water, is borne hither and thither until its parts, meeting together and mutually harmonizing, again become earth; for they can never take any other form. But water, when divided by fire or by air, on reforming, may become one part fire and two parts air (Figure 2); and a single volume of air divided becomes two of fire (6).

The evaporation of water could be explained in terms of its geometrical components (9):



Plato's geometric figures are a monument to man's mathematical approach to understanding nature. It was echoed through the ages by such giants as Johannes Kepler (1571-1630) and Galileo Galilei (1564-1642). Kepler's theory of the solar system was based upon the mathematical relationships of the five regular solids. Johannes Kepler also worked out a theory to explain why snowflakes should be hexagonal and symmetrical (*Chemistry*, Sept. 1971, page 19). Galileo said, "we cannot understand it [nature] if we do not learn the language and grasp the symbols in which it is written. This book is written in the mathematical language, and the symbols are triangles, circles, and other geometric figures."

Certainly, to the modern scientist, mathematics is an indispensable tool. But there are differences between the Platonic and the modern role of mathematics in science. To Plato, ideal forms were more important than real things. He and the Greek civilization of antiquity left to succeeding generations the ideas from which today's efforts to explain natural phenomena evolved. The Platonic theory in its specifics did not survive, but the Pythagorean principles of mathematical harmony and symmetry in nature underlying Plato's ideas have had a pronounced influence on modern science.

Investigators of the properties of crystals have found Plato's and the Pythagorean forms very useful. For instance, such substances as sodium chloride (NaCl), potassium bromide (KBr), lithium iodide (LiI), magnesium oxide (MgO), and a host of other solids have a cubic form, externally and internally. Other examples of regular polyhedra in the solid crystalline state are alum [$\text{KAl}(\text{SO}_4) \cdot 12\text{H}_2\text{O}$], antimony trichloride (SbCl_3), and antimony trifluoride (SbF_3), for example, which occur as regular octahedra. Copper(I) chloride (Cu_2Cl_2) exists either as a cube or as a regular tetrahedron in the



Figure 3. Forms made by packing spheres in the method of Robert Hooke

Figure 4. Crystals of calcite, left and center, shown with Haüy's idea of the relation of natural faces to the stack of tiny rhombohedral units

crystalline state. Dodecahedra and icosahedra are virtually unknown in the world of crystals.

Although the number of crystalline substances occurring as Plato's regular polyhedra is quite small, there is a preponderance of symmetrically shaped crystals in nature that are not regular polyhedra. But Platonic and Pythagorean idealism carry

Figure 5. Bravais lattices

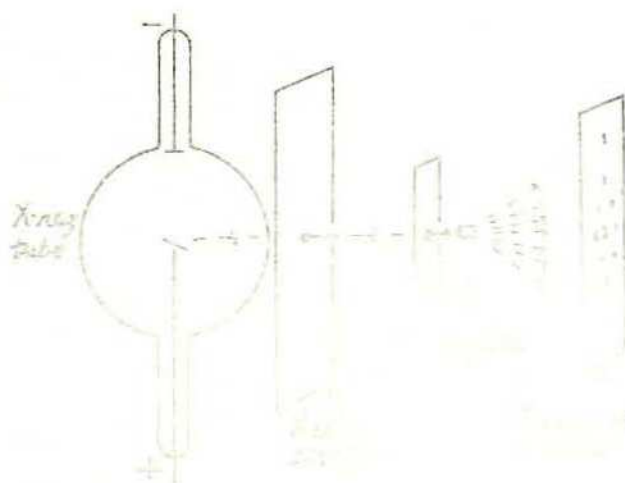


Figure 6. Setup of Friedrich and Knipping to examine crystals with X-rays

over to the fundamental of crystallography that crystals exhibit some form of external regularity resulting from a regular internal arrangement of component atoms or ions.

Robert Hooke in 1665 (2 millennia after Plato) proposed a theory of crystal structure embodying such notions of regularity. He noted the regular cubical shapes found in such solids as rock salt, NaCl, and explained their formation by assuming that crystals were built of uniform, spherical particles arranged in a regular pattern; he did not select a miniature cubical particle as his basic building block. He demonstrated the reasonableness of his model by building a cube of spherically shaped lead shot (3). He also showed how other crystalline forms could be obtained by varying the method of packing spheres (Figure 3). Using the perfect sphere as the basic unit of structure would have been approved by the Pythagoreans. Hooke was proposing a simple explanation, an idealized model consistent with his observed facts.

