Summary

To summarize our consideration of translocation, it is evident that plants have very effective translocation systems capable of rapidly moving very small particles, such as potassium ions, which are only about 2 angstroms in diameter, or of moving relatively large particles, some even as long as 20,000 times the diameter of a potassium ion. At the small end of the size scale the dimensions of particles may not influence their translocation, but when particles farther up the size scale (molecules) are involved, dimensions may become more important. At the large end of the size scale (macromolecules), dimensions may be critical. Although we have learned some facts about mechanisms involved in translocation, many questions still remain. The answers that afford an understanding of translocation from a broad viewpoint will necessarily explain how plants translocate particles that vary so widely in size as well as in other characteristics.

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British Achievements in X-ray Crystallography

Knowledge of the precise geometry of molecules opens new possibilities for understanding chemical reactions.

W. L. Bragg

X-ray crystallography is a technique by which the arrangement of atoms in various types of substances, and particularly in crystals, is deduced by studying the manner in which these substances scatter a beam of x-rays. This study became possible when the German scientist von Laue discovered x-ray diffraction by a crystal in 1912. The rays from a roentgen-ray tube were concentrated in a narrow beam by passing them through a fine hole, and when this beam fell on a crystal, and the scattered rays were recorded by a photographic plate, the photographs showed a symmetrical pattern of spots. Von Laue correctly interpreted this effect as due to the "diffraction" of x-ray waves by the regular pattern of atoms in the crystal.

This discovery was a crucial event in the history of science. In addition to proving conclusively that x-rays are electromagnetic waves like light, and leading to the study of the characteristic x-ray wavelengths emitted by the elements, which played a key part in subsequent research into atomic structures, it made it possible to analyze the structure of matter in a new and very powerful way.

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Optical Grating Principle

The effect is due to the same principle which governs the production of spectra by a diffraction grating. An optical grating consists of a number of fine lines ruled regularly on a glass or metal plate. When light falls on such a grating, each line scatters a wavelet. In certain directions, depending on the spacing of the grating and the wavelength of the light, the wavelets combine so that their crests and troughs coincide, and in these directions a strong beam of light is scattered. In other directions there is no such fit, the waves cancel each other's effects, and there is no scattered beam. This is the principle of "interference" enunciated by the famous Thomas Young in the first years of the 19th century, who first clearly demonstrated the wave nature of light. Many of the most beautiful colors in nature, such as the iridescent sheen on some beetles, the blue of a butterfly's wing or a jay's feather, the play of color in mother-of-pearl or, more strikingly, in an opal, are due not to pigments but to interference.

No new optical principle is involved in x-ray diffraction, but there is a contrast in emphasis. An optical grating is used to analyze light; the grating diffracts light of each wavelength in a characteristic direction. A very simple pattern of regular lines in the grating is used to analyze a complex spectrum consisting of light of many different wavelengths. In x-ray analysis, on the other hand, we wish to analyze the grating. The simplest possible spectrum is used—a monochromatic x-ray beam consisting of a single wavelength. This falls on a complex grating composed of atoms arranged in some kind of regular pattern in three dimensions. The aim is to deduce the atomic arrangement from the directions and intensities of the scattered beams or "spectra."

It would be out of place to outline, in this article, the rather complicated geometry of the effect. It may perhaps suffice to say that every variation of atomic pattern produces a characteristic pattern of x-ray diffraction which we can calculate, so by observing the latter we can deduce the former.

One point may be noted. Nature has been kind to us in providing a scale of dimensions that is just right. X-ray waves are about 1/1000 as long as light waves, and their wavelength is of the same order of magnitude as the

distance between atoms in crystals. This is precisely the right condition for the interference of the waves scattered by the different atoms in the crystal, which are regularly arranged like soldiers drawn up on parade or the pattern of a wallpaper.

