

It is a remarkable fact that *Homo rhodesiensis*, although apparently a more primitive and simian type than *Homo neanderthalensis*, was found still unfossilised, and among animal remains which belong to still living Rhodesian species. The deduction has been made that *Homo rhodesiensis* was living quite out of his proper geological horizon, and was surviving in South Africa long ages after his compeers in Europe had passed away. In fact he was probably still flourishing in the south when his European "contemporaries" had been dead for thousands of years. But there is really nothing singular in such an idea. After all, such a situation is typical of South Africa in more respects than one. Our Bushmen are nothing but living fossils whose "contemporaries" disappeared from Europe many thousands of years ago. The interest of South Africa as a field for anthropological research is partly just this, that it is possibly ten thousand years behind the times, as measured by the standards of European cultures. In this respect our anthropology does not stand alone, for in botany also we have true "living fossils" like the cycads. In South Africa, therefore, certain biological problems can still be studied from life which in Europe can only be deduced with difficulty from the fossil records of the past.

That is by no means, however, the only or the best claim that South Africa can put forward as a fitting place for palæontological study and research. Discoveries already made point to the possibility that South Africa may yet figure as the cradle of mankind, or shall I rather say one of the cradles? As we have seen, it is not only one of the oldest land surfaces but

also, since the end of the Mesozoic period, it has generally enjoyed a fairly habitable though, on the whole, dry climate. While in Tertiary and Pleistocene times most of Europe and much of Asia and North America were intermittently under ice or shallow seas, southern Africa was very much as it is to-day. No wonder, therefore, that it should contain some of the most ancient fossil records of the human race, and that among its living races it should include what are "fossils" in other continents. Its little Bushmen are unique; its little pigmy population that hide in the tropical and subtropical parts are the representatives of the long-vanished human past. Going a little further back, we find in Africa the home of the great anthropoid apes which are nearest to us in the affinities of life. Here then we are clearly near to the great origins. These and other considerations point to the vast importance of Africa from a palæontological point of view, if not to the possibility that here may yet be found some intimate connexion with the far-off beginnings of the human race. The scope for scientific work in South Africa in this department of knowledge is therefore immense.

Science has in South Africa a splendid field of labour: other nations may well envy us the rich ores of this great "scientific divide" which is our heritage. I trust that South African science will rise to the height of its great opportunities, and that this sub-continent will yet earn for itself that scientific leadership of the southern hemisphere to which its central position and its great scientific assets and opportunities entitle it.

### The Crystalline Structure of Inorganic Salts.<sup>1</sup>

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THE examination of crystalline bodies by means of X-rays has enabled us to discover the positions of the atoms in the crystal. In the earlier period of X-ray analysis it was only possible to do this when the atoms were arranged according to a simple pattern of high symmetry. Experience has increased the range of substances to which the new methods can be applied, and we can now assign structures to relatively complex crystals, basing the proposed structure on the manner in which the crystal diffracts the radiation.

The study of the crystalline structure of organic and inorganic compounds has revealed certain broad distinctions between these two classes of crystals. The crystalline arrangement throws new light on those differences in the structure of the molecule which have made it convenient to distinguish organic from inorganic chemistry. No exact line can be drawn between the two classes of crystals, and yet the main features are sufficiently different to make the classification useful. The organic crystal appears to be composed of definite molecules. Inside each molecule the atoms are bound together by forces so local, and so rigid, that an addition to one part of the molecule scarcely affects the rest; these molecules are then massed together by comparatively weak forces into a crystalline structure. The form of the inorganic

crystal suggests that the bonds between atom and atom are not limited to certain directions; the molecule is more fluid, and an addition to one part profoundly disturbs the relationship of all the rest. It must be this molecular fluidity which makes it so hard to apply the ideas of stereochemistry to inorganic compounds although they have been so successful in explaining the organic compounds.

Our powers of X-ray analysis are as yet very incomplete and it is difficult to find the positions of the atoms in complex structures. The complexity of a structure depends on the number of parameters, or degrees of freedom permitted by the symmetry, which fix the positions of the atoms in its pattern. At the present time any structure with more than half-a-dozen of these independent parameters presents a difficult problem. Crystals with two or three parameters are comparatively simple. For several reasons the inorganic salts can be analysed more completely than organic compounds. In the first place, the number of atoms in the inorganic molecule is generally smaller than that in the organic molecule, and owing to the power of readjustment in the former class of compound which has already been mentioned, the atoms often take up a symmetrical arrangement and this symmetry makes the X-ray investigation more easy. Every requirement of symmetry which must be satisfied by the atom reduces the number of variable

<sup>1</sup> Discourse delivered at the Royal Institution on Friday, May 1.

parameters in the structure, and confines the atom to certain planes, lines, or points from which it cannot move. Further, in a series of inorganic crystals it is often possible to replace one atom by another of similar chemical properties without altering the crystalline structure. Now the heavier atoms scatter X-rays more than the lighter atoms. If, therefore, we wish to find the position of the metal atoms in an inorganic salt, and a crystal of the series is available in which the metal has a high atomic weight compared with the other constituents, it is an easy matter to fix its position. The same process can often be carried out with a heavy atom in the acid radical and a light one in place of the metal. In order to aid the X-ray examination we are using a method which is precisely like the staining, by means of suitable dyes, of certain parts of a microscopic preparation. In the organic crystal the atoms of carbon, oxygen, and nitrogen are almost indistinguishable by means of X-rays since they are so close in the periodic table, and, with the exception of one or two compounds, it has so far been impossible to fix their positions.

