The Carbon Atom in Crystalline Structure.¹

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IT is one of the great purposes of research to be able to explain the properties of materials in terms of the properties of their parts. The division into parts may be carried to various degrees of fineness; and the nature of the research, its methods and difficulties, and the expectations of success will depend on the division that is attempted. The properties of a piece of steel may to some extent be explained in terms of the small visible particles, crystalline or not, of which it is composed; the degree of division is determined by the power of the microscope, and results of great value are obtained within this range. But we may have, as a higher ideal, the hope of explaining the qualities of steel in terms of the properties of the atoms of iron and carbon and other constituent elements. This division is far finer than the other; but obviously far more complete and satisfying. The difficulties are great, but so also will be, we may be sure, the ultimate success. Generally it must be our aim to explain the properties of all materials in terms of the atoms, remarkably limited in kind, of which the world is made.

Some progress towards the ideal has been made in the case of the gas and the liquid states; the great effort is yet to be made in the case of the solid. The moving particles of a gas are free from each other's influence for the most part of their time; they can be treated as projectiles the rare encounters of which are but slightly affected by the special and peculiar attractions which they exert on each other when very close together. The properties of gases are to a certain extent explainable in terms of a pure kinetic theory. Complications arise when from any cause the times during which the atoms or molecules are under each other's influence become relatively important, and the consequences depend on the individual peculiarities.

So also in the case of liquids much can be explained on a purely hydrodynamical theory, especially when the ties between atoms and molecules can be dissolved and re-formed continually without waste of energy in the form of heat, that is to say, when there are no viscosity effects. But when viscosity is to be taken account of, then the peculiar and individual actions of the atoms and molecules must be treated as effective. Still more, the phenomena of surface tension are direct manifestations of the forces that the atoms exert on their neighbours; and so in general are all the effects studied by the physical chemist. We are yet very far from being able to unravel them.

It is true that the associations and dissolutions of chemical action are due directly to the characteristic forces exerted by the atoms; and that chemical studies afford a most important means of examining them. Nevertheless, we want more than chemistry gives us if we are to reach our object. For example, we are far from linking up the properties of quartz with the known chemistry of silicon and oxygen.

In general, we know very little of the relation between the properties of the solid material and of the atoms of which it is built. Of the relation between the molecule

and its constituent atoms we do know something, thanks to chemical study. But the wide field of solid structure is in this respect almost unexplored. The reason for this is very simple. The properties of the solid depend upon the structural arrangement of its component atoms, and the arrangement is, at the first attempt, as we may say, crystalline. When groups of atoms or molecules associate and form a solid, they arrange themselves in a regular pattern; the unit of pattern containing only a few groups, usually two, three, four, six or other small numbers. The arrangement is so uniform and so exact as to imply that the group has a definite and characteristic shape, or, in other words, that the forces which one group, atom or molecule exerts on its neighbours are such as to place them at proper distances from itself, and in proper orientations. The crystal is the direct expression of this tendency and is a far more prevalent form of matter than we had thought. The large crystals that we see with our naked eye, and even the small crystals which the microscope reveals to us, are only the favourable cases. Below all that we can see in any way is a universal tendency to crystallisation which the methods of X-ray analysis are now showing to us. The solid which appears to us to possess none of the properties of the crystal is usually a very viscous fluid, or a disordered mass of minute crystals. The crystal is the simple body, the so-called isotropic body is the complex. Consequently, it is the crystal that must first be mastered.

It is only within the last ten years that the direct study of crystal structure has been possible, and the way to this huge field of inquiry been thrown open. The X-rays, to put it simply, if somewhat crudely, are a form of light ten thousand times finer than visible light, and we are now able to see, indirectly it may be, the actual arrangement of the atoms. Here is our chance of making this supreme analysis. We have before us a widespread research, in the course of which we must examine crystal after crystal, learning its structure, that is to say, the pattern according to which its constituent atoms are arranged, and examining the way in which the properties of the individuals determine that pattern; and in turn the pattern determines the elasticities, rigidities, conductivities, dielectric capacities and every other characteristic which the crystal possesses. After that, follows in its turn the crystal conglomerate, the isotropic solid.