This new art of x-ray analysis has cast a flood of light on problems in many branches of science. Chemists are able to tell us the proportions of the elemental atoms which build up chemical compounds. In some cases, in particular in the case of the compounds of the element carbon, they can discover which atom is linked to which. But x-ray analysis goes further; it gives us a map or blueprint of the structure, with each atom in its correct place, so that we can see how it is surrounded by its neighbors and how far away they are. Just as a blueprint explains to an engineer how a machine works, so this map makes it possible for the scientist to understand why bodies possess the properties they do and how they interact with each other.

In *The Ethics of the Dust* Ruskin explained to his class of young ladies what fascinating patterns they would find if only they had a way of magnifying a speck of dust so greatly that they could see the patterns of its building stones or atoms. His fantasy has now become fact.

Scientists in all countries have made contributions to the art of x-ray analysis, but it can be claimed that the United Kingdom has played a leading part. The first analyses were made in the United Kingdom, and up to the present a large proportion of the major advances in applying it to increasingly complex problems have had their origin in British laboratories. In reviewing the structures which have been analyzed we can play a kind of "animal, mineral, and vegetable" game, though these are not quite the categories we want. The convenient ones are "inorganic" (oxides, salts, minerals), "organic" (the compounds of carbon), "metallic" (metals and alloys), and finally "biological" (the vast number of molecules which play a part in life processes).

Inorganic Compounds

Most of the first structures to be analyzed were inorganic, because they were simple. The first of all was the structure of rock salt, or sodium chloride (NaCl), shown in Fig. 1, where
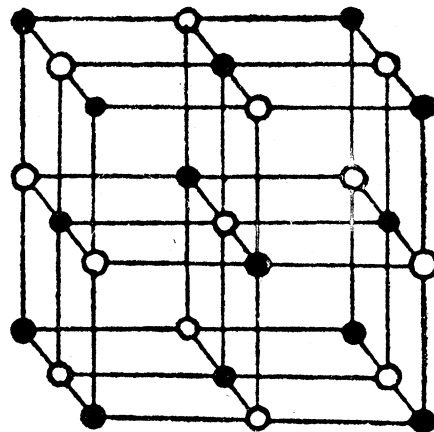

Fig. 1. The structure of rock salt (sodium chloride).

the open and solid "spheres" show the position of the centers of sodium (Na) and chlorine (Cl) atoms. Innocent though this structure may appear, it caused something like a minor chemical revolution. A cornerstone of chemistry is the conception of the molecule, the basis of Dalton's atomic theory. The vast numbers of different chemical compounds are built from comparatively few elements. Dalton postulated that each pure compound is composed of identical molecules, each molecule being a small family party of various atoms united together as a group. For instance, sodium chloride was held to be composed of molecules each containing one atom of sodium and one of chlorine. But, in the structure shown in Fig. 1, where is the molecule? Each sodium atom (Na) is surrounded equally by six chlorine atoms (Cl), and each chlorine atom by six sodium atoms, in a kind of three-dimensional chessboard pattern, and there is nothing to indicate that one sodium atom is particularly linked to one chlorine atom.

