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THE CRYSTAL STRUCTURE OF TRICALCIUM ALUMINATE

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It was predicted a number of years ago on theoretical grounds that many of the complex minerals, such as those of the polysilicic acids, would be found to contain molecules of the component oxides rather than complex ionic groups.[1a] $K_2O{\cdot}Al_2O_3(SiO_2)_6$ was cited as an example. So far, no data have been published which support this view, and, so far as the present authors know, no compounds of this type have been examined by x-ray methods. It was with the hope of obtaining data on this type of compound that this research was undertaken. Tricalcium aluminate ($3CaO{\cdot}Al_2O_3$) was chosen for analysis because it was known to be optically isotropic, thus showing that the crystals have cubic symmetry, and because of its relatively simple composition and its lack of ability to exist in other than the solid state. It is said to melt incongruently at 1535°, giving a melt of the two oxides with an excess of CaO. No method is known by which crystals of tricalcium aluminate can be grown of such size as to permit of goniometric measurements. This has necessitated the use of a very general method of application of the theory of space-groups to the powder method of x-ray crystal analysis. It turns out that tricalcium aluminate does not show the new type of structure originally sought. Instead, it is "mixed ionic," *i. e.*, the metallic elements and the oxygen all enter the compound as separate crystallographic entities. It is with the determination of this type of structure and with the sort of chemical combination which it discloses that this paper has to do.

Preparation of $3CaO{\cdot}Al_2O_3$.—A mixture of CaO and Al_2O_3 of high purity in the molecular ratio of three to one was very thoroughly mixed and ground in an agate mortar. It was then heated for about twenty minutes in a small platinum boat which was directly heated in the air by an electric current to 1350–1450°. Temperatures were measured by an optical pyrometer and were found to be substantially uniform over the

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[1] The material here presented was used by the junior author in partial fulfilment of the requirements for the Ph.D. degree at The Pennsylvania State College, June, 1928.

[1a] Langmuir, THIS JOURNAL, **38**, 2241 (1916).

portion of the boat used. The substance does not fuse at these temperatures but sinters into a light, friable lump. The cycle of grinding and heating was repeated from two to eight times for each sample. Little improvement in the material could be noted after the third cycle. The temperature was not critical within the above limits.

X-Ray Diffraction Data.—X-ray diffraction patterns of the powdered substance, made on the General Electric apparatus, using molybdenum K-alpha radiation, showed strong lines characteristic of a body-centered cube, $a = 3.812$ Å., superimposed upon a weak pattern of CaO and numerous additional faint lines. Since $3CaO{\cdot}Al_2O_3$ is known from optical data to have cubic symmetry,[2] it seemed likely that the body-centered cubic lines mentioned above were due to this substance. It remained to account for the extra lines.

The optical properties of the four compounds of CaO and Al_2O_3 which have been described in the literature[2] ($3CaO{\cdot}Al_2O_3$, $5CaO{\cdot}3Al_2O_3$, $CaO{\cdot}Al_2O_3$ and $3CaO{\cdot}5Al_2O_3$) are given in the "International Critical Tables." Using these data as a basis of identification, the petrographic microscope revealed the presence of large amounts of $3CaO{\cdot}Al_2O_3$, together with smaller amounts of $3CaO{\cdot}5Al_2O_3$ and CaO. $5CaO{\cdot}3Al_2O_3$ and $CaO{\cdot}Al_2O_3$ were absent. Another batch of the material was prepared with about equal molar proportions of the two oxides. The petrographic microscope showed that it contained a much greater proportion of $3CaO{\cdot}5Al_2O_3$. The x-ray diffraction pattern showed a much greater relative intensity of all but three of the lines which had not been accounted for in the previous diffraction patterns. These three lines correspond to interplanar spacings of 3.1 Å., 2.20 Å. and 1.79 Å. These spacings may be derived from a cube whose side is twice that corresponding to the body-centered cubic pattern. These data were taken as conclusive evidence that the body-centered cubic lines, and the three additional faint lines, were due to $3CaO{\cdot}Al_2O_3$ and that the other faint lines were due to CaO and $3CaO{\cdot}5Al_2O_3$.

