CXLIX.—*On Polymorphism, with Especial Reference to Sodium Nitrate and Calcium Carbonate.*

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IN previous communications (Trans., 1906, 89, 1675; 1907, 91, 1150) the authors have submitted a considerable body of evidence indicating that the total volume occupied by a crystalline substance must be regarded as portioned out amongst the atoms of the component elements, consistently with the established homogeneity of crystal structure and the crystal form, according to the following two definite principles. 1. That the polyhedral space appropriated by each atom approximates to the spherical shape so far as the enviroing conditions will allow; this may be conveniently designated the principle of close-packing of spheres of atomic influence. 2. That the volume of the space which, in the case of any given compound, is thus allotted to an atom is approximately proportional to the fundamental valency of the element of which it consists; this may be called the law of valency volumes.

The tendency towards sphericity on the part of the atomic domain has been interpreted as arising from the establishment of equilibrium in the crystal structure of opposing attractive and repulsive forces operative between the component atoms of the molecule. It has been illustrated by constructing close-packed assemblages of spheres of deformable but incompressible material representing the arrangement of the atoms in the crystalline structures concerned, and supposing the assemblages subjected to a general compression from all sides, so as to flatten the spheres into polyhedra and to eliminate the interstitial space; a similar result is obtained by describing tangent planes at the points of contact between the spheres of the assemblage and regarding the spheres as exchanged for the polyhedra enclosed by the planes thus indicated. If, therefore, equilibrium of a structure obtains, it will be indicated by close-packing of the spheres employed to form the assemblage representing the structure; the volumes of polyhedra derived from the spheres, and constituting the spheres of influence of the component atoms, will be approximately proportional to the fundamental valencies of the elements concerned. The propriety of allotting or partitioning up the whole space among the atoms, without leaving interstices, becomes evident directly it is admitted that the atoms exercise individual influence according to some distance law. For every geometrical point within the structure must then be regarded as exposed to the paramount influence of some particular atom or atoms, and if the portion of space throughout which the influence

of a particular atom is paramount is allotted to this atom, the partitioning thus achieved necessarily excludes the presence of interstitial space. This consideration shows that the conception of interstitial space amongst the spheres of atomic influence composing the crystal structure is unnecessary.

The results of the conclusions already put forward are obviously far-reaching and should be subjected to test in the light of phenomena other than those which have led inductively to their formulation. Tests of this kind have already been applied. Le Bas has demonstrated that in the normal paraffins the carbon atom appropriates a volume four times as great as that occupied by the hydrogen atom (*Trans.*, 1907, **91**, 112; *Phil. Mag.*, 1907, [vi], **14**, 324); Jaeger has shown that predictions as to crystalline form based upon the new theory are verified in practice (*Trans.*, 1908, **93**, 517. Compare also Jerusalem and Pope, *Proc. Roy. Soc.*, 1908, **80 A**, 557). Further light is thrown on the subject by, and substantial confirmation of the legitimacy of the methods employed results from, the study of the way in which the new conclusions apply to the crystalline forms of polymorphously related substances; the inquiry thus indicated is included within the scope of the present paper.

It has long been recognised that the polymorphously related forms of a substance are frequently related morphotropically (Pasteur, *Ann. Chim. Phys.*, 1848, [iii], **23**, 267), although the observed relationship is in general confined to a similarity between corresponding angles measured on the several modifications. Relationship of a far more intimate character should, however, exist, if the mode of treatment which we have adopted has any physical meaning. Thus, in accordance with the terminology which we have adopted, polymorphism may be defined as the existence of two or more close-packed assemblages, distinguished by difference of marshalling, all of which are partitionable into units or chemical molecules of practically identical configuration. The discussion of the relation existing between the cubic and the trigonal modifications of silver iodide (*Trans.*, 1907, **91**, 1174) furnishes an illustration of this definition; both these materials are partitionable into molecular units of the same configuration.

The study of the case of silver iodide reveals a peculiarity to which is immediately traced the close morphotropic relationship between its cubic and trigonal forms, namely, that both modifications are to be regarded as built up from identical double layers as figured (*Trans.*, 1907, **91**, 1174, Figs. 19 *a* and *b*). The occurrence of the two modifications of silver iodide is thus to be attributed to the possibility of close-packing the same layers of spheres in accordance with either cubic or trigonal symmetry; the two crystalline modifications originate

in the different packing together of identical unit layers (*loc. cit.*, 1177). It is readily perceived that in all cases where two polymorphously related substances result from two different modes of close-packing of identical layers or sets of layers, it will be possible to convert the axial ratios descriptive of the one modification into those of the other by aid of some simple transposition; this has been already indicated in connection with the two modifications of silver iodide and of zinc sulphide (*loc. cit.*, 1178).

As other known instances in which a close relationship of similar kind occurs between polymorphously related substances, the following may be quoted. The orthorhombic mineral gerhardite,

which exhibits $a:b:c=0.9217:1:1.1562$, is morphotropically almost identical with the synthetic substance, the latter being monosymmetric with $a:b:c=0.9190:1:1.1402$, $\beta=85^\circ 27'$ (Wells and Penfield, *Zeitsch. Kryst. Min.*, 1886, **11**, 303). A similar approximate identity in axial ratios occurs between the two compounds of the composition $\text{NaGHSi}_3\text{O}_8$; the monosymmetric mineral eudidymite has the axial ratios $a:b:c=1.7107:1:1.1071$, $\beta=86^\circ 14'$; whilst epididymite, having the same composition, is orthorhombic with the axial ratios $a:b:c=1.7274:1:1.0680$. The double propionate of calcium and barium, $2\text{Ca}(\text{C}_3\text{H}_5\text{O}_2)_2, \text{Ba}(\text{C}_3\text{H}_5\text{O}_2)_2$, crystallises in the cubic system and forms two series of isomorphous mixtures, of cubic and tetragonal symmetry respectively, with the double propionate of calcium and lead, $2\text{Ca}(\text{C}_3\text{H}_5\text{O}_2)_2, \text{Pb}(\text{C}_3\text{H}_5\text{O}_2)_2$, which crystallises in the tetragonal system with $a:c=1:0.9787$ (Fitz and Sansoni, *Zeitsch. Kryst. Min.*, 1882, **6**, 68). It is obvious that the latter substance is pseudo-cubic, and that its equivalence parameters approximate very closely to those of the truly cubic calcium barium salt. Carbon tetrabromide, CBr_4 , is dimorphous, crystallising above 47° in the cubic system, and below that temperature in the monosymmetric system with $a:b:c=1.7414:1:1.9617$, $\beta=125^\circ 3'$ (Zirngiebl in *Groth, Chem. Kryst.*, 1906, **1**, 231); as Groth has noted, the latter modification is pseudo-cubic, and if the observed forms $\{001\}$, $\{10\bar{1}\}$, and $\{110\}$ are assigned the indices $\{11\bar{1}\}$, $\{1\bar{1}1\}$, and $\{111\}$, and are referred to a set of anorthic axes, the axial ratios $a:b:c=1.0260:1:1$, $\alpha=89^\circ 44'$, β and $\gamma=90^\circ 33'$, are obtained. The monosymmetric form is thus almost identical dimensionally with the cubic modification.

