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LARGE MOLECULES IN SCIENCE AND LIFE[1]

By Professor HUGH S. TAYLOR
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IT is a striking characteristic of the gaseous substance, acetylene, with which Father Nieuwland spent so much of his later scientific life, that, under the influence of a variety of agencies, light, radioactive rays, cathode rays, the silent electric discharge and, also, even contact agents such as a copper catalyst, the gas changes to an insoluble yellowish solid known as cuprene. It received its name because Sabatier, who prepared it from acetylene with the aid of a copper catalyst, thought that it contained copper. It is now known that it contains no copper, but, within the error of analysis, a one to one ratio of carbon to hydrogen, as does acetylene. How different the properties! In place of a highly reactive gas we have a chemically inert solid, the linkages of which are all so mutually satisfied that it has hitherto resisted all efforts to bring it into solution in any known solvent, although hundreds of such have been tried. All the properties of the simple molecule, with the study of which Father Nieuwland spent so many happy and fruitful days, have disappeared in the formation of something which we may speak of as giant molecules, each particle of the cuprene composed of three-dimensional arrays of the carbon and hydrogen atoms of which it is composed. Acetylene is the simplest of the compounds from which, in these hectic days of industrial-scientific progress, large molecules or polymers, with a fascinating range of properties, may be prepared, synthetic rubbers, plastics, fibers and the like.

It is not alone, however, in the industrial scientific field that the large polymeric molecules possess great significance. In biological systems and in organic matter generally, it is now known that highly polymerized systems constitute an important fraction of such material and that their properties, including tensile strength, elasticity and flexibility, durability, resistance to chemical change, hardness, confer on such bodies a

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[1] An address delivered at the Father Nieuwland Memorial Exercises at the University of Notre Dame on January 10, 1937.

wide variation of desirable properties. In inorganic systems also, as in diamond and graphite, silica and the silicates, including varieties with such divergent properties as crystal quartz, mica sheets, asbestos fibers, we find examples multiplied of the manifold properties which may be conferred on material of the same unitary composition when built up by repetition of the unit in one, two or three dimensions into the larger aggregates of naturally occurring minerals and products.

Science to-day is facing boldly the difficult problems that the investigation of such complexities of structure bring in their train. The wonderful achievements in the organic chemistry of biologically important compounds with the syntheses of such substances as the vitamins and hormones can not obscure the fact that the problems that still lie ahead, involving the molecules of an entirely higher order of complexity, the proteins, the viruses, enzymes, cellulose, require for their solution the best cooperative efforts of the biologist, the physicist, the organic and inorganic chemist; nor is it beyond the bounds of possibility that the mathematician with his specialized knowledge in the field of topology will also be called in to assist. Only in special cases will the ordinary synthetic and analytic studies of classical organic chemistry suffice for the problem in hand. Greater progress will occur when such is combined with kinetic, stereo-analytical and colloidal techniques that the other sciences will contribute.

In the field of inorganic matter it is the diffraction of x-rays by solid matter that has been, in the past two decades, so intensely revealing. These rays of light, commensurable in wave-length with the distances between atoms in the solid structures studied, have revealed the diamond, hardest of known substances, as a tetrahedral array of carbon atoms in one giant molecule, each atom equally spaced from four neighbors arranged at the corners of a tetrahedron of which the fifth atom occupies the center. The distance from carbon atom to carbon is identical with that between carbon atoms in the paraffinic hydrocarbons of a straight run Pennsylvania gasoline, with about the same energy of bonding. This is a strong bond, and it is the symmetry of this bonding in all directions throughout the diamond aggregate that confers upon it its two conspicuous properties, its intense hardness and its lack of volatility. In graphite, this symmetry is destroyed and the analysis of the atom spacing reveals the causes of the new properties. There is a hexagonal array of carbon atoms in flat planes similarly spaced to the carbon atoms in a benzene ring, but between planes the distance is from two to three times that between atoms in the ring. It is along this plane of great distance that cleavage can occur, accounting simply for the flaky characteristics of the mineral.

In crystal quartz and in the silicates, the x-ray reveals a similar regularity of architecture. The silicon atom in this case is always located between four oxygen atoms. In certain silicates, this array of five atoms, SiO_4, forms a tetrahedral array similar to that discussed in the case of diamond. The oxygen atoms may, however, act as bridges between two silicon atoms and numerous possibilities result. Two tetrahedra may be linked through one common oxygen atom which is common to two silicons and form a unit, Si_2O_7, to build into a more complex structure with other units. Three may form a ring, Si_3O_9, and six may form another type of ring, Si_6O_{18}. If the edges of two tetrahedra are linked by two common oxygen atoms a chain or filament or fiber, with a formula $(SiO_3)_n$, where n may be indefinitely long, is formed. Two chains linked side by side give a band of which the unit composition is Si_4O_{11}. Sheets, like mica, belong to the class of linked tetrahedra, each tetrahedron sharing three corners, with composition $(Si_2O_5)_n$. If all four corners are shared with other tetrahedra (as in diamond) the extension occurs in three dimensions, crystal quartz results and the composition is a giant molecule $(SiO_2)_n$.