The interpretation of the crystal structure of tricalcium aluminate, therefore, resolves itself into a search for those structures which can quantitatively account for the body-centered cubic pattern and for the three faint lines mentioned above. The first step is the determination of the number of "molecules" per unit crystal cell.

The Number of Molecules per Unit Cell.—Since tricalcium aluminate is available only in a finely divided and relatively impure condition, a precision measurement of its density is not possible. An approximation sufficiently close for the determination of the number of molecules per unit cell was made, however, by observing the behavior of the substance in liquids of various densities. The observations were made by filling a

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[2] Shepherd, Rankin and Wright, *Am. J. Sci.*, **28**, 293 (1909); Rankin and Wright, *ibid.*, **39**, 1, (1915).

fine capillary tube with a suspension of the powder in a mixture of methylene iodide and mesitylene of previously determined density. A petrographic microscope was mounted with its optical axis horizontal, and the tube containing the suspension was mounted vertically on the microscope stage. With a liquid whose density was 2.89 most of the tricalcium aluminate particles moved downward, and those of $3CaO{\cdot}5Al_2O_3$ moved upward. A partial separation of the two was obtained by centrifuging the suspension. Complete separation could not be obtained because of the mechanical union between particles due to the sintering process. The relatively pure $3CaO{\cdot}Al_2O_3$ thus obtained was dried and used in subsequent determinations. This powder was found to fall in a liquid of density 2.94 and to rise in one of density 3.07. In a liquid of density 3.005 the particles went up and down in about equal numbers. The density of $3CaO{\cdot}Al_2O_3$ is therefore between 2.94 and 3.07 and is probably very close to 3.00. The number of molecules per unit cube (a = 3.812 Å.) is given by the density and molecular weight as 0.373 ± 0.004. This is very nearly equal to $^3/_8$. No other common fraction whose numerator and denominator are small integers comes within the precision of the data. Since the number of "molecules" in a unit cell must be a whole number, it is evident that the edge of the unit cell must be a multiple of 3.812 Å. A cube of twice these dimensions (*i. e.*, a = 7.624 Å.) would contain three "molecules." A smaller cell cannot possibly contain a whole number of "molecules" without conflicting with the x-ray data. Furthermore, there are no data from the diffraction patterns which require that it be larger. This means that for crystallographic purposes the formula of tricalcium aluminate should be $9CaO{\cdot}3Al_2O_3$. The three faint lines mentioned above might be accounted for quantitatively within the precision of the data by assuming that they are caused by first-order diffraction from 2 1 1, second-order diffraction from 1 1 1 and third-order diffraction from 1 1 0, respectively. It will appear later that all three can be accounted for in this way.

The Crystal Structure.—Since the body-centered cubic pattern from the tricalcium aluminate is on the basis of a cube of one-half the dimensions of the unit cell, it must be considered to be essentially an accidental result of the atomic arrangement within the unit cell and, as such, it imposes no symmetry limitations upon the cell as a whole. Since no crystals large enough for symmetry observations or Laue photographs could be made, none of the usual methods for establishing the space-group is available. This means that every possible arrangement of the atoms consistent with cubic symmetry must be considered as a possibility until it is shown to be in conflict with known facts or data.

The procedure used in writing down the possible arrangements was essentially the same as that used by Wyckoff in his treatment of calcite[3]

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[3] Wyckoff, *Am. J. Sci.*, 50, 317 (1920).

except that the process is greatly complicated by the fact that all cubic space-groups must be considered and that there are many more atoms to place in the unit cell. In considering the possible combinations of groups of equivalent points occupied by a given kind of atom, it is obviously necessary to consider only those numbers which represent groups of equivalent points in cubic symmetry, namely, 1, 2, 3, 4, 6, 8, 12 and 16. Furthermore, those which do not have variable parameters, namely, 1, 2 and 3, need not be considered more than once. Bearing these limitations in mind, the possible combinations for the six Al ions are found to be 6 all alike, 4 of one kind and one each of two others, 4 of one kind and 2 of another, 3 of one kind and 3 of another, and 3 of one kind, 2 of another and one of another. These combinations may be expressed more conveniently by merely writing the possible numbers totaling 6, bearing in mind the limitations mentioned above. The possible combinations for Al are, then, 6, 4–1–1, 4–2, 3–3 and 3–2–1. This code will be followed in the subsequent discussion. Reference to the summary table[4] of equivalent points in the various space-groups of the cubic system shows that all of these are possible except the last. The 3–2–1 combination is impossible because there is no one space-group which contains arrangements of both 2 and 3 equivalent points.