An especial interest is attached to all that we can discover by the new methods of crystal analysis concerning the nature and properties of the carbon atom. It is not one of the more common elements. While oxygen is calculated to form half the materials of the earth's crust, silicon a quarter, and aluminum about a sixteenth, only about a thousandth is composed of carbon. But it is the carbon atom which more than any other impresses its character on the materials of which living bodies are composed. The very term, organic chemistry, which is given to the subject that is largely occupied with the study of the carbon compounds, is an expression of the importance of the carbon atom in the living organism. Not only is the carbon

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atom of supreme importance in the constitution of our bodies and of their unconscious actions, but also in a great proportion of the external activities in which we are engaged. We must be especially eager to know what we may learn of the behaviour of the carbon atom when it takes part in the constitution of the solid body, and in the first place of the crystal which is the simplest form of the solid. The only fact which makes us hesitate is the vastness of the number of known crystalline compounds, giving us a bewildering choice of material on which to work.

We come to this study with certain expectations founded on the large labours of the organic chemist and their rich harvest of results. We expect the carbon atom to display, for example, a definite tetravalency, a power of attracting to itself under certain circumstances, at least four other atoms and no more, all bound in a similar way to the central carbon; as, for example, when the carbon atom draws to itself four atoms of hydrogen and the methane molecule is formed. Yet, in other circumstances, the carbon atom seems fairly content with a smaller number, as when in the benzene ring each carbon is attached to two other carbons and only one hydrogen, and the benzene molecule has very little general attraction for another benzene molecule. Again in the carbon dioxide molecule, the carbon atom is satisfied by the companionship of two other atoms only, and we should like to know what rearrangement has been made of its activities to permit the formation of this self-contained molecule, so independent that it forms a gas. Also, what further change has been made when the molecule of carbon monoxide is constituted? In other words, what is the explanation of the single, double, and triple bonds known to the chemist? We hope to be able to throw light on all these conditions, and the questions to which they give rise, by the study of the carbon atom as it is built into the crystal, where we can examine the exact nature of its environment and can relate thereto the properties of the crystal.

There are two crystalline forms composed of carbon alone, diamond and graphite, and we naturally turn to their examination first. The diamond structure was, in fact, one of the first to be examined by the new methods. Its structure is very simple and symmetrical, and answers at once our expectation that we should find in some circumstances a perfectly tetravalent behaviour. Each carbon atom is surrounded by four others, which are grouped about it in perfect symmetry; the atom shows no attraction for more than four. A sphere can, of course, be surrounded by twelve other similar spheres, and if the attraction between any two atoms could be represented merely by a central force, we should expect the close packing which gives the full quota of neighbours. Since there are only four, the force exerted by one carbon atom on another cannot be represented by central forces only. Further, the hardness and rigidity of the diamond show us that the forces are mutually oriented; that they are primarily exerted along four lines drawn from the centre of a tetrahedron to its corners and that there is a strong resistance to any relative change in those directions. All these new points are in excellent agreement with known chemical facts. The carbon atom is to be represented by a tetrahedron rather than a sphere.

The disposition of the atoms in the diamond shows that they may be divided into two classes, any member of one class being the reflection of the other—with appropriate shift—in any one of three planes which are the cube faces of the crystal. To put this in another form, each diagonal of the cube crystal passes through the vertex and the middle of the base of each class of atom, but members of the two classes face opposite ways. The X-rays detect the difference between the two kinds, from which we conclude that the scatterers of the X-rays participate in the tetrahedral grouping. Yet the difference is only slight, so that if it is the electrons that scatter, they are close to the centre, which seems unlikely; or else they have an extended movement about their average positions at the corners, so that their diffracting effect is small; their action is like that of broad faint rulings on a diffraction grating.