The inorganic salts are interesting not only because we know more about their structure, but also because they lend themselves more readily to mathematical treatment. We may compare this case of crystal equilibrium to the engineering problem of calculating the stresses to which the members of a girder system are subjected. If the number of constraints is the minimum requisite for rigidity, these stresses can be directly calculated by simple laws of mechanics. If the whole structure is too rigid, much more detail must be known about the structure in order to calculate the stresses. The inorganic crystal represents the structure with the minimum number of constraints. We can try to explain the properties of the crystal as a whole by making certain simple assumptions about the forces between the atoms. It is certain that the real atomic properties are more complex than those represented by these simple assumptions, but it is interesting to see how far one can get towards an explanation with their aid. For example, a number of crystalline properties can be explained by assuming an atomic model of the following kind.

(a) The atom consists of a symmetrical electronic structure surrounding the nucleus in which the charges on the electrons and on the nucleus do not balance, so that the sum of the charges is sometimes positive, sometimes negative.

(b) When the atoms approach within a certain distance of each other a force of repulsion between their outer electronic structures sets in very rapidly and prevents closer approach.

(c) When the atom is placed in an electric field it becomes polarised. Its positive and negative parts are drawn in opposite directions and it is surrounded by a field like that of an electrical doublet.

With the aid of these assumptions, qualitative explanations have been given of the formation of inorganic compounds (Kossel) and quantitative explanations of the heats of formation, heats of solution, latent heats of evaporation, and elastic properties of the inorganic crystals (Born and Landé, Madelung, Fajans, and others). Their highly interesting investigations have been applied to crystals of a symmetrical and

simple type, such as the rock-salt structure. The quantitative agreement between calculated and observed data is most striking and shows that the assumptions which have been made are not far from the truth. I do not wish to discuss their results here; I quote them to show how far this atomic model explains the facts, as I wish to use it in examining the more complex salts which we have analysed by X-rays.

The force which causes two atoms to repel each other when they approach closely is very interesting. We do not know its origin, but it is clear that it sets in very sharply and increases rapidly as the centres of the atoms get closer together. This is so much the case that each atom in the crystalline structure appears to be surrounded by a domain which it occupies to the exclusion of other atoms. We cannot define the size of this domain exactly because the distance of closest approach of two atoms will always depend on the strength of the force driving them together, but the domain varies within narrow limits for the range of forces ordinarily present in a crystal. A knowledge of the domain associated with the atoms and molecular groups is most important in crystal analysis since it limits the possible configurations and confines the atoms to certain regions where they do not overlap too greatly. In a Friday evening discourse at the Royal Institution four years ago, I gave some empirical figures for the radii of these atomic domains and tried to show how these figures could be used to aid crystal analysis. I wish to take this opportunity of saying that I have considerably altered my views on this question; other workers who have dealt with the subject have given alternative estimates of the domains, which I believe to represent the physical facts far better than did my original figures, and in addition a more complete knowledge of crystal structures has shown how elastic the atomic domain is and what care is necessary in using the conception to help analysis. Nevertheless, its very great importance must not be lost sight of, for it is one of the principal aids we have in tackling a difficult crystal structure.

We do not know the exact dimensions of the electronic orbits, but such estimates as can be formed suggest that in a crystal such as rock-salt there are large spaces between the outermost orbits of neighbouring atoms. Each atom has its system of orbits quite distinct and widely separated from those of its neighbours. This is generally true where the charged atoms are of a symmetrical type and held together by electrostatic attraction. On the other hand, where the chemical evidence points to a linkage of the homopolar type, crystal analysis shows the atoms close together as if the electronic orbits were actually linked up.

A series of atomic structures such as  $O^{--}$ ,  $F^-$ ,  $Ne$ ,  $Na^+$ ,  $Mg^{++}$ ,  $Al^{+++}$  are supposed by Kossel to have a common configuration resembling that of neon itself. The charges on the atoms are due to the addition or removal of electrons required to give them the correct number for a neon structure. The scale on which the atoms are built must diminish from oxygen to aluminium, owing to the increasing nuclear charge,  $Al^{+++}$  being on about one-half the scale of  $O^{--}$ . The idea of an atomic domain can only be a very rough approximation to the truth, for in actual fact there must be a different law of force for

every given pair of atoms; in this approximate sense, interatomic distances in simple crystalline structures are in agreement with the supposition that they obey an additive law and that the dimensions of the domain are proportional to those of the atomic structures in a series such as has been given above. I directed attention to this additive law as an empirical fact in the discourse referred to above, but made the domain of the positive ions too large and those of the negative ions too small. A better interpretation of the significance of the law was given by Wasastjerna in a paper on the "Radii of Ions" in which due weight was given to the relative dimensions of the electronic structures. Recently, Jones, in a series of highly interesting papers, has linked up the fields which give the repulsion between atoms of an inert gas, and the fields of the corresponding ionic structures in crystals.