A similar treatment of the nine positions required for the Ca ions leads to the combinations 8–1, 6–3, 4–3–1–1 and 4–4–1. Each combination for Al must now be considered with each combination for Ca, and the space-groups compatible with both are written down. As may be seen in Table I, the entire list includes only five space-groups. This whole process is then repeated for the possible combinations for the 18 oxygen ions. The results are listed in Table II. Although there are only five space-groups involved, there are so many combinations possible within each space-group that the total number of possible arrangements is very large. For instance, if Ca is taken at 8c and 1a,[5] and Al at 6a, there are over 30 configurations of O possible. Since Al may also be at 6b, 6c or 6d, this number is increased four-fold. Placing Ca at 8c and 1b again

TABLE I

SPACE-GROUPS POSSIBLE FOR VARIOUS ARRANGEMENTS OF CA AND AL

Combinations for calcium	Aluminum at 6–0	Aluminum at 4–1–1	Aluminum at 4–2	Aluminum at 3–3
8–1	$T_h^1 O^1 O_h^1$	none	none	$T_h^1 O^1 O_h^1$
6–3	$T^1 T_h^1 T_d^1$, $O^1 O_h^1$	$T^1 T_d^1$	none	none
4–3–1–1	$T^1 T_d^1$	none	none	none
4–4–1	$T^1 T_d^1$	none	none	$T^1 T_d^1$

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[4] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Pub. No. 18, Carnegie Inst. of Wash., **1922**, p. 176.

[5] These arrangements are expressed in the code used by Wyckoff, refs. 3 and 4, pp. 103 *et seq.*

doubles this figure. Such a systematic procedure involves a number of duplications, but it was followed rigidly to lessen the chances of error. The total number of possibilities tabulated was about 1500.

TABLE II

SPACE-GROUPS POSSIBLE FOR VARIOUS ARRANGEMENTS OF O WITH COMBINATIONS OF CA AND AL ALREADY FOUND POSSIBLE

Combinations for oxygen	6–8–1	6–6–3	6–4–3–1–1	6–4–4–1	8–3–3–1	4–4–3–3–1
12–6	$T_h^1O^1O_h^1$	$T_h^1T^1T_d^1$, $O^1O_h^1$	$T^1T_d^1$	$T^1T_d^1$	$T_h^1O^1O_h^1$	$T^1T_d^1$
12–4–1–1	none	$T^1T_d^1$	none	none	none	none
12–3–3	$T_h^1O^1O_h^1$	none	none	$T^1T_d^1$	none	none
8–8–1–1	none	$T_h^1O^1O_h^1$	none	none	none	none
8–6–3–1	$T_h^1O^1O_h^1$	$T_h^1O^1O_h^1$	none	none	none	none
6–6–6	$T_h^1O_h^1O^1$	$T^1T_h^1T_d^1$, $O^1O_h^1$	$T^1T_d^1$	$T^1T_d^1$	$T_h^1O^1O_h^1$	$T^1T_d^1$
6–6–3–3	$T_h^1O^1O_h^1$	none	none	$T^1T_d^1$	none	none
6–4–4–3–1	none	$T^1T_d^1$	none	$T^1T_d^1$	none	none
6–6–4–1–1	none	$T^1T_d^1$	none	none	none	none

There were no possibilities with O at 16–2, 16–1–1, 12–4–2, 8–8–2, 8–6–4, 8–6–2–2, 8–4–4–2, 8–4–4–1–1, 6–6–4–2 or 6–4–3–3–1–1.