The hexagonal and orthorhombic modifications of silica are dimensionally related. Quartz, with $a:c=1:1.0999$, may be referred to a set of orthorhombic axes, in which $b/a=\tan 60^\circ$, and the form $\{100\}$ is changed to $\{011\}$; the axial ratios then become $a:b:c=\cot 60^\circ:1:1.0999/\cos 30^\circ=0.5774:1:1.2701$. In the orthorhombic mineral tridymite, with $a:b:c=0.5774:1:0.9544$, the occurrence of

the forms {043} and {443} allows the latter indices to be changed to {111}; the axial ratios then become $a:b:c = 0.5774:1:1.2716$. These values are almost identical with those calculated from the hexagonal modification of the substance. It has been pointed out by Beckenkamp (*Zeitsch. Kryst. Min.*, 1901, **34**, 569) that quartz and tridymite can be referred to the orthorhombic parameters, $a:b:c = 0.5774:1:0.9545$, and $0.5774:1:0.9544$, respectively.

The following instances, although of equal weight, are not so obvious as the foregoing, and, apparently for this reason, have not been previously remarked.

The accurate goniometric data furnished by Miers for the red silver ores (*Min. Mag.*, 1888, **8**, 37; 1893, **10**, 215) afford examples of polymorphous relationships very similar to, but even more striking than those existing between quartz and tridymite. The minerals of the composition, Ag_3SbS_3 , are the hemimorphously rhombohedral pyrrargyrite, with $a:c = 1:0.7892$, and the monosymmetric fire blende, with $a:b:c = 1.9465:1:1.0973$, $\beta = 90^\circ$; the data for pyrrargyrite may be referred to a set of rectangular axes by transposing so that the forms {101} and {001} become respectively {011} and {010}. The axial ratios for the two minerals then become:

Pyrrargyrite..... $a:b:c = 1.9007:1:1.0974$, $\beta = 90^\circ$

Fire blende..... $a:b:c = 1.9465:1:1.0973$, $\beta = 90^\circ$.

On performing the same simple transposition with the axial ratio of the hemimorphously rhombohedral proustite, Ag_3AsS_3 , with $a:c = 1:0.8039$, values are obtained which approximate to the axial ratios of the monosymmetric xanthoconite of the same composition, namely:—

Proustite..... $a:b:c = 1.8671:1:1.0774$, $\beta = 90^\circ$.

Xanthoconite..... $a:b:c = 1.9187:1:1.0152$, $\beta = 88^\circ 47'$.

The examples quoted above refer to cases in which two modifications of the same composition are sufficiently stable at the ordinary temperature to allow of goniometric measurement; it is, however, clear that dimensional correspondences such as those pointed out above should be also observed amongst cases of isopolymorphism. One illustration may be quoted in this connexion. Rubidium nitrate is pseudo-hexagonally orthorhombic with $a:b:c = 1.7366:1:0.7108$ (Jaeger, *Zeitsch. Kryst. Min.*, 1907, **43**, 588) and, owing to the equivalence of rubidium and sodium, should be isopolymorphously related to the rhombohedral sodium nitrate, which exhibits, $a:c = 1:0.8276$. On referring the latter rhombohedral axial ratio to orthorhombic axes by transposing, so that

$$a:b:c = \tan 60^\circ:1:0.8276 \cos 30^\circ = 1.7320:1:0.7151,$$

values almost identical with those for rubidium nitrate are obtained. Thus:

Rubidium nitrate.....	$a:b:c = 1.7366:1.07106.$
Sodium nitrate.....	$a:b:c = 1.7320:1.07151.$

The numerous cases quoted above, in which the goniometric constants for two polymorphously related substances can be immediately referred to practically the same set of axial ratios, suggest the existence of a relation between the respective assemblages similar in character to that worked out for silver iodide. Stated in general terms, the conclusion must be drawn that where such dimensional coincidences obtain as between two polymorphously related assemblages, the latter are composed of practically identical layers or blocks of the aggregated spheres of atomic influence. It is, however, desirable to make the conclusion more obvious by constructing the assemblages representing some pair of polymorphously related substances, and for this purpose it is convenient to select the isopolymorphously related substances, sodium nitrate and potassium nitrate. The first of these is rhombohedral with $a:c = 1:0.8276$, and the latter orthorhombic with $a:b:c = 0.5910:1:0.7010$. The examination of these cases is the more important in that they are related by the second geometrical property to the two polymorphously related modifications of calcium carbonate (Trans., 1906, 89, 1732); the rhombohedral calcite shows $a:c = 1:0.8543$, and the orthorhombic aragonite exhibits $a:b:c = 0.6224:1:0.7206$. The whole method of treatment is subjected to a somewhat crucial test in being applied to these intimately related cases, and the more especially in that many data are available concerning the crystal structures of these well known substances.

In order to pave the way for this somewhat complicated investigation, it is convenient first to treat a case in which the assemblage is more easily derivable and which is closely related to that of sodium nitrate; for this reason the crystal structure of the tetartohedrally cubic barium nitrate is next discussed.

Barium Nitrate, Ba(NO₃)₂.

A close-packed assemblage having the valency composition of the tetartohedrally cubic barium nitrate is related to a closest-packed assemblage consisting entirely of bivalent spheres of influence, of which three-fourths are oxygen, through the second geometrical property previously defined (Trans., 1907, 91, 1151 and 1204). If the remaining one-fourth of the spheres are removed from the assemblage and for each bivalent sphere abstracted, a sphere of volume three, representing a tervalent nitrogen atom, is substituted, additional

spheres have, according to the property referred to, to be inserted in the proportion of a valency volume unit for every substituted sphere, in order to produce close-packing without remarshalling in the altered assemblage. This requirement is met by adding a univalent sphere for every group $-\text{NO}_3$ or a bivalent sphere for every pair of such groups. A composition of the kind under consideration, namely, $\text{Ba}(\text{NO}_3)_2$, is thus attained.

When the cubic closest-packed arrangement of equal spheres is subjected to the above substitution, it appears that the most symmetrical method of selecting one-fourth of the spheres for replacement is one already described by the authors (Trans., 1907, 91, 1197, Fig. 30). The centres of the spheres thus selected for removal form

FIG. 1.

a cubic space-lattice, and the process of substitution can be carried out in harmony with cubic symmetry in the following manner.

