

CXIV.—*Contributions to the Theory of Isomorphism based on Experiments on the Regular Growths of Crystals of One Substance on those of Another.*

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Introductory.

EXAMPLES of the regular growth of one mineral on another have long been known ; they may be grouped into three classes : (1) one mineral is a paramorph of the other, so that they have the same percentage composition, for example, rutile on anatase ; calcite on aragonite ; hornblende on augite, and, conversely, augite on hornblende ; (2) one mineral is a decomposition product of the other, in which case they have some elements in common, for instance, barytes on witherite ; (3) the two minerals neither have similarity of composition nor belong to the same crystallographic system ; as examples of this type, the combinations rutile on mica and tourmaline on mica may be cited. A complete list of all such occurrences has been compiled by Mügge (*Neues Jahrbuch für Mineralogie, Beilage-Band*, 1903, 16, 335).

In the examples of regular growth among minerals, it is not usually possible to confirm the observations by experiments, for it is difficult to prepare synthetically the appropriate pairs of compounds. But when we turn to soluble substances the crystallisation can be watched and controlled. It is necessary, however, that the substance which has to receive the deposit shall not be acted on by the solution containing the other. Since the best examples of insoluble crystals are found in nature as minerals, it follows that the simplest way of studying the deposition of substances on each other is to experiment with soluble salts and minerals.

Although experiments of this kind have been previously made, they were isolated and had no definite end in view. The following investigations were made in order to ascertain whether the orientating influence of one crystal on another is due to some similarity of structure. Comparative experiments may enable us to discover the requisite conditions for the formation of regular growths, and may throw some light on the crystal structure of the substances concerned.

The first experiments on regular deposition were made by Wakkernagel in 1825 (*Kastner's Archiv f. d. gesammte Naturlehre*, 1825, 5, 293), who asserted that he obtained a regular deposit of lead nitrate on alum, and of alum on boracite. He also varnished some of his crystals, and observed the same regular deposit as on an unvarnished

crystal; he was therefore of the opinion that a crystal possesses a sphere of activity ("Wirkungskreis"). A regular deposit of lead nitrate on alum from an aqueous solution of the former is *a priori* absurd, for lead sulphate is immediately formed and deposited on the alum crystal. Kopp (*Ber.*, 1882, 15, 1653) repeated Wakkernagel's experiments, and could not obtain any regular deposition in either of the above cases; he also showed (*Annalen*, 1855, 94, 118) that growth on a varnished crystal begins at the edges or quoins, that is, at those points which remain uncovered owing to the shrinkage of the varnish. The idea of a sphere of activity, however, was not given up immediately; Bombicci (*Mem. Acad. Bologna*, (3), 7, 123), for example, in 1876 asserted that if a beaker containing a solution of sodium nitrate be placed on a piece of calcite, the latter exerts an "iso-orientating influence" to such a degree that the crystals of sodium nitrate appear in the beaker with their edges parallel to the edges of the calcite!

Frankenheim (*Pogg. Ann.*, 1836, 37, 516; 1860, 111, 1), in 1836, observed that if a drop of a solution of sodium nitrate be allowed to evaporate on a cleavage-piece of calcite, small rhombohedra appear which are definitely orientated. The edges of the rhombohedra are approximately parallel to those of the calcite-cleavage. He also tried old cleavages, and, finding that the deposition was not regular, concluded that the calcite must be freshly cleaved.

Frankenheim then proceeded to try other minerals with good cleavages and found that potassium iodide, bromide, and chloride separate out as definitely orientated equilateral triangles on a fresh cleavage-piece of mica, whereas on a glass plate they crystallise in cubes. He says "in biaxial mica one side of the triangle is always nearly parallel to one of the elasticity-axes of the mica." The deposition is regular on uniaxial micas also; the orientation of the triangles is twofold, one being derivable from the other by a rotation of 180° . The cubes which accompany these triangular forms are stated to be parallel to one another if the mica-cleavage be fresh. The corresponding sodium salts did not give regular growths. Again, sodium nitrate is deposited in similarly orientated triangles on mica and on gypsum; finally, calcium sulphate grows regularly on fresh cleavages of gypsum.