Again, in the case of the very simple crystals, good quantitative agreement between calculation and observation of crystal dimensions can be obtained by certain simple assumptions about the nature of the repulsive field due to their electronic structures. In the more complex crystals the concept of an atomic domain is by itself sufficient to explain the general configuration of the crystal. Cases which are especially interesting are those where the domain of one ion is much larger than that of the other. The structure of aluminium oxide,  $\text{Al}_2\text{O}_3$ , is an example. Since the oxygen ion is so much larger than the aluminium ion, the structure is that of a series of oxygens in a close-packed arrangement (hexagonal) with aluminium atoms in the interstices acting as a cement to bind the whole together. In spinel,  $\text{MgAl}_2\text{O}_4$ , the oxygen atoms are in a cubic close-packed arrangement. In cadmium iodide,  $\text{CdI}_2$ , the large iodine atoms are in hexagonal close-packing with cadmium atoms lying between alternate layers perpendicular to the hexagonal axis. Tin tetraiodide is another case where a quite complex structure approximates closely to a cubic close-packed arrangement of iodine atoms. Such crystals give a great deal of information about the forces between atom and atom.

In a few cases it has been possible to determine the shape of the acid radical. In  $\text{CO}_3^{--}$  and  $\text{NO}_3^-$  the oxygen atoms are arranged at the corners of an equilateral triangle around the central atom, and the arrangement must be very nearly the same in  $\text{ClO}_3^-$ . Though we do not know the arrangement of the oxygen atoms round the sulphur atom in  $\text{SO}_4^{--}$  with such certainty, they must be nearly at the corners of a

regular tetrahedron, and the arrangement also holds in such groups as  $\text{ClO}_4^-$ ,  $\text{MnO}_4^-$ ,  $\text{SeO}_4^{--}$ . In an ion such as  $\text{PtCl}_6^{--}$  Wyckoff has shown that the six chlorine atoms are arranged at the corners of a regular octahedron around the platinum atom. The simple geometrical shape in each case is interesting, and it is difficult to avoid the conclusion that the outer atoms are all related in the same way to the inner one. Kossel regards the inner atom as having a large positive charge, and holding the negatively charged outer atom by electrostatic attraction. Although the actual bonds may be of a more complex type, it is interesting to see how much this idea explains. The dimensions of the group are in accord with the idea that the large oxygen ions are grouped around a relatively small atomic structure with a high positive charge in the centre, and that the size of the group is mainly determined by the repulsive forces between the oxygens. Certain optical properties can be explained by the same conception. The refractivity of the acid group is got by assigning a value of about 3.3 to the ionic refractivity of each oxygen, and a very small value to the central atom. The strong negative double refraction of carbonates and nitrates, where the groups of oxygen atoms lie in parallel planes, is explained quantitatively by the influence on each other of the oxygen atoms arranged in a triangle. On the other hand, most sulphates have a very small birefringence. This may be explained by the regular tetrahedral arrangement of oxygens around the sulphur, for such a group on account of its symmetry is optically isotropic.

The problem of the other type of binding between atoms, in which the electronic structures seem to fuse together so that the atoms approach each other closely and are rigidly connected, has yet to be solved. In acid groups such as  $\text{CO}_3^{--}$  and  $\text{SO}_4^{--}$  the atoms may retain separate electronic systems, or the other type of binding may have come into play. In any case the atoms must be greatly distorted by their unsymmetrical location. X-rays can only tell the positions of the atomic centres, the skeleton of the structure, since the interference between waves scattered by the electrons is so complex. The centres can be fixed with considerable certainty, however, and cases of undoubted homopolar combination can be examined. The interest of the inorganic structures lies principally in the fact that they can be analysed with some degree of completeness, and it is to be hoped that they will tell more about the binding forces. They present a fascinating series of problems for solution.

## Southampton Meeting of the British Association.

### LOCAL ARRANGEMENTS.—II.

VISITING members of the British Association are requested to book for Southampton West Station, where men wearing distinctive armllets will be in attendance on the station platforms to render assistance to members on arrival and to afford information. The idea of a special train from Waterloo on the Tuesday, the day before the opening of the meeting (as previously announced), has been dropped because the existing means of communication to Southampton, on further examination, were found to be amply sufficient. Baggage may be deposited at

the Reception Room if desired for conveyance to the address in Southampton where the member will be staying. Tickets of membership may be obtained at the Reception Room.

The Reception Room is at King Edward VI. Grammar School in the Marlands, two minutes' walk from the West Station. Here the following facilities will be provided for members: ticket and information bureau, where a representative of the Southern Railway will be in attendance; telephones; smoking and writing room; ladies' rest rooms; post office;