The other crystal of pure carbon is graphite. There is no clear evidence at present of the existence of any other form, although certain curious carbon materials have not been fully examined. The structure of graphite has recently been re-examined by Bernal, who was able to obtain single crystals of sufficiently perfect form. The results of his work show that graphite is a hexagonal crystal, as Hull had supposed from an examination by the Lowder method. It consists of layers of carbon atoms, each layer separated from the next by $3.40 \text{ \AA.U.}$, as has long been known. In each layer, the carbon atoms are arranged in a hexagonal network; the long uncertain point as to whether the atoms of one sheet are all exactly in one plane or are in two planes making a puckered network, seems now to be decided in favour of the former alternative, as Debye has suggested. In this case, each carbon atom is very strongly tied to three neighbours, all in one plane; the distance between the centres is $1.44 \text{ \AA.U.}$ as against $1.54 \text{ \AA.U.}$ in the diamond. The distance between a carbon atom in one layer and its nearest neighbour in the next is more than twice as great.² The curious properties of graphite show that the forces between atoms in the same sheet are exceedingly strong, while the forces between sheet and sheet are very small. It is clear that the carbon atom is now exerting its attraction on other atoms in quite a different manner from that which was followed in the diamond. If the electrons are in some way responsible for these forces, their arrangement must have been altered. The atom is no longer tetrahedral.

The extraordinary success of Bohr's theory in regard to radiation is a constant inducement to attempt a correlation between his arrangement of electron orbits with the display of the atomic forces, although it does not seem possible at present to make more than vague and preliminary attempts in this direction. According to Bohr, there are four electron orbits which we may naturally associate with the tetravalency of the atom; but the four are not all alike, being different, two and two. Thus the tetravalency is not fully symmetrical. The radiating carbon atom which is the subject of the theory is not, however, attached to other atoms, but is free; and we may well suppose that the internal

² Since this was written, a paper by Hassel and Mark has appeared in the *Zeitschrift für Physik*, describing experiments which lead to exactly the same result as that of Bernal. The latter's paper appears in the *Proceedings of the Royal Society*.

arrangements are modified by structural requirements. There may be a real difference, implying perhaps a different energy content between the free atom with its two pairs of outer orbits, the atom in graphite with three like orbits and one odd, and the atom in diamond with all four alike. The electron of the odd orbit in graphite would naturally travel far and be loosely attached to the nucleus; and in this, as has been suggested by Shearer and Bernal, we may find the explanation of the colour, the opacity, and the conductivity of graphite.

We now come to cases in which other atoms beside the carbon enter into the structure; and first to calcite. The X-ray analysis shows that the carbon atom is now surrounded symmetrically by three atoms of oxygen, all alike.

The compact group of one carbon and three oxygens possesses a double negative charge; the calcium atom possessing the corresponding amount of positive electricity. It has been suggested by Kossel that the arrangement is governed by the tendency for the oxygen atoms to surround themselves in each case by the full complement of eight electrons, and that this is effected by stripping the calcium atom of two electrons and the carbon atom of four. On this theory, there is no parallelism with the graphite structure, though in both cases the carbon atom is surrounded by three other coplanar atoms, similarly situated. The carbon atom has now lost all four of the electrons that were moving in outer orbits and is reduced, in external appearance, to helium. It is to be treated as exerting a central electrostatic force due to a positive charge of four units.

It is well known that a vast number of organic substances are based on a substructure consisting of a ring of six carbon atoms, or a chain of carbon atoms of any length. The simplest ring compound is the famous benzene molecule; benzene does not, however, lend itself very readily to analysis because benzene is liquid at ordinary temperature and when frozen does not form good crystals. But there are the two substances, naphthalene and anthracene, of which the former has been imagined by the organic chemist to consist of a double ring, represented by two hexagons in the same plane, having one side and two corners in common. The latter consists of three hexagons in a line, the naphthalene model extended by one more hexagon. Both these substances crystallise well, a very marked characteristic of each being the tendency to split into thin flakes. All these molecules are bounded by hydrogens. They must be considered as simple subjects for attack, because the ring is so common a feature of organic substances, and the single, double and triple rings form a series of comparable members. A curious point of obvious interest is the connexion of each carbon atom with three, and only three, other atoms. Why has the fourth bond apparently disappeared?