The next work was done by de Senarmont (*Compt. rend.*, 1854, 38, 105), who obtained regular growths of sodium nitrate on certain natural faces of calcite, namely, rhombohedral forms, both steeper and fatter than the form $\{100\}$, on the hexagonal prism and the scalenohedron $\{20\bar{1}\}$.

In 1877, O. Lehmann (*Zeit. Kryst. Min.*, 1, 490) described some 14 cases of regular growths of pairs of salts simultaneously deposited from solution.

Kopp (*Ber.*, 1879, 12, 917) somewhat later obtained regular growths of sodium nitrate on the following forms of calcite:

$$\begin{aligned} +R^3 = \{20\bar{1}\} &= v; & -2R = \{11\bar{1}\} &= f; \\ \infty R = \{2\bar{1}\bar{1}\} &= b; & -\frac{1}{2}R = \{110\} &= e; \end{aligned}$$

but Friedel (*Ber.*, 1872, 5, 483) could not obtain a parallel deposition on "prismatic crystals."

In 1871, Rose (*Ber.*, 4, 104) reported that Mitscherlich had obtained a zonal growth of sodium nitrate on dolomite from Traversella, and that he himself had observed a parallel growth by hanging a crystal of aragonite from Bilin in an aqueous solution of potassium nitrate. The latter experiment was repeated by Kopp (*loc. cit.*, p. 918) with a negative result, whereas the former observation was repeated by Tschermak (*Min. Mitth.*, 1882, 4, 118), who remarks that the zone crystals are "rarely" formed in the case of dolomite, never with chalybite or magnesite.

Zemiatshensky (*Zeit. Kryst. Min.*, 1894, 22, 77) confirmed Frankenheim's observations with regard to potassium iodide and mica, and also obtained regular growths of cubes of potassium iodide on gypsum.

Mügge (*loc. cit.*) also repeated Frankenheim's observations; he used two varieties of mica with large and small axial angle, namely, muscovite from an unknown locality and meroxene from Vesuvius. He found the regular growths with potassium chloride are more difficultly obtained than those of potassium bromide and potassium iodide. Sodium chloride, even with the addition of urea to encourage an octahedral habit, gave quite irregular growths. He was unable to trace any regularity in the growth of potassium iodide and gypsum.

Gaubert (*Bull. Soc. franç. Min.*, 1904, 27, 225) has recently observed that crystals of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ grow in regular positions on the rare minerals, uranocircite, autunite, meta-autunite, chalcilite, and metachalcilite; a face (010) of the salt is in contact with (001) of the mineral, and an edge (010) (001) of the former is parallel to either an edge (010) (001) or an edge (100) (001) of the latter.

H. B. Hartley has informed the author of an interesting case of regular growth observed by him. Triphenylmethane crystallises with one molecule of aniline, benzene, thiophen, or pyrrole, of crystallisation, in steep rhombohedra; triphenylmethane itself is orthorhombic. Sometimes regular growths are obtained in which the anhydrous substances crystallise on both ends of the rhombohedra, with the axis-*c* of the former parallel to the principal axis of the latter.

As regards the exact orientation of sodium nitrate on calcite, various contradictory results have been published. Frankenheim

gives nine positions, the most important of which are those where two faces are in contact with

- (1) An edge of each parallel,
- (2) An edge perpendicular to an edge of the calcite,
- (3) Corresponding diagonals parallel.

De Senarmont found that the diagonals only are parallel. Finally, Miers, as a result of measurements by means of his inverted goniometer, is of the opinion that a face and an edge are parallel.

(I) *Sodium Nitrate—Calcite Group.*

Parallel Growths on Fresh Cleavage-pieces of Calcite.

The method of study first used by the author was to allow drops of saturated solutions to evaporate on cleavage-pieces viewed under the microscope. Frankenheim's observation, that a cleavage-piece must be fresh to get a parallel growth, was confirmed; the rhombohedra of sodium nitrate quickly appear on the calcite, and, so far as the difference of angle allows, the orientation of the rhombohedra is exactly parallel to that of the calcite.

Sometimes some of the crystals of sodium nitrate are not parallel to the calcite, but are in twin position thereto—the twin axis is the rhombohedral zone axis [100]. It is interesting to note that, so far as the author is aware, no examples of calcite (or of sodium nitrate) twinned according to this law have been observed.