It was found possible to eliminate most of these possibilities by a consideration of the packing-sizes of the ions involved and the space available in the unit cell. Ionic dimensions have been published by Bragg[6] and by one of the present authors.[7] According to Bragg the ionic radii are Ca = 2.1 Å., Al = 1.45 Å. and O = 0.6 Å. According to Davey they are Ca = 1.4, Al = 0.9 and O = 1.0 Å. Davey's values were used in this work for two reasons: first, that they give the distance from Al to O in Al_2O_3 as 1.9, in agreement with the published data of Bragg, and second, that they give a smaller total distance for Ca + O and for Ca + Al, so that they tended to retain certain of the possibilities which would have been thrown out on the basis of Bragg's values. Thus any error introduced by our limited knowledge of the packing dimensions of ions was clearly on the safe side. The procedure of finding whether or not space was available in a given configuration was greatly facilitated by drawing each of the arrangements of equivalent positions involved on tracing cloth. In this way any combination of arrangements could be superimposed and viewed against a bright light. In this manner the ions placed along any one dimension of the cube could be picked out readily.

As an example of this procedure, consider the structure in which Ca is at 8c and 1a, Al at 3a and 3b and O at 6a and 12d. This places $^1/_2$ Ca, 1 O and $^1/_2$ Al along half the cube edge. This requires a space of 1.4 + 2.0 + 0.9 = 4.3 Å. where only 3.8 Å. are available. The structure is obviously an impossibility if the ions have anything like the packing

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[6] Bragg, *Phil. Mag.*, **40,** 236 (1920).

[7] Davey, *Phys. Rev.*, **22,** 716 (1923); *Chem. Rev.*, **2,** 349 (1926); *Gen. Elec. Rev.*, **29,** 274 (1926).

radii assigned to them above. In making these eliminations, the packing dimensions assumed for the ions were not regarded as strictly inflexible. No structure was eliminated unless the available distance involved was exceeded by at least 10%. This procedure eliminated all but about 40 of the original 1500 possible structures. It remained to eliminate as many of these as possible on the basis of x-ray evidence. Among the 40 arrangements allowed by the ionic dimensions were a number of duplications, but these were carried through as a check. In general, however, each of these structures actually represents a number of possibilities which cannot be distinguished experimentally because of the similar dimensions and scattering power of Al and O ions. In the present state of our knowledge of diffracting power, we are hardly justified in distinguishing between Al^{+++} and O^{--} on x-ray data alone. It was therefore assumed that interchanging places between the 6 Al ions and 6 of the O ions has no effect on the diffracting power of the crystal planes. Were this assumption not made, the number of structures to receive individual examination would be much larger than forty.

After it had been decided that the unit cell must have a length of 7.624 Å., repeated attempts were made to detect a first-order diffraction from the 1 0 0 planes for d = 7.624 Å. These attempts gave uniformly negative results. This fact served to eliminate a considerable number of otherwise possible structures without an intensity calculation. In accordance with the general practice, the diffracting power of a plane was taken as proportional to the total number of electrons in the ions which were situated in that plane. The diffracting powers of 1 0 0 planes were calculated for all the forty structures. Those whose 2 0 0 planes were obviously too thinly populated with electrons to cut out the first order from d_{100} = 7.624 Å. were discarded. However, because of the lack of definite knowledge of the correct basis for calculating diffracting powers, no structures were discarded on this basis unless the 2 0 0 planes had less than three-fourths the electron population of the 1 0 0 planes. Repeated attempts to find experimental evidence of a second-order diffraction from d_{100} = 7.624 Å. gave negative results. A few additional structures were therefore eliminated because it was inherent in the structure that the ions were distributed in the space between the 1 0 0 and 2 0 0 planes in such a way as unavoidably to produce such a second-order diffraction.

When all possible eliminations had been made by simple inspection of 1 0 0 planes, there remained only 18 structures, of which 9 were duplicates of the other 9. For instance, the structure having Ca at 8c and 1a, Al at 6d and O at 6b and 12d, may be transformed into the structure having Ca at 8c and 1b, Al at 6a and O at 6c and 12e by merely changing the origin of coördinates from a corner of the unit cube to its body-center. From this point on the duplicates were combined, leaving 9 structures for which intensity calculations must be made. In those cases where two arrangements differed only in having one variable parameter more or less (for instance, 12e and 12n), only the more general arrangement was considered. Similarly, the combination of 6b and 6c was used instead of the special case represented by 12f.