The X-ray analysis shows that the unit of pattern of both naphthalene and anthracene contains two molecules arranged so that their long axes are parallel to one another and that they are the reflection of each other in the single plane of symmetry which the crystal possesses. In fact, the crystal can be considered as a set of parallel flakes, like the monomolecular layers of Langmuir. In each flake the molecules stand not quite

at right angles to the flake, but lean over like wheat in a field blown by the wind. The difference between the anthracene and the naphthalene structures lies only in the length of the molecule, which makes the flake thickness of the former greater than that of the latter. Moreover, the actual increase in length which is found by the X-ray measurement is exactly what it should be if, in the first place, the one molecule consists of three benzene rings in a row and the other of only two, according to chemical theory, and in the second place, the width of the ring is the same as that of the carbon ring which is found everywhere in the diamond structure. We might suppose, in fact, that the molecule of naphthalene as built into the crystal structure was simply carved out of the diamond without alteration and then fringed with hydrogen atoms. A similar set of atoms carved out of the graphite flake would do equally well so far as length is concerned, because the graphite layer is, according to Bernal, the diamond layer pressed flat without any sideways extension. But if the carbon atoms were in the supposed graphite condition, it might be expected that naphthalene would be a conductor and be opaque like graphite, which is not the case. The direct analysis itself is not yet able to say whether the three attachments of each carbon atom to its neighbours in the same molecule are all on one plane. It is to be remembered that there are attachments between each molecule and its neighbours in the same layer, but these must be far weaker than the bonds binding together the atoms in the same molecules; they are stronger, however, than the end-to-end attachments which break on the cleaving of the crystal. These last must be feeble because the crystal cleaves so easily.

So far, therefore, the result of the analysis of these crystals is, in the first place, to give confidence in the existence of a mutual support between the established organic chemistry and the new methods of analysis; and to show us also how closely the behaviour of the crystal may be connected with its general structure. As to details, the indication seems to be that the carbon atom has—at least nearly so—the same characteristics as the atom of the diamond; but that one of the four valencies is unused. We have even some grounds for saying that the unused valency, or the unoccupied corner of the carbon tetrahedron, is that which lies on the face of the molecule, not on its edge. The crystal of naphthalene tetrachloride, *i.e.* naphthalene with four added chlorine atoms, shows the same structure as that of naphthalene, and has very similar dimensions except that it has broadened by an amount which would correspond closely with the result of adding the chlorines at the places indicated.

Measurements have been made of some of the dimensions of other crystals containing ring molecules, and the results fit in, so far as they go, with the idea that the ring is an actual structure of definite dimensions and form, slightly altered it may be by additions or substitutions of other atoms or groups of atoms, or strained because it has to be fitted into its place in the crystal, nevertheless recognisable in its different circumstances, as the chemist would expect. To settle these points more satisfactorily, to turn guesses into certainties is, of course, the work that is before us.

Very interesting results are obtained by Müller and

Shearer from the study of the long-chain molecules of the fatty acids, hydrocarbons, and similar substances. It appears that when these substances in the solid state are pressed on to a flat surface, they form flaky crystals like graphite or naphthalene, and it becomes easy to measure the thickness of the monomolecular layer. The experimental results are beautifully definite, and their interpretation can be given with great chance of being correct. It seems probable that the molecule is perpendicular to the layer, not slanting. If it were the latter, one would expect the amount of slant to be variable so that it would not be possible to connect the thickness of the layer with the length of the molecule only. Now, it is a remarkable fact that the thickness of the layer grows at a uniform rate as the chain is increased by the addition of carbon atoms, and that for very nearly all, if not all, the different kinds of chain molecules that have been examined, this rate has one or other of two values. For every two carbon atoms that are added the increase in length is either 2.50 Å.U. or 2.00 Å.U. very nearly.