The answer, as is now realized, is that the structure is composed of charged atoms or ions, sodium being positive and chlorine negative. It is the electrical attraction of these opposite charges which holds the structure together, and of course each positive tends to be surrounded by negatives, and vice versa. The equality in numbers of sodium and chlorine atoms comes, not from paring of one sodium with one chlorine atom, but from the fact that the electrical charges must balance. So there is no molecule; it is as if, having found that the numbers of ladies and gentlemen at dinner parties is generally equal, we had falsely
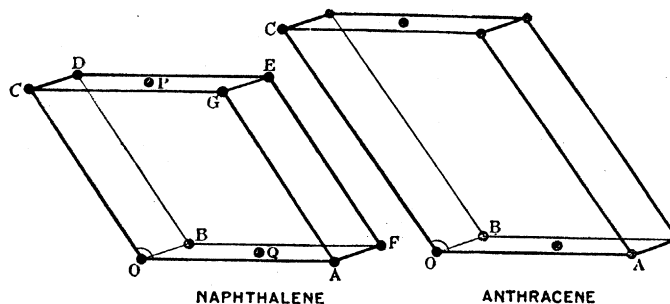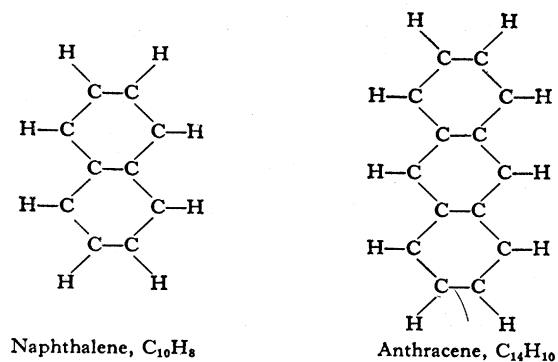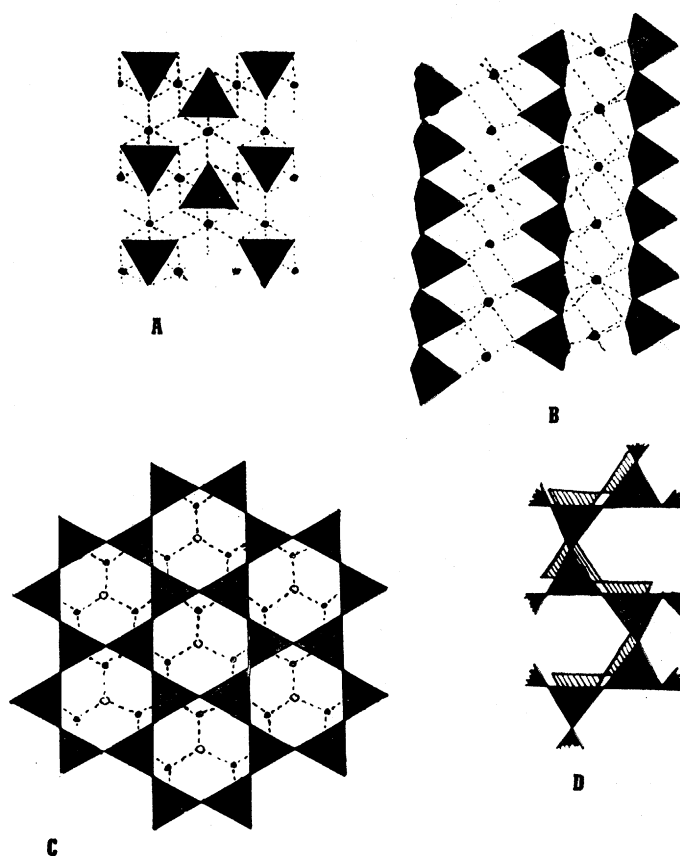
Naphthalene, $C_{10}H_8$

Anthracene, $C_{14}H_{10}$

NAPHTHALENE   ANTHRACENE

Fig. 2 (left). Schematic representation of the main silicate structures. (*A*) Isolated groups; (*B*) chains; (*C*) sheets; (*D*) three-dimensional frameworks. Fig. 3 (above). Naphthalene and anthracene.

concluded they were all necessarily married couples, instead of realizing that it was because each lady liked to have a gentleman on either side, and vice versa. It was a hard fight to get the idea accepted. I remember well how we were begged by the chemists to find some inclination, however slight, of a sodium atom to the chlorine atom to which it properly belonged!