The difference in approach between Hooke's selection of the sphere as the ultimate particle in the sodium chloride crystal and Plato's choice of the cube as the ultimate particle in all solids is indicative of the two different intellectual climates in which each lived. Plato was a mathematical idealist, Hooke lived in an era where the role of observation had grown much stronger. After observing the macroscopic cubic structure of rock salt, Hooke proposed a model to fit his idea of the facts.

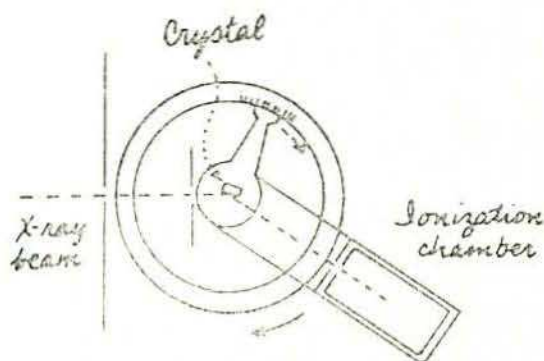


Figure 7. Bragg equipment for studying crystals with X-rays

From 1784 to 1822, René Haüy addressed himself to the study of crystal structure (7). He introduced the experimental technique of cleaving crystals repeatedly until no change in shape resulted in the pieces upon further cleavage. His extensive observations indicated that all crystalline substances were aggregates of one of three basic polyhedral building blocks—the rhombohedron (of which the cube is an example), the tetrahedron, and the triangular prism. The calcite crystal (Figure 4, left) was postulated by Haüy as an aggregate of cubic building blocks (Figure 4, right).

In 1848, Auguste Bravais modified Haüy's model by proposing an open lattice of spherical units; each sphere occupied the center of each polyhedron in Haüy's model (Figure 5). Over a hundred crystalline varieties were recognized and organized into 14 basic space lattices (7).

Evidence to support the Bravais model was provided by Max von Laue in 1912. He first assumed that the atoms in a cubic crystal such as NaCl were spheres arranged in a lattice framework just as postulated by Bravais. He predicted that passing a beam of X-rays through these crystals, and allowing the emergent rays to fall on a photographic plate, would result in a symmetrical diffraction pattern. The following year, Walter Friedrich and Paul Knipping performed a series of experiments by sending X-rays (Figure 6) through a variety of crystals and they obtained the patterns which had been predicted by von Laue (2).

Sir William H. Bragg and his son, William L. Bragg, developed an improved technique for studying effects of crystals on X-rays (2). They used the crystal as a reflector of a beam of X-rays and noted how a reflected beam varied in intensity as the angle between the incident beam and the crystal surface varied (Figure 7). From their data they concluded that certain crystals, such as diamond, were composed of a lattice network of carbon atoms (Figure 8).

The Braggs' basic assumption was that the structural units of crystals are spheres arranged in symmetrical geometric patterns, a very Pythagorean opinion. Modern theory suggests that geometric arrangement of ions in an ionic crystalline solid depends mainly on the charges of the ions and the ratio of the ionic radii. In nonionic crystals the geometric structure may depend on directed localized covalent bonding or hydrogen bonding, or van der Waals forces. The mobility of the electrons in metals, and the nondirectional nature of the bonding enable atoms to assume close-packed arrangements. Thus, a great variety of crystalline forms exist; in fact, about 20 000 crystalline species are known (3).

In the realm of molecular geometry, rather than crystallography (1), the Platonic figures have become the architectural models of a number of molecules (3). The tetrahedron is accepted as the structural configuration of the methane (CH_4) molecule and the carbon tetrachloride (CCl_4) molecule, for example.