The oxygen spheres remaining after the removal of one-fourth of the original number may be regarded as forming distinct octahedral groups of six so arranged that the centres of the groups are symmetrically situated at the centres of half the cubic cells outlined by joining the points of the cubic lattice formed by the centres of the removed spheres; since the centres of the spheres remaining are at the centres of the cube faces, either of the two sets of cubes in edge contact (Fig. 1), which together make up the entire number, can be selected as containing the centres of the octahedral groups (Trans., 1907, 91, 1170, Fig. 16). Let now the scale of the system of cube cells be increased uniformly while keeping the centres of the octa-

hedral groups of spheres at the centres of the selected half set of cubes ; since each original block or unit of eight bivalent spheres, consisting of an octahedral group of six and the two which have been removed, is ultimately to be replaced by a unit representing the molecular composition $\text{Ba}(\text{NO}_3)_2$, the requisite increase of scale is given by the volume ratio of these two units, namely, $16 : 20 = 4 : 5$. The arrangement of the octahedral groups in a single layer of cells thus expanded is shown drawn to scale by the medium-sized circles of Fig. 2. This diagram shows the projection of the contents of one set of alternate layers of cells ; the projection of the other set on the same area would

FIG. 2.

be represented by a similar figure in which the two kinds of filling of the squares have changed places. The relation between the two projections is indicated by the non-continuous circles of Fig. 4, *a* and *b*.

In the system of cubic cells of Fig. 2, when containing only the octahedral groups of six bivalent spheres, two kinds of principal cavities are present, one at the centres of the set of cubes in edge contact not containing the group centres, the other, just twice as numerous, at all the cube angles. The latter cavities are of such a shape and size as accommodate spheres larger than those representing the trivalent nitrogen, and the cavities at the cube centres can similarly accommodate spheres smaller than those of a bivalent atom ;

the positions and sizes of spheres such as fill the cavities are shown in projection in Fig. 2.

The assemblage thus completed, of which one layer is depicted in Fig. 2, has the composition indicated by $\text{Ba}(\text{NO}_3)_2$, if the small, the medium, and the large spheres respectively represent the spheres of atomic influence of barium, oxygen, and nitrogen; if constructed from incompressible, deformable spheres, and subjected to a general pressure, the equilibrium condition reached would show but little modification of the arrangement prevailing before the application of pressure, and would, just as before, display holohedral cubic symmetry. As, however, the small spheres used are much smaller than those of the bivalent size which should represent barium, and the large spheres are larger than those of the trivalent nitrogen size, it has to be ascertained what modification of the type of arrangement will occur when the spheres used are replaced by others representing barium, oxygen, and nitrogen, in accordance with the valency rule; the respective volumes of these spheres must be then approximately in the ratio 2 : 2 : 3.

As the nitrogen spheres of volume three are too small to fill the cavities provided for them, it is evident that some relative movement of the octahedral groups of six oxygen spheres can occur without obstructing the introduction of nitrogen spheres of the proper magnitude; thus a certain slight symmetrical movement of the octahedral groups can take place which uniformly reduces the size of the nitrogen cavities so that each just suffices to contain a sphere of the correct volume three, and this movement is found to increase uniformly the magnitude of the cavities allotted to the barium spheres so that each will now accommodate a sphere of approximately the correct volume two. The symmetrical change thus involved is described below; whilst it results in the retention of cubic symmetry by the assemblage, it involves a degradation of the class of symmetry obtained to that of the tetartohedral cubic system to which barium nitrate belongs.

In the skeleton assemblage of octahedral groups of six oxygen spheres represented by the medium-sized circles of Fig. 2, one-fourth of the trigonal axes are selected as a set of non-intersecting trigonal axes having the relative positions already described (Trans., 1907, 91, 1183), the directions of these axes in their cells being indicated by the letters a, b, c, and d, on Fig. 3, according to the convention previously adopted. All the remaining trigonal axes are destroyed by a similar slight movement of each octahedral group, O_6 , along its selected trigonal axis; the displacement of any single group determines those of all the others, since they are derived from the first by the coincidence movements characterising the system of symmetry. The movements

of the original octahedral groups whose projections are given by the non-continuous circles of Fig. 4, *a* and *b*, are, both in direction and approximately in extent, expressed by the shift required to bring the continuous circles of the figure to coincidence with the non-continuous circles; the diagram represents the movement as a mere translation of each group along its trigonal axis in the appropriate selected direction without change of orientation, but a slight similar rotation of the octahedral groups about their trigonal axes accompanying the translation conduces towards the closeness of the final packing of the assemblage. This rotation component is not represented in the diagram in order to avoid complication; its introduction leads to no change of the type of symmetry.

The corners of the cells of the partitioning, having the same relative arrangement as that of the cell centres, are, like them, made up of two sets whose position relations are indicated by the two kinds of cubes previously distinguished in Fig. 1. Before the screw movements referred to occur, the cavities at the cell corners of both the

FIG. 3.

component sets are identical, and have identically the same relation to the assemblage of groups, but after the movements the two sets of cavities are distinguishable, for whilst those of each set are similarly changed, the change experienced by the cavities of one set differs from that experienced by those of the other set. The octahedral groups, O_6 , and the barium spheres are found to have approached the nitrogen spheres of one set along the common trigonal axis, and thus to have receded from the original places of the other set along this axis; these latter nitrogen spheres have, however, approached the barium spheres, and the total number of contacts is nearly the same for both sets of nitrogen spheres. The cavities at the cell corners for the accommodation of the barium spheres, which have been increased in size by the movement of the octahedral groups of oxygen spheres, remain identical with one another; all the spheres of the assemblage have experienced some shift from their original positions indicated in Fig. 2.

It is established by the foregoing that the assemblage of spheres of the magnitudes indicated by the valency relations of the elements

composing barium nitrate, $\text{Ba}(\text{NO}_3)_2$, is not in equilibrium in the holohedral cubic arrangement of the type shown in Fig. 2, and that, if

FIG. 4.

a. *b.*

forced into an arrangement of this highly symmetrical type, it will, in seeking equilibrium, pass into some less symmetrical arrangement.

It is shown that passage to an equilibrium arrangement of the tetartohedral cubic type, numbered 1 in Barlow's list (*Zeitsch. Kryst. Min.*, 1894, **23**, 1), can occur in the manner described above; the movements of the octahedral groups of oxygen spheres which lead to this equilibrium arrangement destroy all the elements of symmetry excepting those about a set of non-intersecting trigonal axes, and such other elements of symmetry as are involved in the existence of those axes.

When the equilibrium is pictured by an appropriately constituted assemblage of deformable spheres it is clear that, as in all other cases, the greatest flattening must occur of those spheres the actual contacts of which are relatively fewest, since the pressure on these spheres will be concentrated at a relatively small number of points on their surfaces. In harmony with this, the barium spheres, which have but six actual contacts each, must be more flattened than the others; the effect of this, like that of the movements, is to make a larger size of sphere available for the purpose without endangering the equilibrium.

The twinning of barium nitrate crystals, which occurs on {111}, does not appear to call for special remark, as it is traceable to the same kind of symmetrical disposition about a layer perpendicular to a trigonal axis as produces twinning in the case of the root assemblage to which the structure has just been referred (compare *Trans.*, 1907, **91**, 1187). Consequently, if the root assemblage is twinned before the change is made in accordance with the second geometrical property, an equilibrium arrangement of the barium nitrate spheres of influence, which is derived from this twinned assemblage of equal spheres, will be that appropriate to the twinned form of the crystalline substance.