The idea of inorganic compounds being composed of ions has given a new slant to inorganic chemistry. It has its most striking application in the structure of the minerals. The most common elements, which form by far the greatest proportion of the earth's crust, are oxygen, silicon, and aluminum. Sand, for instance, is mostly silica or quartz, a substance made up of silicon and oxygen in such a way that there are twice as many oxygen ions as silicon ions. These are highly charged ions with strong attractions. Silicon is al-
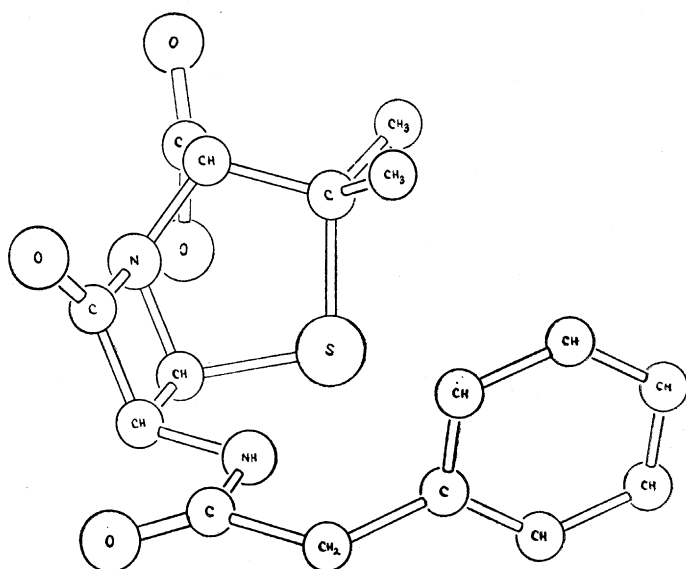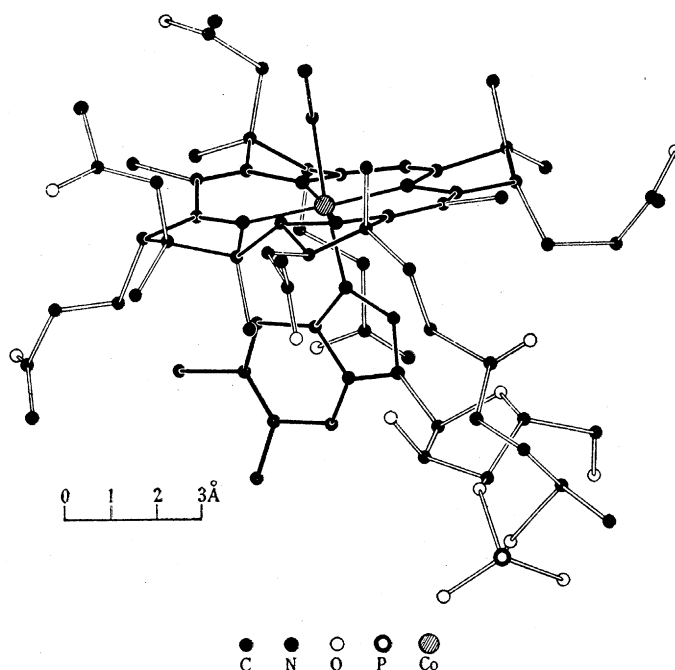

Fig. 4 (above). Structure of penicillin. Fig. 5 (right). Structure of vitamin B_{12}.

C   N   O   P   Co

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SCIENCE, VOL. 131

ways surrounded by four oxygen atoms at the corners of a tetrahedron; aluminum, sometimes by six at the corners of an octahedron (like two pyramids joined base to base) and sometimes by four, like silicon. The framework of the common minerals, the silicates, is a kind of fabric of these tetrahedra and octahedra linked by the oxygen atoms at their corners.

We may compare these two types to the purl and plain stitches in knitting, which in suitable combinations can produce such complex patterns. The tetrahedra are the strongest stitches, and it can be seen at once that there must be four main types of pattern which can be built with them. They can either be separate, or joined corner to corner in a long string, or joined by three corners to make sheets, or joined by all corners to make a three-dimensional framework (see Fig. 2).

These are precisely the four great families of silicate minerals. The first is represented by the dense olivines (the jewel peridot is an olivine); the second, by such fibrous minerals as asbestos; the third, by mica and the minute spangles which form clay; the last, by the felspars, of which the pink or gray opaque crystals in a granite are an example.