Alumina can replace silicon in these structures, the tetrahedron acquires a negative charge and so can associate in the crystal architecture with positive metal units. The felspars are of this structure. Zeolites, such as permutit, are more open structures containing water molecules within the crystal architecture; these open structures permit replacement of the positive units, a circumstance which determines their use for water softening.

From such deductions based upon x-ray analysis of inorganic matter there is a ready transition to the corresponding structures in naturally occurring and synthetic organic materials. The continuous linkages of molecules having one reactive group at each end will give rise to linear aggregates, filamentary or chain-like in character. Under favorable circumstances this type of reaction may give rise to ring formation or cyclization, with alternative spacial configurations of the resultant products. Molecules with a greater number of reactive units in the initial structure, so-called polyfunctional molecules, offer greater varieties of structural growth, extending into three dimensions. Acetylene may be regarded as having four-fold functionality and the cuprene would represent a three-dimensional growth of the aggregate. Divinyl acetylene, on the other hand, $CH_2 = CH - C \equiv C - CH = CH_2$, illustrates the acetylene molecule in process of linear growth, with only half of its unsaturation contributing to the change. Oxygen, sulfur and nitrogen are important atom links in such aggregates of large organic molecules. Sulfur atoms are important links in the chains of atoms present in the technically important "thiokol."

The study of jellies, and of the gels which result from them by controlled removal of the water content, represents another avenue of approach to the problems of large molecules employing the technique of the colloidal chemist. Here also x-ray investigations are an invaluable supplement to the physico-chemical studies of such structures. They reveal the structure or its absence in the aggregates obtained. Completely amorphous, crystalline and half-crystalline structures have been observed. The physical characteristics of the jelly undoubtedly depend on the same type of orienting forces, if quantitatively less strong, as are involved in the building up of the more robust structures. The zeolites may be thought of as a half-way house between the jelly and the large-molecule crystal.

The techniques of colloid-chemistry are invaluable also in the determination of the distribution of sizes amongst the polymer aggregates. In this regard, mainly due to the brilliant leadership of Svedberg, our knowledge is rapidly growing. By measurements of the rate of settling of the particles dispersed in a suitable liquid medium, either under the action of gravity or under the influence of centrifugal forces which may rise to many tens of thousands of times the force of gravity, we can learn whether the individual particles of a product, natural or synthetic, are uniform or non-uniform. If uniform, the rate of settling will be uniform and reveal itself as sharp-edged sedimentation. If the material be non-uniform, the lighter particles settle more slowly and a blurred boundary is obtained in the process. Size-classifications can be obtained in the latter case. The outstanding results of such studies by Svedberg and his collaborators lie, however, in the observations made with naturally occurring proteins, many of which, after suitable purification and under stable conditions, are found to be remarkably uniform in size. This implies that the units are identical chemically, are, indeed, single macromolecules. Svedberg's researches reveal, moreover, that the molecular weights of different proteins show a surprisingly simple relationship with one another. One series of proteins have a molecular weight of about 34,500. Another group have a value of about 68,000; a third averages 104,000, another group 208,000. Some have molecular weights of as high as 5,000,000.

In the general field of the large molecules, included under the term protein, the greatest scientific activity now obtains. Here, at its best, is exemplified, at the moment, that cooperative international effort in science in such marked contrast to the divisive, competitive struggles that separate nations in other fields. A great concentration of skills is being brought to bear upon the problem. The shapes and sizes and surface properties are being studied by observations of insoluble protein films on water. The velocities of protein reactions are being followed, practically and theoretically, in an effort to elucidate the mechanisms of interaction. Stanley's studies of the crystalline tobacco leaf virus are revealing the conditions necessary to the multiplication of protein material. Crystalline pepsin and trypsin, typical protein enzymes are steadily compelled to reveal the complexities of their structure and behavior. More recently still, from the ranks of the mathematician, from a topographical approach, Dr. Wrinch is discussing the pattern of protein structure, two-dimensional cyclol layers capable of extension in three dimensions by linkage front to front and back to back by side chains and hydroxyls, respectively, in a manner made familiar by the study of Langmuir and Miss Blodgett with oil films on saturated barium carbonate solutions. The pattern of the protein surface is being linked with the structure of the physiologically active substances, such as the carcinogens, sterols, sex hormones, as the substrate on which these latter may be superposed. Finally, the same protein pattern may be built up into closed globular structures which would define the uniformity of molecular weight determined by Svedberg in his studies and the particular magnitudes for these weights which the measurements reveal. All these varying techniques are available to assist the synthetic organic chemist in the development of his own rich efforts, so well exemplified in the person of him who to-day we have come from near and far to honor.

ENGINEERING IN AN AMERICAN PROGRAM FOR SOCIAL PROGRESS.[1] II

By Dr. KARL T. COMPTON
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CONSERVATION OF NATURAL RESOURCES

We turn now to the third great feature of the American program for social progress, which is the conservation of our natural resources. To this end the Federal Administration has maintained a National Resources Committee which has made an extensive survey into every aspect of national resources, including soil, water, minerals, timber, waterways and even manpower. There can be nothing but approval of this

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[1] Address on Commemoration Day at the Johns Hopkins University, February 22, 1937, celebrating the twenty-fifth anniversary of the founding of the School of Engineering at the Johns Hopkins University.