The above discussion of the crystal structure of barium nitrate naturally also holds for the other tetartohedrally cubic nitrates of the bivalent metals, namely, strontium and lead nitrates. The case has been selected as an illustration of the second geometrical property because the crystal structure concerned belongs to the same system of symmetry as the parent closest-packed assemblage from which it is derived, namely, the cubic system, and the process is therefore comparatively easy to trace. The application of the same property to other cases in which this latter relation does not exist is referable to a modifying cause which is described in connexion with the examples which follow.

Sodium Nitrate, NaNO₃.

The modification of sodium nitrate stable at the ordinary temperature belongs to the holohedrally rhombohedral system and exhibits

$\alpha = 102^\circ 47'$ or $\alpha : c = 1 : 0.8276$ (Brooke, *Ann. Phil.*, 1823, **21**, 452). A close-packed assemblage of the valency composition of this salt is connected with a closest-packed assemblage of bivalent spheres of influence by the second geometrical property, in just the same way as is the assemblage representing barium nitrate. In both cases each of one-fourth of the total number of bivalent spheres is replaced by a sphere of trivalent size; the sodium nitrate assemblage is derived by adding, in accordance with the second geometrical property, one sphere of univalent size, representing sodium, for each trivalent nitrogen sphere so added, whilst the barium nitrate assemblage has been derived by similarly adding one bivalent sphere, representing barium, for each two nitrogen spheres. Double as many cavities have thus to be provided for the accommodation of the sodium spheres as had to be found for the barium spheres, but as the former are approximately of one-half the size of the latter, the total volume of the spheres representing the metallic element is the same in both cases.

When the cubic cells of the root assemblage are enlarged to the same extent as in the previous case, namely, in the volume proportion of 4 : 5, the required number of large cavities is provided by moving the oxygen spheres until their centres occupy the points of bisection of the enlarged cell edges; the process of expansion, which may be supposed to draw the oxygen spheres equally away from all the cell corners, will similarly enlarge all the cavities at the centres of the octahedral groups of six oxygen spheres surrounding those corners. The magnitudes of the spheres which just fit into the cavities occurring in a skeleton assemblage of oxygen spheres thus expanded are shown in Fig. 5. The larger spheres are, as in the previous case, larger than the trivalent spheres to be accommodated, although the disparity is now less; the small spheres centred at the cube corners are, on the other hand, much smaller than the univalent spheres which have ultimately to replace them. The assemblage of Fig. 5, like the parent assemblage, is of the holohedral cubic type of symmetry, and it has to be ascertained what modification of it results when nitrogen spheres, of trivalent magnitude, and sodium spheres, of univalent magnitude, are used in place of those depicted. Inspection of Fig. 5 shows that the length of the edge of a cube cell is the sum of the diameters of a small sphere, centred at the cube corner, and an oxygen sphere situated at the middle of a cube edge. On substituting the small and the large spheres by sodium and nitrogen spheres of the magnitudes indicated by the valencies, whilst retaining the kind of arrangement, the cell edges must necessarily be increased in length, since the univalent sodium spheres are larger than the small spheres of the assemblage of Fig. 5; the volume of the cell has, however, to

remain unaltered because it represents the molecular valency volume, 10, of sodium nitrate. The retention of the method of grouping, and the preservation of the same volume, will thus involve a distortion of the cube cells to rhombohedra, since this is the kind of distortion which, whilst keeping the edges of the cells equal, gives them greater length in proportion to the cell volume. It is therefore established that for the prescribed cell volume, if the grouping above described is adopted, rhombohedral space-lattices will take the place of the cubic ones found in the assemblage of Fig. 5. The amount of distortion, upon which the angle of the rhombohedron depends, will evidently be that which gives maximum closeness of packing under the given

FIG. 5.

conditions; it remains to ascertain, first, whether the arrangement thus reached is a stable one, and, if not, what modification should take place in order that it may become stable, and, secondly, the nature of the symmetry displayed when stable equilibrium is reached.

In the passage of the assemblage of Fig. 5 to rhombohedral symmetry, one of the four trigonal axes becomes the principal axis of the modified system, and it is convenient to depict the latter by its projection upon the plane perpendicular to this principal axis. An assemblage of rhombohedral form, in which the trivalent nitrogen spheres are centred at the cell centres, the bivalent oxygen spheres have their centres at the points of bisection of the cell edges, and the univalent sodium spheres are centred at the cell corners, is thus repre-

FIG. 9.

sented in Fig. 6.; the projections of three successive layers on the same area of a plane perpendicular to the trigonal axis are depicted, and are marked a, b, and c, respectively. The fourth layer has the same projection as the first, the fifth as the second, and so on. The spheres representing sodium, which lie immediately above and below each plane of centres of the nitrogen and oxygen spheres, are in each case indicated by continuous and non-continuous circles respectively; each sodium sphere is thus depicted twice over, so that those represented by continuous circles in Fig. 6a are also represented by discontinuous circles in Fig. 6b. The assemblage is of Barlow's type 52a₁. Trigonal axes pass through all centres of nitrogen and sodium spheres; digonal axes lie in the directions indicated by the straight lines in the figures, through all the nitrogen spheres, and also, parallel to these lines, through the centres of the sodium spheres. Centres of symmetry occur at all the sphere centres and midway between the centres of pairs of sodium spheres in planes parallel to those of the diagrams. The packing of the assemblage described is not so close as that of the closest-packed assemblage of equal spheres; the scale selected for the diagrams is obtained by making the content of the unit rhombohedral cell equal to the valency volume 10 of the salt, and the angles of this cell those of the cleavage rhombohedron of the crystalline mineral. Thus, if A is the longer face diagonal of this rhombohedral cell and C its axial body diagonal, since the content of the rhombohedron is $A^2C/2\sqrt{3} = 10$ and $A : C = a : c$, the values, $A = 3.472$ and $C = 2.873$, are obtained. These values are used as the scale to which the diagrams are constructed, and they involve a rather considerable flattening of the spheres at some of their contacts. If the volumes of the spheres representing sodium, oxygen, and nitrogen are respectively in the ratio of 1 : 2 : 3, and the rhombohedron angle adopted is that observed upon the crystals of sodium nitrate, the arrangement is seen to be practically stable as depicted by a stack of deformable spheres under pressure.