These minerals, and others like them, are held together by strong forces and hence have a high melting point, and they are relatively light; hence, as the earth cooled, they came to the top and formed the crust on which we live. A knowledge of structure has turned complexity into order and simplicity. The dynamics of the structures were elucidated by the American scientist, Linus Pauling, but the main story of the silicates was worked out in the United Kingdom.

Organic Compounds

If the idea of the molecule was found to be inappropriate in inorganic compounds, it received ample support when organic compounds came to be analyzed by x-rays. These compounds are for the main part composed of carbon, oxygen, nitrogen, and hydrogen. The atoms are bound together by links which are strong and which are localized, as if each atom had places in its surface to which another atom could be bolted. The groups of atoms so linked together into a chemical molecule are bound by comparatively weak forces to

neighboring molecules, hence they can be regarded as separate entities in a real molecular sense. This is in contrast to the inorganic compounds, which form a continuous structure of alternating positive and negative ions.

The analysis of organic compounds began with my father's work on naphthalene and anthracene, illustrated in Fig. 3. Organic chemists had shown that the former of these consisted of two benzene rings and the latter, of three benzene rings fused together. The distance between carbon atoms had been ascertained from the structure of diamond. The "unit cell" or box containing each pattern element of a crystal can be directly found by x-ray analysis, and my father was able to show that the box on the left could just contain two naphthalene molecules, that on the right, two anthracene molecules, of the form postulated by organic chemistry. X-ray analysis of organic compounds developed rapidly after this start, at first in the main confirming and making precise the pictures of organic molecules deduced by the methods of stereochemistry, and latterly revealing molecular structures which had hitherto defied chemical analysis. In contrast to this start, Figs. 4 and 5 show two recent triumphs, the positions of the atoms in moleclues of penicillin and vitamin B12, determined by Dorothy Hodgkin and her colleagues by x-ray analysis in her Oxford laboratory.

Alloys

The story of alloys is very fascinating and involves quite new ideas. The basis of Dalton's atomic hypothesis was the law governing the definite proportions in which atoms combine to form compounds. This gave rise to the conception of family parties of atoms, the molecules, which we have seen to have been inapplicable to inorganic compounds but applicable to organic compounds. In alloys, the law of combining proportions no longer holds. When one metal is alloyed with another—for instance, zinc with copper —a series of different structures is formed, depending upon the proportions of zinc and copper in the alloy. Each structure is not characterized, however, by a definite ratio of the two elements; on the contrary, there is a certain range of proportions, often quite extensive, for each structure.

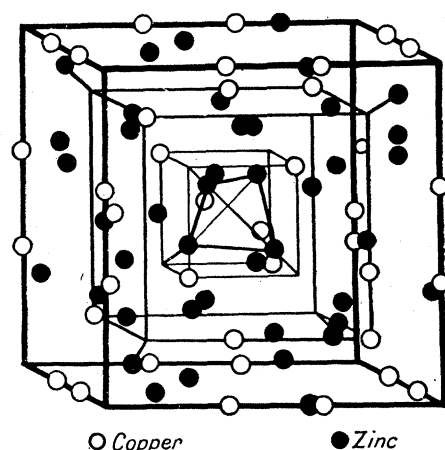The reason for this is clear if we

O *Copper* ● *Zinc*

Fig. 6. Structure of brass, an alloy of copper and zinc.

consider the peculiar nature of a metal. A metal atom is characteristically electropositive—that is to say, it has one or more electrons which are very easily detached from the atom, leaving it a positive ion. When metal atoms come together to form a metal structure, these loosely held electrons cease to belong to individual atoms and become a continuous electron sea with the positive ions embedded in it. The structure is held together by the electrostatic attraction between the positive ions and the enveloping negative electron sea. There are no bonds between atoms; that is why a metal can be distorted without breaking.