In making the intensity calculation the customary assumption was made that the amplitude of the radiation scattered by a given plane is proportional to the electron population of that plane. This population was determined in the usual manner on the basis of $O^{--} = 10$, $Al^{+++} = 10$ and $Ca^{++} = 18$. The resultant amplitude from a given form was taken as the vector sum of the amplitude from the individual coöperating planes. This was determined by the graphical addition of vectors in the same manner as the addition of alternating currents which have a known phase difference.[8] The intensity of the resultant beam was calculated from the formula[9,10]

$$I = R^2 j \left(\frac{d}{n}\right)^m$$

where R is the resultant amplitude, j is the number of families of planes of the form, n is the order of diffraction and d is the fundamental spacing of the form, taking the edge of the unit cube as unity, and regarding the unit cell as being simple cubic. These calculations showed clearly that six of the nine structures are quite incompatible with the x-ray data. For example, the structure with Ca at 8c and 1a, Al (or O) at 3a and 3b,

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[8] In this connection see A. Schuster, "The Theory of Optics," Chap. 1, Edw. Arnold, London, **1909**, **1919**, or any standard book on alternating currents.

[9] Because of our inexact knowledge of diffracting power this equation can be used only to show qualitatively the relative intensities of diffraction. The simpler the plane form to which it is applied the more reliable are the results. It may be used quite successfully for the 1 0 0 planes—and seems to apply for the 1 1 0 planes. For the 1 1 1 planes the packing radii of the ions are so large in comparison with the interplanar spacing that the calculated results can only be depended upon to show that a line is present or absent in the diffraction pattern. There is a tendency to make the diffracted beam of orders higher than the first abnormally weak. For this reason the formula shows whether the second and fourth orders of 1 1 1 are present and whether the first and third orders are absent, but it does not give the relative intensity of the second and fourth orders.

It is well known that certain crystals act as though the resultant amplitude of the diffraction beam depends upon the square-root of the electron population. For this reason attempts were made to repeat the above calculations on this basis. In no case where this was tried were we able to retain a structure which had been rejected in the original calculations.

[10] Bragg uses $m = 2.0$; Wyckoff uses $m = 2.35$; McKeehan uses $m = 3.0$. None of these seem to be entirely satisfactory. Our Table III was calculated using $m = 2$, merely for the sake of convenience in making the large number of calculations required. It is clear that Table III could have been made to show greater *apparent* agreement by using a different value for m but it does not follow that such a change would have increased the probability of the correctness of our ultimate solution.

O (or Al) at 6d and O at 12d gave a calculated intensity of 380 for the first order of d_{100} = 7.624, and 257 for the fourth order, even when such parameters were used as to give the weakest possible first order and the strongest possible fourth order. Since experimentally the first order is absent and the fourth order is strong, this structure is in direct conflict with the experimental data and must be discarded. Similar calculations on the 1 0 0 planes for the rest of the 9 structures eliminated all but three.

In the case of the three remaining structures it was necessary to make intensity calculations for the first four orders of the 1 0 0, 1 1 0 and 1 1 1 planes. These calculations were made for a large number of different values for the variable parameters which were allowed by the space available for the ions, and by the symmetry requirements of the atomic arrangements. The best fit in intensities was found in the structure illustrated in Fig. 1, in which Ca is at 8c and 1a, Al at 3a and 3b and O at 6d and 12f.[11] The calculated intensities are shown in Table III. It will be noted that they indicate the presence of the three faint lines mentioned at the beginning of this article.

TABLE III

CALCULATED AND OBSERVED INTENSITIES FOR THE MOST PROBABLE ARRANGEMENT

Line	Calculated intensity	Observed intensity
100 1st order (d_{100} = 7.624)	75	Absent
100 2nd order	0.1	Absent
100 3rd order	14.1	Absent
100 4th order	1750	Strong
110 1st order	26	Absent
110 2nd order	1420	Very, very strong
110 3rd order	80	Very faint
110 4th order	1500	Weak
111 1st order	163[a]	Absent
111 2nd order	1067[a]	Weak
111 3rd order	69[a]	Absent
111 4th order	552[a]	Faint
211 1st order	4754[a]	Weak
211 2nd order	735[a]	Very strong

[a] Note statements in the text as to the weight to be put on numerical results for these planes.