The marshalling shown above to be common to the cubic and the rhombohedral form of assemblage is the simplest possible of spheres of the three sizes indicated by the valencies, and present in the proportion represented by the composition, NaNO_3 , of the salt; the assemblage described is fairly close-packed. A slight adjustment is, however, possible, which increases the closeness of the packing without changing the marshalling; its occurrence involves the loss of some of the elements of symmetry, but retains the original crystal symmetry, namely, holohedrism of the rhombohedral system. The adjustment in question consists in moving each oxygen sphere along the line joining the two nitrogen spheres between which it lies until it touches one of them; all these movements are made symmetrically, and the result is depicted in Fig. 7. In this diagram six different projections of six

consecutive layers of nitrogen and oxygen spheres on the same area are shown by the sections a, b, c, d, e, and f, respectively; the sodium spheres which lie between the layers are, as before, indicated twice over, and the projections a, c, and e present the opposite orientations to those of b, d, and f. In order to obtain a relative molecular volume comparable with that of the closest-packed assemblage of equal spheres, less flattening of the spheres at their points of contact is now requisite; the conversion of the component spheres into polyhedra by a general compression consequently involves less departure from sphericity than before the adjustment.

It is suggested that the assemblage thus finally arrived at is in stable equilibrium when the rhombohedron angle closely approximates to that of sodium nitrate. The scale employed in the diagrams represents the rhombohedral unit cells as of the valency volume, $W = 10$, of sodium nitrate, and the unit of volume has therefore the same content as a dodecahedral cell of a closest-packed assemblage of spheres of univalent magnitude; the rhombohedron angle is represented as having the observed value of $\alpha = 102^\circ 47'$.

The elements of symmetry remaining after the final adjustment are (a) all the original trigonal or principal axes, (b) those of the digonal axes which intersect both nitrogen and oxygen spheres, and (c) the centres of symmetry situated at the centres of the sodium spheres, and those which lie in the planes of the latter but midway between them; the other elements of symmetry previously enumerated are destroyed by the adjustment. The type of symmetry presented is that numbered $52a_2$ in Barlow's list (*Zeitsch. Kryst. Min.*, 1894, 23, 47).

Reference has been already made to the fact that the rhombohedral sodium nitrate and the orthorhombic rubidium nitrate are, dimensionally, so closely related that the axial ratios of the former can be transposed into a form almost identical with those of the latter, namely:

Rubidium nitrate	$a : b : c = 1.7366 : 1 : 0.7106$.
Sodium nitrate	$a : b : c = 1.7320 : 1 : 0.7151$.

From this close correspondence it is concluded that the rhombohedral sodium nitrate is divisible into similar layers of a form which can be employed in building up the orthorhombic structure of rubidium nitrate.

The Rhombohedral Form of Calcium Carbonate.

Calcite, the holohedral rhombohedral modification of calcium carbonate, CaCO_3 , is crystallographically so nearly identical with sodium nitrate that the resemblance is greater than that commonly displayed by the crystals of isomorphous substances. This resemblance, as already indicated (*Trans.*, 1906, 89, 1731), is associated with a relationship in composition between the two substances which affords

FIG. 7.

a simple illustration of the second geometrical property of close-packed assemblages. In the derivation of the cubic assemblage of Fig. 5, in connexion with sodium nitrate, from the cubic closest-packed assemblage of spheres each of volume two, the unit cubic cells of the latter were expanded in the volume ratio $8:10=4:5$, because the group of four bivalent spheres of total volume 8 in the latter assemblage were to be replaced by the group, NaNO_3 , of valency volume, $W=10$. On expanding the original cubic cells to an extent determined by the greater valency volume, $W=12$, of calcium carbonate, namely, in the ratio $8:12=2:3$, and, as before, introducing spheres of the largest

FIG. 8.

possible size into the two kinds of principal cavities thus made, the arrangement of Fig. 8 is obtained; in this the large spheres are rather larger than those representing quadrivalent carbon and the small spheres are smaller than those representing the bivalent calcium sphere. On replacing the large and small spheres by quadrivalent carbon and bivalent calcium spheres, keeping the cell volume constant, the assemblage passes to the rhombohedral one of Fig. 9, just as is described above in connexion with sodium nitrate. A final slight adjustment such as led to closer packing by movement of the oxygen spheres in the sodium nitrate assemblage also leads to closer packing in the case of the calcite assemblage; the rhombohedral assemblage representative of calcium carbonate is depicted in the six sections of Fig. 10.

The marshalling of the assemblages of rhombohedral symmetry which have been derived for sodium nitrate and calcite is still that of the original assemblage of bivalent spheres from which they were derived. In the latter assemblage each fourth sphere of volume two was replaced by a nitrogen sphere of volume three, an operation which, when not accompanied by remarshalling, left cavities capable of accommodating an equal number of sodium spheres of volume one; the sodium nitrate assemblage was thus derived. When each fourth bivalent sphere in the original assemblage was replaced by a carbon sphere of volume four, without remarshalling, cavities were produced which accommodated an equal number of calcium spheres of volume two. The relations here described afford a simple illustration of the second geometrical property of close-packed assemblages; the case differs somewhat from that exemplified by the cubic barium nitrate in that, in the present one, a marshalling of highest symmetry, the cubic, is compelled to assume the lower crystal symmetry of the rhombohedral system. The reason of this is that in certain linear directions the assemblage is unyielding and resists compression, namely, along the edges of the cubic space units as above explained; it is traceable to the fact that all the centres of the constituent spheres occupy singular points of a highly symmetrical character and are thus similarly related to many surrounding spheres. The only final adjustment which, whilst it allows a slight contraction to occur in the linear directions referred to, does not diminish the closeness of the packing to a greater extent in other directions, appears to be the one above described involving the movement of the oxygen spheres; it is noteworthy that this does not further lower the crystal symmetry.

Twinning of Sodium Nitrate and Calcite.

Crystals of sodium nitrate and calcite can be artificially sheared without destroying their identity in such a manner as to reproduce the original crystal form; this property will now be shown to characterise the assemblages attributed above to these substances.

The six sections of Figs. 7 and 10 represent projections of the assemblages on the basal plane (111); in any one of these sections, for instance, 7b, the six sodium spheres, three above and three below, surrounding immediately any nitrogen sphere, together with the two sodium spheres shown above and below that nitrogen sphere in the two adjacent sections, 7a and 7c, mark the eight apices of a cleavage rhombohedron of the crystal. The planes containing two opposite edges of a cleavage rhombohedron, which do not contain the principal axis, constitute the form $\{110\}$, and are the gliding planes on which sodium nitrate and calcite crystals can be sheared and artificially

twinning with such facility. The projection of a section of the sodium nitrate assemblage of Fig. 7 upon the plane (110) is shown in the lower part of Fig. 11; thus regarded, the assemblage is made up of similar layers each containing nitrogen, sodium, and oxygen spheres in equal numbers, with centres all lying in the same plane, and between which are intercalated layers consisting of the remaining two-thirds of the oxygen spheres. The continuous circles of this part of Fig. 11 represent a layer of the first kind, consisting of nitrogen, sodium, and oxygen spheres, and the next layer of identical composition is represented by the similar arrangement of non-continuous circles; the oxygen spheres intercalated between the pair of such layers are indicated by double non-continuous circles. An elevation of the system of which the stratum thus represented forms a part, and showing a double layer, the plane of which is perpendicular to that of the lower part, is depicted in the upper part of Fig. 11. Where the double circles are of two kinds, continuous and non-continuous, they do not represent a single sphere, but a larger and a smaller sphere one behind the other.