The octahedral shape has been assigned to the cobaltic hexammine ion, $\text{Co}(\text{NH}_3)_6^{3+}$, and the sulfur hexafluoride molecule, SF_6 , as well as to such ions as PbCl_6^{2-} and FeCN_6^{3-} . Elementary boron and carborane ($\text{B}_{10}\text{C}_2\text{H}_{12}$) are recognized icosahedral structures. Some of the hydrate clathrates of water are classed as dodecahedrons. Despite these examples of regular polyhedra in the modern geometry of matter, the number of nonregular polyhedra serving as molecular models far exceeds the regular polyhedra, and the modern scientist is not constrained to limit his theories to Platonic polyhedra.

William Hyde Wollaston in 1808 maintained the Pythagorean definition of beauty when he wrote: "If we suppose the limit to the approach of particles to be the same in

Clathrates are inclusion compounds in which an atom or molecule is trapped in a crystalline cage

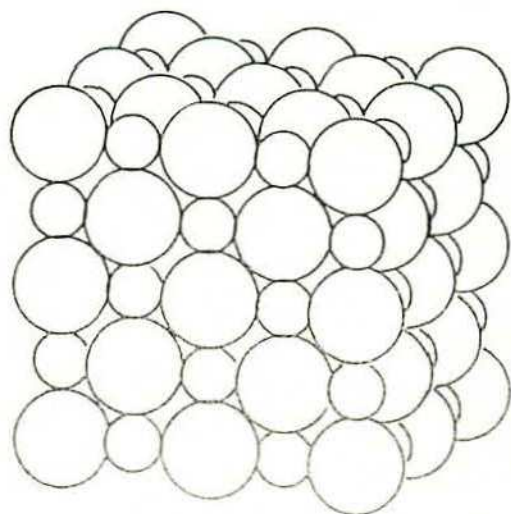


Figure 8. Structure of sodium chloride (NaCl) crystal composed of sodium and chloride ions (smaller balls represent sodium ions; larger ones, chloride ions)

all directions, and hence their virtual extent to be spherical (which is the most simple hypothesis), when different sorts combine . . . in the proportion of two to one, the two particles will naturally arrange themselves at opposite poles. . . . If there be three, they might be arranged with regularity, at the angles of an equilateral triangle . . . when the number of one set of particles exceeds in the proportion of four to one . . . a stable equilibrium may take place if the four particles are situated at the angles of four equilateral triangles composing a regular tetrahedron" (1).

On extending Wollaston's reasoning, we find that the geometric figure formed by the symmetrical and stable arrangement of one species of spherical particles around a single centrally placed spherical particle would depend mainly upon the ratio between the two species of particles, assuming the deranging force of other adjacent particles is negligible. Four such combinations could and do give rise to regular polyhedra: A ratio of 1:4 would give a tetrahedron with one central particle and four particles at the vertices (CH_4 , CCl_4); 1:6, the octahedron (S_6 , PCl_6^-); 1:8, the cube: (CsCl); 1:12 the icosahedron (MoAl_{12}).

Many other ratios are possible that are not expressed as regular polyhedra, although

their forms are geometrically symmetrical. Thus, in the BF_3 molecule the ratio of 1 to 3 gives rise to a trigonal planar figure, as Wollaston predicted. The NH_3 molecule has a ratio of one N atom to three H atoms, but it forms a trigonal pyramid. A ratio of 1:5 is found in the trigonal bipyramid molecule of PCl_5 . Like the overwhelming majority of molecules or complex ions that have been investigated, BF_3 , NH_3 , and PCl_5 have geometrical symmetry but they are not the Platonic regular polyhedra.

To determine the possible geometrical form of a molecule, one must today consider the electronic configuration of the central atom in a molecule and that of the peripheral atoms that surround it as well as the number of electron pairs that can form. Directed valence, bond distances between atomic nuclei, internal motion in molecules, such as rotation about covalent bonds, and repulsions among electron pairs, bonding and nonbonding in the valence shell of the central atom also must be considered. Consequently, it turns out that conditions for the formation of regular polyhedral molecules are very unfavorable.

Thus, the kind of mathematical harmony and symmetry predicted by Pythagoras and postulated by Plato clearly does not govern the geometry of all matter. Nevertheless, their idealized forms and their notions of symmetry served as simple and convenient models from which our more complex and sophisticated theories were developed. Ω

Suggested Reading

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