As was mentioned previously, it is not possible to distinguish with certainty between Al and O ions on the basis either of dimensions or of diffracting power. The assignment of certain of the positions in Fig. 1 to Al and of other positions to O was made on the basis of electrostatic considerations. For instance, in Fig. 1 the x-ray data would permit Al to be at 6d and six of the eighteen O at 3a and 3b. However, since there

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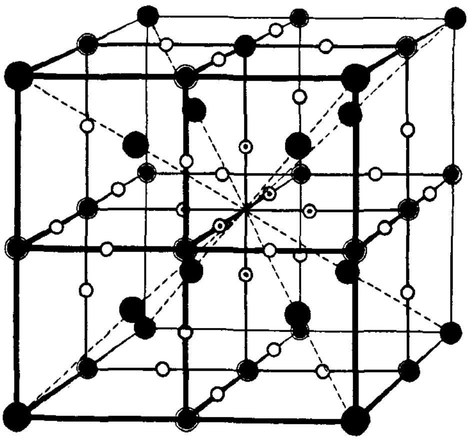
[11] The presence of Al at 3a and 3b leaves room for O at 6b and 6c only at a point half-way between 3a and 3b. This changes 6b and 6c into the special case of 12f.

are O ions at 12f, we would then have five O ions in a row along a direction parallel to the edge of the cube (d_{100} = 7.624 Å.). Such an arrangement is highly improbable from electrostatic considerations. Similarly, the Al might have been placed at 6b (or 6c) with the O at 3a, 3b and 6c (or 6b). This also places five O in direct contact with one another, and is therefore a highly improbable structure. Furthermore, there is some theoretical basis for expecting that Al would have a somewhat greater equivalent scattering power than O, especially in the higher orders and from forms of small spacing. If this be true, the Al at 3a and 3b would cause a fainter 1 1 1 second-order diffraction than the calculated value given in Table III. This would give a still better match with the experimental data.



●, Ca; ◉, Al; O, O at 12f; ⊙, O at 6d.
Fig. 1.

It has already been stated that, although the theory of space-groups permits a variable parameter for 12f, the dimensions of Al and O ions fix this parameter in Fig. 1 at u = 0.25. Arrangements 6d and 8c have variable parameters. The best intensity match is obtained when u for Ca at 8c = 0.24 and u for O at 6d = 0.31. Intensity calculations show that these parameters are not particularly critical, especially in the case of O at 6d, which may well be somewhat closer to Al at 3a.

The two other structures which were mentioned as possibilities both have Ca at 8c and 1a. One has 6a, 6b, 6c and 6d for Al and O, while the other has them at 6a, 6b, $6b_2$ and 6d. These two structures are closely related, since 6c may be derived from 6b by a single rotation of 90°. While the calculated intensities of these two structures are somewhat less satisfactory than those of the one shown in Fig. 1, the degree of reliability of the laws of scattering with complex crystals is so uncertain that they must be considered as possible structures. In any case, the same general chemical conclusions can be drawn from all three structures.

Chemical Significance of the Structure.—It is obvious that there is no particular grouping of ions in any of the three structures of which Fig. 1 is typical. There is no indication of those groups which might have been expected to be present, such as CaO, AlO_3, Al_2O_3, Al_2O_6, etc. The entire structure is built up of Ca, Al and O ions as units. The ionic nature of the compound is evident from its crystal structure. Figure 1 shows that the O at 12f are in every case midway between two Al at 3a and 3b, and that each O at 6d is equidistant from four Ca at 8c. Similarly, every Al at 3a is equidistant from each of four O at 12f; every Al at 3b is equidistant from four O at 12f; every Ca at 8c is practically (within 4%) equidistant from six O at 12f, and every Ca at 1a is equidistant from twenty-four O at 12f. Every Al at 3a is equidistant from four Ca at 1a and is equidistant from eight Ca at 8c. Every Al at 3b is equidistant from two Ca at 1a and is also equidistant from eight Ca at 8c. Similarly, every Ca at 1a is equidistant from six Al at 3b and every Ca at 8c is practically equidistant from 3 Al at 3a and from 3 Al at 3b.