In the building up of the sodium nitrate assemblage in the manner indicated by the compositions and relative arrangement of the three layers depicted in Fig. 11, a choice of orientation is offered after each layer composed of nitrogen, sodium, and oxygen spheres has been deposited. Thus, starting with the layer represented by non-continuous circles in Figs. 11 and 12, the succeeding layers may be deposited as indicated by the double non-continuous and continuous circles either of Fig. 11 or of 12; the orientation of the one mode of growth is opposite to that of the other and is further illustrated by the projections shown in the upper parts of Figs. 11 and 12. The latter diagrams, in which most of the component spheres lie in contact in straight lines, indicate clearly how, by a simple rolling movement of the spheres upon each other, the orientation of Fig. 11 can be converted into that of Fig. 12.

The mechanism of the artificial twinning of sodium nitrate is thus clearly indicated, and the only further requisite is that the shear of the portion on one side of a gliding plane, (110), shall take place without dislocating the connexion with the unaltered portion on the other side of this plane. If the assemblage under treatment were the unmodified more symmetrical one of Fig. 6 the symmetry of arrangement would ensure this; as it is, some mutual adjustment of the intermediate oxygen spheres has to occur in the modified assemblage at the twin plane. The nature of this adjustment is indicated in the discussion of the crystal structure of potassium nitrate given below.

In connection with the derivation of the rhombohedral sodium
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nitrate assemblage it has been shown that the marshalling of the final arrangement is still that appropriate to an assemblage of spheres in cubic symmetry. The passage from cubic to rhombohedral symmetry necessitates the distinction of one of the four trigonal cubic axes as

FIG. 11.

the principal or trigonal axis in the rhombohedral assemblage; after one of the four trigonal cubic axes has been thus distinguished from the other three as a direction of symmetry it is still possible, by the operation of some influence such as is involved in a shear of the above-described kind, to convert either of the three previously dis-

carded trigonal cubic axes into the principal axis of the rhombohedral assemblage. The change thus effected does not when completed alter the configuration of the assemblage, but brings about a change of orientation which corresponds exactly with that produced by the

FIG. 12.

artificial twinning of sodium nitrate. It is obvious, without the exhibition of further diagrams, that the mechanism which illustrates the artificial twinning of sodium nitrate elucidates in precisely the same way the artificial twinning of calcite.

Potassium Nitrate, KNO₃.

Potassium nitrate crystallises in the orthorhombic system with $a:b:c=0.5910:1:0.7010$, and crystallographically closely resembles aragonite, the orthorhombic modification of calcium carbonate, just in the same way as the rhombohedral substances sodium nitrate and calcite resemble each other; the two orthorhombic crystal forms, like the two rhombohedral ones, are connected through the second geometrical property (Trans., 1906, **89**, 1732).

The marshalling of the orthorhombic assemblage suggested for potassium nitrate is derived by an intimate molecular twinning of the rhombohedral assemblage above assigned to sodium nitrate, the change of orientation from stratum to stratum occurring at every corresponding layer of the three kinds of spheres which lies parallel to one plane of the form $\{110\}$. It has been shown in connexion with artificial twinning that the stratum of the sodium nitrate assemblage, which is parallel to the plane (110), and is depicted in the lower part of Fig. 11, is capable of alteration by shear; the shear produces identically the same arrangement of the constituent spheres, but changes the orientation, and it was suggested that a portion of the rhombohedral assemblage can be sheared without dislocating its connexion with the unsheared portion, if a slight adjustment of the spheres occurs at the gliding plane which becomes the twin plane. When every one of the layers composed of three kinds of spheres, as shown in the lower part of Fig. 11, becomes a twin plane, the marshalling of the assemblage represented in Figs. 11 and 12 becomes transformed into that represented in Fig. 13. The close resemblance of the constituent layers of Fig. 13a to those of the rhombohedral assemblage as shown in Fig. 11 is very apparent, and the requisite adjustment of the two-thirds of the oxygen spheres, which makes the twin planes planes of symmetry, is seen to be slight. Fig. 13b depicts the projection on a plane perpendicular to that of Fig. 13a, and a comparison with Figs. 11 and 12 suffices to indicate how the intimate twinning occurs.

The assemblage of Fig. 13 is of orthorhombic symmetry, and satisfies the conditions embodied in the axial ratios and other geometrical data of the orthorhombic potassium nitrate; it is indeed drawn to the scale of the equivalence parameters of the substance, calculating the latter values from the axial ratios in the form $a:b/2:c$, and taking the valency volume $W=10$. The equivalence parameters of potassium nitrate are thus calculated as $x:y:z=2.152:1.821:2.553$, and these values are marked on Fig. 13. The process of twinning by which the assemblage has been derived is, of course, to be regarded as a mere

geometrical device; its only physical meaning is that it shows that the isopolymorphously related substances, the rhombohedral sodium and the orthorhombic potassium nitrate, can be built up as the results

FIG. 13b.

FIG. 13a.

of alternative modes of superposing layers of similar configuration. The potassium nitrate assemblage described possesses the symmetry of Barlow's type $54a_2$; it contains digonal screw axes in the three

directions mutually at right angles, namely, (1) perpendicular to the plane of Fig. 13a, through points such as A_1, A_2, A_3, A_4 , (2) parallel to the plane of Fig. 13a through the centres of the smallest, and also through those of the largest, spheres, and (3) parallel to the direction of y , midway between the planes of set (1) and also midway between those of set (2). Centres of symmetry lie on the axes (1) in planes containing the axes (3).

A rhombohedral modification of potassium nitrate can exist (Frankenheim, *Pogg. Ann.*, 1837, **40**, 447), but is so unstable at the ordinary temperature that no goniometric measurements have been made; the crystallographic dimensions of the orthorhombic and rhombohedral modifications of the salt cannot therefore be directly compared. Such a comparison can, however, be instituted between the dimensions of the rhombohedral sodium nitrate and the isopolymorphously related and orthorhombic potassium nitrate. According to the relation suggested above as holding between the assemblages of these two substances, the length of the rhombohedron edge, the longer semi-diagonal of a rhombohedral face, and the distance between two opposite rhombohedron edges which intersect the obtuse angles constitute three rectangular dimensions which should be approximately reproduced as the equivalence parameters, $x:y:z$, of the corresponding orthorhombic assemblage; the ratio of these is identical with the axial ratios $a:b/2:c$ of the orthorhombic substance. A closer comparison of the same kind can be made between the axial ratios of the two polymorphously related forms of calcium carbonate, because the assemblages representing these substances must be related in just the same way as the rhombohedral sodium nitrate and the orthorhombic potassium nitrate assemblages figured above. The rhombohedral calcite, with $\alpha = 101^\circ 55'$, and the orthorhombic aragonite, with $a:b:c = 0.6224:1:0.7206$, are depicted by sets of diagrams corresponding exactly feature by feature with those given above for sodium and potassium nitrates. In the unit rhombohedron cell of calcite, the length of the rhombohedron edge, the longer semi-diagonal of a rhombohedral face, and the distance between two opposite rhombohedron edges which intersect the obtuse angles should therefore be approximately in the ratio of the axial ratios $a:b/2:c$, determined on aragonite.