Cleavage-pieces from crystals of various habits and derived from different localities were then tried, in order to see whether the directive force varies at all. The varieties included opaque, milky, brown, argillaceous, and pink-manganiferous calcites; also dog-tooth spar and calcite from the Oxford Clay: no difference could be traced with all these varieties, a parallel growth being always obtained on a fresh cleavage surface, but never on an old one.

The only varieties which did not yield parallel growths were fibrous calcite and "Schieferspath," but it is difficult, if not impossible, to obtain a good cleavage surface in either of these varieties. Neither could a parallel growth be obtained on a specimen supposed to be "red calcite"; this, however, on analysis, was found to be a dolomite. The parallel growth of sodium nitrate is a most delicate test for calcite.

A solution of sodium nitrate, containing a little potassium nitrate, placed on calcite, gives on evaporation a parallel deposition of rhombohedral mixed crystals; the amount of potassium nitrate must be small, otherwise orthorhombic prisms of potassium nitrate containing sodium nitrate make their appearance in irregular positions. Retgers (*Zeit. physikal. Chem.*, 1889, 4, 599) has shown that sodium nitrate forms an isodimorphous series of mixed crystals with silver

nitrate, the rhombohedral crystals containing up to 52.32 per cent. molecules of silver nitrate. The author prepared mixtures by the same procedure as that followed by Retgers, and allowed the solutions to crystallise on calcite-cleavages. All the rhombohedral mixtures formed parallel growths just as readily as pure sodium nitrate ; but the crystals are extremely deliquescent, and the author has not yet succeeded in obtaining reliable angular measurements. The specific gravity of the crystals increases with the increase of silver nitrate contained, that of the end-mixture having the value 2.982 (Retgers). The molecular volume calculated from this value and the "average molecular weight" of the mixture is 38.6. The crystals do not grow parallel on dolomite.

Connections between Parallel Growth and the Nature of the Cleavage Surface.

Since the growth on an old cleavage surface is irregular, experiments were made with a view to cleaning the surface to such an extent that parallel growths would be formed. It was found that water, benzene, polishing, or even grinding with water on a ground glass plate, had not the desired effect. Etching an old cleavage surface with hydrochloric or nitric acid increases the regularity of the deposit, and the number of parallel crystals seemed to increase with the duration of etching : the periods of time employed were five, thirty, eighty, and one hundred and eighty seconds. Conversely, the number of parallel crystals decreases on etching a freshly cleaved surface, and even on immersion in distilled water for a period of a week.

G. T. Beilby (*Proc. Roy. Soc.*, 1903, **72**, 218) has recently shown that the structure of calcite undergoes a deformation if a cleavage surface be stroked several times in the same direction with a clean chamois-leather. When viewed with a high power, the surface seems to be unaltered, but on etching with a 0.2 per cent. solution of hydrochloric acid for ten to fifteen seconds, ridges and furrows, parallel to the direction of stroking, become visible. He has found the same to hold good for metals when polished, and is of the opinion that a crystalline surface-film flows and becomes amorphous. The effect of the above deformation on the subsequent growth of sodium nitrate was studied, and it was found that the change due to stroking, with or without subsequent etching, is not of such a fundamental character as to prevent the parallel deposition of crystals ; no difference between the orientating action of the stroked and the unstroked part of the surface could be detected.

Growth on a Reusch-twin of Calcite.

The effect of artificial twinning upon the glide plane $e - \{110\}$, on the subsequent growth of sodium nitrate on calcite was next studied. The sodium nitrate was deposited in parallel position on both the faces which constitute the re-entrant angle of the twin-crystal. If, however, the sodium nitrate be first deposited, and the calcite be then subjected to twinning, the crystals either fall off or retain their old orientation, as might be expected.

Magnetic Experiments.

Since calcite and sodium nitrate are both diamagnetic, experiments were made in order to see whether a magnetic field has any effect on the parallel orientation of sodium nitrate, when the calcite is placed in the position exactly opposite to that it would take up if freely suspended in the field.

Mr. H. E. Hurst kindly assisted the author in these experiments.