Tricalcium aluminate certainly has no grouping which would justify its name. From its crystal structure it would appear to be a mixed oxide and not a salt in any sense of the word. It is distinctly different from solid solutions or mix-crystals, which are either isomorphous substances or simple replacements of one kind of atoms by another kind. In this latter case the structure of one or the other is retained with usually only a change in the lattice dimensions. In the case of tricalcium aluminate the original structure of neither oxide is retained. The structure of tricalcium aluminate is also distinctly different from that of crystals containing complex ions. The complex ionogens whose structures have been determined support the Wernerian conception of secondary valence. $NiCl_2 \cdot 6NH_3$,[12] $K_2Zn(CN)_4$,[13] K_2PtCl_4,[14] $NaClO_3$,[15] etc., are examples of this type of compound. In each of these the complex ion has been found to act crystallographically as a unit, thus confirming the evidence, already strong, from solutions. Tricalcium aluminate, on the other hand, shows the Ca, Al and O to act as crystallographic entities, each surrounded as symmetrically as possible by the other two. In terms of the most probable of the three structures discussed above (see Fig. 1), all six Al ions lie at the intersections of a physical three-dimensional lattice work in such a way as to put an O midway between each pair of Al. This lattice work uses up 12 of the O, so that the lattice work contains two O for every Al. Figure 1 shows, however, that there are no AlO_2 groups existing as physical entities in the crystal. The crystallographic effect might be described as a sort of rectangular sponge of Al and O in the interstices of which are the Ca and the rest of the O ions.

The type of crystal structure reported in this paper for tricalcium aluminate therefore belongs to the fifth type of chemical combination, listed below, *viz.*, (1) ionic compounds (NaCl) (Bragg) in which the crystal is built up of simple ions of an electrolyte; (2) electron-sharing compounds (Al_2O_3) (Bragg) in which the crystal is built up of neutral

[12] Wyckoff, THIS JOURNAL, **44**, 1239 (1922).

[13] Dickinson, *ibid.*, **44**, 276 (1922).

[14] Dickinson, *ibid.*, **44**, 2404 (1922).

[15] Dickinson, *ibid.*, **43**, 2045 (1921).

molecules; (3) geometrical compounds (Cu_3Au) ($CuAu_3$) (Bain) in which definite proportions are an accident of symmetry in homogeneous atomic dispersions; (4) Wernerian compounds ($CaCl_2I$) (Wyckoff) (K_2PtCl_4) (Dickinson) in which the crystal is built up of both simple and complex ions; (5) mixed ionic compounds ($3CaO{\cdot}Al_2O_3$).

There remains to be discovered a sixth type,[1] namely, the molecular compound in which molecules of the constituents crystallize together without losing their original identity. As in the case of Type 3, it may be expected that this will be an accidental effect of the symmetry of a homogeneous molecular dispersion of one substance in the other.

Acknowledgments.—It is a pleasure to express our appreciation to the General Electric Company, Schenectady, N. Y., the Calumet Baking Powder Company, Chicago, Ill., and to the Aluminum Company of America, New Kensington, Pa., for placing at our disposal facilities without which this research would have been exceedingly difficult, if not impossible; and to Dr. E. A. Harrington, who first showed that the x-ray diffraction pattern of an impure tricalcium aluminate contained lines corresponding to those from a body-centered cube.

Summary

1. The most probable crystal structure of tricalcium aluminate has been determined and the alternate possibilities stated.

2. The structure of tricalcium aluminate has been shown to be mixed ionic.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

THE THEORETICAL EVALUATION OF THE ENTROPIES OF AQUEOUS IONS

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It has been suggested by Latimer and Buffington[1] that the entropy change, ΔS, for the process

$$\text{Ion (gas)} = \text{Ion (aq.)}$$

is a function of the charge, e, on the ion, and the radius, r, of the ion cavity in the water solution; $\Delta S = f(e^2/r)$. This relation was noted from an inspection of the experimental values of the entropies of solution and was stated in the form of an empirical equation. The theoretical evaluation of this function will be considered in this article.

The total entropy of hydration may be considered as due to two effects: $\Delta S_{(1)}$, the entropy change arising from the polarizability of the medium,

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[1] Latimer and Buffington, THIS JOURNAL, **48**, 2297 (1926).