The same conception explains the nonexistence of a law of combining proportions. There is no longer a need to balance the numbers of positive and negative atoms, as in an inorganic crystal, because each atom brings with it its own balancing charge in the electrons it contributes to the structure. We may liken it to one of those parties of the type where the number and balance of the guests is not of prime importance because each brings his own supply of drink. An important factor in determining the phase structure is the ratio of the number of electrons to the number of atoms. When zinc is added to copper, each zinc atom brings two electrons with it, while the copper has one, so the electron-atom ratio is increased. The phase structure, at first simple, assumes more complex forms as the amount of zinc increases. Scientists in many countries contributed to this story, but the work on complex alloys by Bradley in Manchester, and on the influence of the electron-atom ratio by Hume-Rothery in Oxford, was outstandingly important. Figure 6 shows an example of Bradley's analysis.

Biological Molecules

Biological molecules are essentially organic compounds like those already described, but for convenience they are considered in a separate class because of their size and complexity. The molecule of hemoglobin, for instance, which colors our blood red and has the task of conveying oxygen from our lungs, which absorb it when we breathe, to the muscles and other parts of the body where it is needed, has a molecular weight of 68,000 and contains about 12,000 atoms. Protein molecules, of which hemoglobin is an example, are for the most part composed of carbon, oxygen, nitrogen, and hydrogen, like all organic compounds, and also contain a few atoms of special kinds such as sulfur.

It appears that each type of protein molecule has a specific task to perform. It may be quite a simple one, like that of carrying oxygen, but the complexity of the molecule may be ascribed to the need to do this task at just the right place and in just the right way. We are reminded of the contrast between the simple letter delivered at our door and the complex of delivery van and postman, and indeed all the organization behind them, which insures that the letter reaches the right address.

A whole group of proteins called enzymes is concerned with the various chemical tasks in our bodies. Another group of biological molecules comes under the heading of "nucleic acid." It appears to be their task to act as the templates on which new protein is manufactured, and as the types of protein made determine the nature of the organism, they are the carriers of the hereditary factor in a parent, which determines the nature of the offspring.

The successful application of x-ray analysis to the study of these biological molecules is one of the wonders of modern sicence. A vast amount of brilliant research on their constitution had been done by chemical techniques; the x-ray work is based on this foundation, but it has performed its typical function of giving precision to the picture. It has been thrilling to see that x-ray analysis can be applied to such very complex bodies.

Protein Structure Analyzed

The leading x-ray group in Great Britain has been the research unit directed by Perutz and Kendrew in Cambridge and supported by Britain's Medical Research Council. Their work resulted in the first successful analysis of a protein structure (by Kendrew), the myoglobin molecule which acts as a storehouse of oxygen in muscle. It would have been almost inconceivably difficult to tackle a molecule containing 3000 atoms (myoglobin is about one-quarter the size of hemoglobin) by the x-ray techniques which had served for simple molecules.

Success was attained because of a discovery by Perutz that certain heavy atoms such as mercury, iodine, or gold could be chemically attached to specific points of each molecule without disturbing the crystal structure.

It is relatively easy to discover the positions in the structure of these heavy marker atoms, which scatter the x-rays far more powerfully than the light atoms of the organic complex. By noting the differences which they cause in the x-ray diffraction, it is possible to apply an analysis which reveals the protein structure.

It is a massive frontal assault. Vast numbers of measurements have to be made, and the results are fed into electronic computers which perform in a few seconds calculations which would take as many weeks if made by human beings. The results are just now coming off the production line, and it is a very exciting time.

Another extremely important success of the Cambridge unit was the establishment of the structure of nucleic acid by Crick and his American colleague Watson. This structure has suggested a fascinating mechanism for the processes of heredity.

Why is this so important? It is again a question of the precise picture. The functions of these molecules must be dependent upon their geometry. They must fit each other in just such a way that the right parts are brought into conjunction and can interact chemically. We hope to understand such processes when we know the structure; we hope to see how the enzymes act, why vitamins are necessary, what hormones do, why certain substances are poisonous. As in other and simpler realms of x-ray analysis, we can confidently hope that this new knowledge will result in a new flood of light being cast.