The rhombohedron angle of calcite is $74^\circ 55'$, and from this the plane angle, $A_1A_2A_3$, of the face of a calcite rhombohedron, $AAAAA_1A_2A_3$ (Fig. 14), is calculated as $78^\circ 5'$. The longer diagonal of the rhombohedron face is A_2A_4 , and, in the plane $A_2BA_4B_1$, which contains this diagonal and is perpendicular to the rhombohedron edge AA_1 , the length BB_1 is the distance between two opposite rhombohedron edges which intersect the obtuse solid angles of the rhombo-

hedron; the plane angle BA_2B_1 is the rhombohedron angle $74^\circ 55'$. Taking $OA_2=1$, $OB=\tan \{(74^\circ 55')/2\}=0.7662$, and $A_1A_2=AA_1=1/\cos \{(78^\circ 5')/2\}=1.2875$; one-half the latter value is 0.6437 . The axial ratios,

$$a:b:c = 0.6437:1:0.7662,$$

are thus obtained by calculation from the axial angle of calcite for comparison with the axial ratios of aragonite, namely,

$$a:b:c = 0.6224:1:0.7206.$$

It is obvious that the two sets of axial ratios are of the same order of magnitude.

The rhombohedral sodium nitrate is characterised by a rhombohedron angle of $73^\circ 30'$, from which the plane angle is calculated as $77^\circ 14'$. A

FIG. 14.

calculation similar to that made in the case of calcite leads to the axial ratios,

$$a:b:c = 0.6399:1:0.7467,$$

for comparison with the axial ratios of the orthorhombic potassium nitrate, namely,

$$a:b:c = 0.5910:1:0.7010.$$

As is to be expected from the difference in the metal present in the rhombohedral and orthorhombic salts, the last two sets of ratios are not in such fair agreement as those calculated from the rhombohedral and orthorhombic modifications of calcium carbonate. The reason why a greater discrepancy is observed among the equivalence parameters of the rhombohedral and orthorhombic carbonates than obtains in many other cases quoted may well be that when fitted together in different ways, the component layers in the structures have to experience a slight internal adjustment; the nature of this adjustment is shown, in the case of the nitrates and carbonates now under consideration, by comparing Figs. 11 and 13. A closer agreement is

presented in the case of the polymorphously related forms of silver iodide; the component layers are of a less complicated character in this case, and can be fitted together in the two different ways without any apparent internal adjustment.

The scheme now put forward embraces, in addition to the rhombohedral and orthorhombic nitrates mentioned above, the rhombohedral minerals of the compositions MgCO_3 , FeCO_3 , ZnCO_3 , and MnCO_3 , and the hemihedrally rhombohedral dolomite, $\text{CaMg}(\text{CO}_3)_2$, and also the orthorhombic minerals of the compositions BaCO_3 , SrCO_3 , and PbCO_3 , together with the isomorphous mixtures $(\text{BaCa})\text{CO}_3$, classed under the name bromlite. The monosymmetric barytocalcite, $\text{BaCa}(\text{CO}_3)_2$, with $\alpha:b:c=0.6255:1:0.7717$, $\beta=106^\circ 8'$, is morphotropically closely related to calcite (Arzruni, *Physik. Chem. d. Krystalle*, 1893, 295), and its structure may hence probably be derived by distortion from that of the latter. The relation between the dimensions of the rhombohedral sodium nitrate and the orthorhombic rubidium nitrate has been already pointed out (p. 1531). In connexion with the structure of dolomite, it should be noted that the unmodified assemblage depicted in Fig. 9 was suggested some years ago by one of the authors as the probable scheme of arrangement of the component atoms in calcite; the observation that dolomite, $\text{CaMg}(\text{CO}_3)_2$, displays a lower form of symmetry, namely, rhombohedral tetartohedral, with centro-symmetry, led to a reconsideration of the question and to the adoption of the slightly modified form shown in Fig. 10. When, in the latter, half the layers of calcium spheres are replaced by layers of magnesium spheres similarly situated so that layers wholly composed of one of these two kinds alternate with layers composed of the other kind, the digonal axes of Fig. 10 are destroyed, and the lower form of symmetry presented by dolomite is obtained. The dolomite assemblage thus produced has the symmetry of Barlow's type 51a₁.

The slight differences in axial ratios or axial angles observed between members of the various isomorphous series of salts discussed above are, as in previous cases, to be attributed to the volumes appropriated by the spheres of atomic influence not being precisely proportional to the whole numbers representing the fundamental valencies of the elements concerned; the volumes of the spheres of atomic influence of the several bivalent elements thus differ slightly among themselves. It has been shown (Trans., 1907, 91, 1193) that in the case of the halogens such divergencies can be traced consistently throughout a whole series of compounds with the result that a definite conclusion is reached that the volume for iodine is the greatest, and those for bromine, chlorine, and fluorine are respectively smaller and smaller. Whether a particular salt belonging to the series dealt with above

will assume the orthorhombic or the rhombohedral form will, it is suggested, depend on which form of symmetry, with the precise volumes assumed by the spheres of atomic influence under the prevailing conditions, will lead to the least departure from sphericity of the latter.

Both the calcite and aragonite assemblages described above may be homogeneously partitioned into highly symmetrical units having the composition CaCO_3 and the configurations depicted in Fig. 15, *a* and *b*; both assemblages may be regarded as built up by homogeneously fitting together either kind of these units in accordance with the appropriate crystal symmetry, slight distortion being practised where necessary, as in cases previously described. The rhombohedral sodium nitrate and the orthorhombic potassium nitrate assemblages described and figured above each similarly yield two kinds of highly symmetrical unit; these possess the composition NaNO_3 or KNO_3 , and possess

FIG. 15.

configurations identical with those depicted in the case of calcium carbonate.

The intimate structural relationship existing between the rhombohedral forms of sodium nitrate and calcium carbonate has been traced in the foregoing pages to the operation of the second geometrical property of close-packed assemblages. A case of exactly the same kind is furnished by the morphotropic relationship between the orthorhombic sulphates of the bivalent metals and perchlorates, &c., of the alkali metals, *e.g.*, between barium sulphate, BaSO_4 , and potassium perchlorate, KClO_4 . When, in the assemblage appropriate to barium sulphate, the bivalent barium sphere of influence is replaced by the smaller univalent sphere of influence of potassium, the simultaneous substitution of the bivalent sulphur sphere by the univalent chlorine sphere can occur, in accordance with the second geometrical property, in such a manner that the original marshalling is retained; the axial ratios are in this case but slightly altered and the crystal symmetry remains

unchanged (compare Barker, *Min. Mag.*, 1906, 14, 235; 1908, 15, 50). It is important to note that potassium permanganate, KMnO_4 , is isomorphous with potassium perchlorate, KClO_4 , so that the manganese sphere of influence appropriates a volume comparable, for purposes of close-packing, with that of the univalent chlorine. The isomorphism existing between the rhombohedral calcite, CaCO_3 , and rhodocrosite, MnCO_3 , shows, however, that the bivalent sphere of influence of calcium is crystallographically replaceable by the manganese sphere. These apparently contradictory indications, namely, that manganese can replace either a bivalent or a univalent atom, point to the conclusion that the manganese sphere appropriates in an assemblage a volume intermediate between those occupied by a univalent and a bivalent atom; the correctness of this conclusion is strongly confirmed by a consideration of the complex valency relations of manganese.