If we were to suppose that every carbon atom in the chain had four points on it, disposed like the corners of a regular tetrahedron, at any one of which an attachment could be made to a neighbour, in other words, if we supposed the atom to be as in diamond, then a chain of carbon atoms would take one or other of three forms, one of which is a screw. Putting the distance between the centres of two carbon atoms equal to the distance found in the diamond, namely, 1.54 Å.U., it can readily be calculated that the length of chain *A* (Fig. 1) is 2.50 Å.U. for every two atoms

FIG. 1.

added, and of chain *B*, 2.05 Å.U. The agreement with experiment seems to be more than a coincidence, and it may be provisionally assumed that in these chains either the *A* or the *B* form is adopted, and the linkage of carbon atoms with their neighbours is on the diamond plan. In other words, if *PQR* are the centres of three atoms, the angle *PQR* is equal to the angle between two of the lines joining the centre of a tetrahedron to the corners.³

One of the most striking results is the fact that the length of the main body of the chain is independent of the nature of any additions to its ends or replacement of any of its side hydrogens by an oxygen atom as in the ketones. Even the removal of two or four hydrogens from the body of the chain leaving two carbons connected, respectively, by a double or a triple bond, makes no appreciable difference in the length. It would not have been a matter of surprise if such treatment had caused a bend in the chain, on account

³ A minute but perfect crystal of stearic acid has recently been examined by the X-ray method by R. E. Gibbs, who has found it to belong to the monoclinic class. The long molecules are not perpendicular to the cleavage plane, but are inclined at about an angle of 63°. This result is not necessarily in contradiction with any of the above suggestions.

of the relative shifting of points of attachment on the carbon atom that might be due to other points of attachment being unused. The removal of a pair of hydrogens from the chain makes no more difference to the chain than the stripping of an opposing pair of leaves from the stem of a plant.

A very curious point in the behaviour of the long chains is their apparent doubling in length when one end is formed of a so-called active group, as, for example, in the case of the fatty acids. When this is the case two chains join end to end, the active groups being together, and again the result is just the same as if two sticks were joined into one, the process of joining being concerned with nothing beyond the two active ends. This form of structure is illustrated in a very interesting way in the X-ray spectra. If a section is made of a substance consisting of layers of these doubled molecules, so as to show their stratification, then there will be a uniform distribution of diffracting centres—electrons—throughout the mass, with alternating thin layers of excess through the active ends, and thin layers of deficiency through the inactive ends, the methyl groups. This has the curious effect of intensifying the odd orders of the diffraction spectra. To understand this, it is only necessary to remember that if we were to make a series of fine rulings on a diffraction grating which exactly interleaved the stronger original rulings, the result would be the strengthening of the even orders; such an effect is found in the case of rock salt and was an important help in the determination of its structure. If now the additional rulings, instead of being like the original but weaker, could be of reversed effect, a deficiency instead of an excess, it would be the odd, not the even orders that would be strengthened. The same effect is found in the case of the ketones. When the substituted oxygen is in the middle of the chain, each layer of hydrocarbon molecules shows a generally uniform distribution of electrons with an excess at the middle where the oxygen atom is placed, and a deficiency at either end. When the substituted oxygen is not in the middle, the reinforcement of the odd orders disappears.

These many observations of the behaviour of the long-chain molecules seem to point to the conclusion that the carbon atom in the chain is, like the carbon atom in the diamond atom, possessed of four points of attachment regularly disposed about it, and that the non-use of one does not alter the disposition of the others.

It is scarcely necessary to consider in any detail the points given by structures like tartaric or succinic acid as to the behaviour of carbon atom. It is enough to say that, while the full interpretation may be yet to come, the general indications are in accordance with what has already been said.

These first tentative conclusions as to the behaviour of the carbon atom in the solid body are of interest, in spite of the fact that so little, relatively, has been accomplished in the solution of the structure of organic crystals. What remains to be done must have great consequences, and what little has been done already seems to possess many points of novelty and of interest, and these two facts taken together may be sufficient justification for this attempt at a review of the present position of the inquiry.