The magnetic field was obtained by putting the pole pieces of an electromagnet 1.5 mm. apart by means of a slip of ebonite. The crystal was then inserted between the poles. The field was measured by placing a small coil of known diameter and number of turns, connected to a D'Arsonval ballistic galvanometer, in the gap. The deflection of the galvanometer when the coil was suddenly withdrawn was noted, and from this, by standardisation of the galvanometer, the field strength was calculated and found to be 18,000 electrodynamic units. The results were all of a negative character, for it was found that the magnetic field has no effect whatsoever; nor has it any orientating effect on the crystallisation of sodium nitrate on glass or on dolomite.

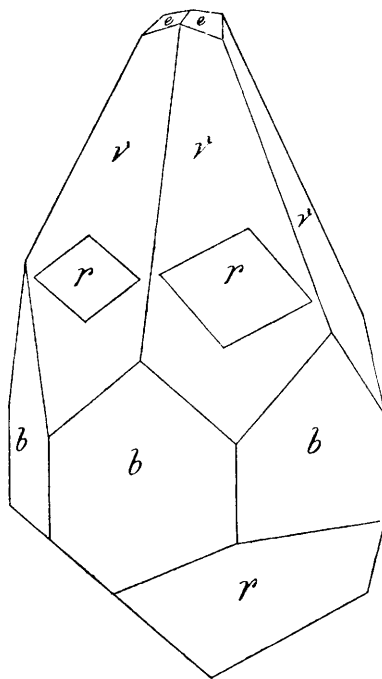
The author was afterwards made aware of the fact that Porter (*Proc. Roy. Soc.*, 1904, '73, 5) has made more elaborate experiments on the orientating action of a magnetic field on crystallo-genesis, and he also concluded that no effect could be traced.

Regular Growths on Natural Faces of Calcite.

Attempts were then made to produce regular growths of sodium nitrate on natural faces of calcite; here, of necessity, the surface is by no means clean. At first the drop-method was used, but no regular growths could be obtained on the scalenohedron $v - \{20\bar{1}\}$, on $e - \{110\}$, or on the hexagonal prism $b - \{2\bar{1}\bar{1}\}$, or on steep scalenohedra. Another method of deposition was therefore tried. A crystal exhibiting the forms v , b and e was hung in a hot saturated solution which was allowed to cool slowly for a week. The result was negative; but on repetition, using the same crystal, the scalenohedral faces were found

to be covered with hundreds of microscopic rhombohedra which were parallel, the crystals on all the scalenohedron faces being symmetrically arranged (Fig. 1). An edge $r:r$ of each crystal of sodium nitrate made a (mean) angle of 80° with the acute edge $v:v$. Now the angle between the edge $r:r$ and the above edge $v:v$ of the calcite is (by calculation) $78^\circ 56'$, and therefore differs by 1° only from the angle made by the edge $r:r$ of the sodium nitrate. Since the above angle is the mean of several readings which varied by 2° , and since the angles for

FIG. 1.

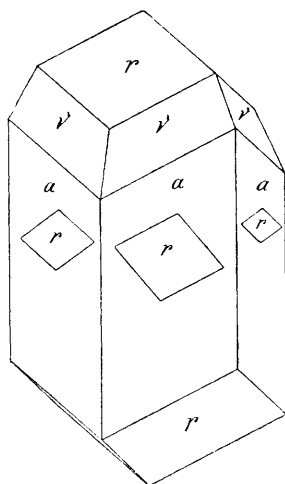


sodium nitrate are slightly different from those of calcite, we may say that one edge of the rhombohedron of sodium nitrate lies in the rhombohedral zone of the calcite. In addition, a rhombohedral face of the former is in contact with a scalenohedral face of the latter, consequently the other rhombohedral edges of the calcite and sodium nitrate were not parallel to one another. The form $e\{-110\}$, which terminated the crystal, was very rough and apparently corroded, and no regular growths were obtained either on it or on the faces of the form $b\{-2\bar{1}1\}$.