The Polymorphous Forms of Silica.

A very simple structure may be attributed to the constituent layers from which the crystalline polymorphous forms of silica, quartz, and tridymite are built up; this simplicity of layer structure, as in the case of silver iodide, is consistent with the close numerical correspondence between the axial ratios of the two minerals which has been already remarked (p. 1530). The assemblages appropriate to the two substances consist of spheres of the bivalent magnitude repre-

FIG. 10.

a.

FIG. 16 (continued).

b

c.

senting silicon and oxygen ; the silicon spheres are regarded as slightly larger than those of oxygen, but the mean valency volume of a sphere of the assemblage is taken as 2. The equivalence parameters for the trigonal trapezohedral quartz and the orthorhombic tridymite are

conveniently calculated from the axial ratios in the form previously given, namely,

	$a : b : c.$	$x : y : z.$
Quartz	0.5774 : 1 : 1.2701	1.466 : 1.269 : 3.224
Tridymite	0.5774 : 1 : 1.2716	1.465 : 1.269 : 3.227

first, however, dividing the length b by two; the valency volume, for the molecule SiO_2 , is taken as $W = 6$.

In the case of quartz the spheres of the appropriate assemblage present the marshalling of the cubic closest-packed assemblage of equal spheres (Trans., 1907, 91, 1152), one-third of those of a triangularly arranged layer consisting of silicon spheres and two-thirds

FIG. 17.

of oxygen spheres. The nature of the assemblage is shown by the three consecutive layers of Fig. 16, a, b, and c, and the corresponding elevation of Fig. 17; the symmetry of the assemblage thus constituted is that of the trigonal trapezohedral crystal class to which quartz belongs.

The triangular arrangement of spheres in a layer of Fig. 16 is that depicted in Fig. 18, in which the lightly shaded spheres represent those of silicon. On mutually arranging layers of this kind in accordance with the marshalling of the cubic closest-packed assemblage, that is to say, giving the layers the relative arrangement indicated by Fig. 16, a, b, and c, the resulting assemblage presents the appearance shown in rough perspective in Fig. 19. It will be seen that the spheres of one kind form staircase spirals in this assemblage,

and that, depending upon the configuration of the mutual arrangement of the first three layers, an assemblage representing either right- or left-handed quartz may be built up. The two kinds of interpenetrant

FIG. 18.

twinning commonly observed with quartz follow immediately from the mode of regarding the structure now put forward.

FIG. 19.

The assemblage representing the orthorhombic tridymite is derived by arranging layers identical with those of Figs. 16 and 18 in the marshalling of the hexagonal closest-packed assemblage of equal

spheres; it is illustrated in plan and elevation by Fig. 20 and in the rough perspective sketch of Fig. 21. This assemblage possesses holohedral orthorhombic crystal symmetry, and, as is seen from Fig. 21, the spheres of one kind form zigzags, devoid of enantio-morphism, within the structure. The equivalence parameters stated

above are indicated as the translations in the diagrams representing the two minerals.

In the diagrams relating to the last two assemblages, as in those given for calcium carbonate and related substances, certain spheres are more or less flattened at the points of contact with others, but the

flattening is small in amount. The cause of the occurrence of this kind of modification will be interpreted in various ways in different cases. Thus, if two kinds of spheres can be distinguished in an assemblage such that the one kind makes but few contacts with neighbouring spheres whilst the other kind makes a large number of such contacts, flattening of the former should occur in order that the mutual arrangement of the centres of the spheres shall be preserved in the assemblage derived by the application of a general pressure which eliminates the interstitial space. Whilst the representation of flattening such as this is thus rendered necessary in certain cases, in others the flattening is associated with a discrepancy between the dimensions of the assemblage as measured and as deduced. In the case of the polymorphously related forms of silica the latter applies, but our ignorance of the exact volume relationship holding between the

FIG. 21.

spheres of atomic influence of silicon and oxygen hinders any precise investigation of the matter.

In a previous paper (Trans., 1906, 89, 1686) we have shown that the discussion of the equivalence parameters elucidates immediately the remarkable morphotropic relationship observed between chondrodite, $\text{Mg}_3(\text{SiO}_4)_2, 2\text{Mg}(\text{F}, \text{OH})$, humite, $\text{Mg}_5(\text{SiO}_4)_3, 2\text{Mg}(\text{F}, \text{OH})$, and clinohumite, $\text{Mg}_7(\text{SiO}_4)_4, 2\text{Mg}(\text{F}, \text{OH})$. These minerals form a homologous series of which the first member is proectite,

and the homologous increment has the composition of forsterite, Mg_2SiO_4 . In calculating the equivalence parameters of these substances we originally assigned to silicon the valency volume $W=4$, which is in disaccord with the volume, $W=2$, given to it in the present paper. It happens, however, that in the humite series, both the first member and the homologous increment contain silicon in such

proportions as to render the morphotropic relation very insensitive to a change in the valency volume assigned to this element. It consequently results that the calculation of the equivalence parameters based on the value $W=4$ or 2 for silicon gives an almost constant value for the ratio z/W . The alternative values thus obtained are given below.

For $Si=4$:

	W.	x	:	y	:	z .	z/W .
Chondrodite	38	2·4249	:	2·2323	:	7·0199	0·18473
Humite	54	2·4278	:	2·2475	:	9·8965	0·18327
Clinohumite	70	2·4349	:	2·2540	:	12·7547	0·18221

For $Si=2$:

Chondrodite	34	2·3367	:	2·1510	:	6·7644	0·19895
Humite	48	2·3343	:	2·1610	:	9·5155	0·19824
Clinohumite	62	2·3384	:	2·1646	:	12·2491	0·19756

The values of z/W obtained with the volume $Si=2$ agree distinctly better among themselves than do the values got with $Si=4$. These and other indications which suggest that the fundamental valency of silicon is 2 are significant because, if they are to be trusted, it would appear that carbon is the only element which has a fundamental valency so large as 4. The exceptional nature of carbon and the fact that this element is not known to be isomorphously replaceable by any other lend support to this suggestion.

As before, the author's thanks are due to the Committee of the Municipal School of Technology for permitting the blocks illustrating the paper to be made in the school, and to Messrs. Chas. W. Gamble and R. B. Fishenden, of the Photographic and Printing Crafts Department, for the care with which they have carried out the work.

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