Since the forms r and v both lie in the rhombohedral zones, it was

thought that other forms lying in those zones might produce a regular deposit. The best form for this investigation was the rare prism form $a\{-1\bar{1}0\}$; a crystal with good faces of this form was thoroughly cleaned by allowing to cool in a hot saturated solution for a week. On taking it out and allowing the solution adhering to it to evaporate, small rhombohedra of sodium nitrate were obtained in a definite orientation. The forms on the calcite were a , r , and v , and the orientation was the one expected, namely, a face r of the sodium nitrate in contact with the prism a , and an edge $r:r$ parallel to the edge $a:v=r:r$ of the calcite (Fig. 2). On this crystal, no regular growths were observed

FIG. 2.



on the scalenohedron faces; it may be here remarked that the only face which never fails to give a regular growth is a fresh cleavage surface. Only crystals free from cleavage cracks were employed in this connection, as it is conceivable that minute cleavage surfaces, if present, would cause a regular deposition.

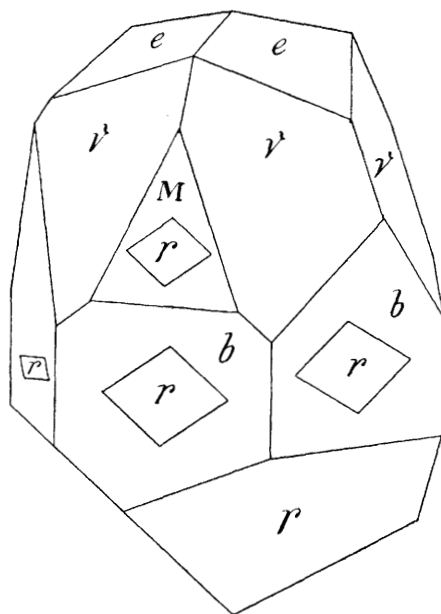
Repeated attempts were made with various crystals exhibiting the ordinary prism $b\{-2\bar{1}1\}$ to obtain regular deposits; these were for a long time uniformly unsuccessful. This led the author to the conclusion that regular growths could only be obtained on faces lying in the zones $[rr]$. The experiments were repeated later, however, with crystals from Egremont, Cumberland, which have been described by Miers (*Min. Mag.*, 1889, 8, 149) and produced a regular growth. In addition to $b\{-2\bar{1}1\}$, the crystals exhibited v , e , and a rare rhombohedral form $M=\{3\bar{1}1\}$ or $\{04\bar{4}1\}$ (Dana); bM measured $=13^{\circ}58'$, calculated $14^{\circ}13'$

(Fig. 3). Both the forms b and M were found to be covered with rhombohedra, so orientated that the longer diagonal of each rhomb was parallel to the edge $b : M$ of the calcite (compare Fig. 3).

Growths on the Rhombohedral Carbonates, Isomorphous with Calcite.

The other rhombohedral carbonates of the calcite group were then brought into the scope of this inquiry, and both methods, drops viewed under the microscope, and the cooling of hot saturated solu-

FIG. 3.



tions in beakers containing cleavage-pieces of the minerals, were used. Not a single case of parallel growth, however, has been obtained.

The dolomites used included pearlspar and specimens from Traversella. The chalybites included specimens from Wheal Maudlin, Alston, Aberdeen, Traversella, and Neudorf, Harz. Diallogite from Hungary, calamine from the Thüringerwald, breunnerite and rhodocrosite have all given negative results. The monoclinic, pseudo-rhombohedral baryto-calcite also induced no regular orientation.

Discussion of Parallel and Regular Growths.

The experiments on the calcite group prove conclusively that similarity of rhombohedral angle is not the predisposing cause for the

parallel deposition of sodium nitrate, for the difference between the rhombohedral angle of calcite and sodium nitrate is far greater than between sodium nitrate and the other rhombohedral carbonates.

The question immediately arises whether this is due to a difference of symmetry or of internal structure of the minerals. Now there seems to be no doubt that dolomite possesses a lower type of symmetry than calcite, for, to mention only one piece of evidence, etching figures point to the absence of the three principal planes of symmetry possessed by calcite. Dolomite therefore belongs to the diopside class (hexagonal alternating).

The question as to the symmetry of the other rhombohedral carbonates of this group is still an open one. According to Tschermak (*Anzeiger d. Akad. d. Wiss. zu Wien*, 1880, No. 19), both symmetrical and unsymmetrical etching figures are obtained by the action of hydrochloric acid on chalybite and magnesite, the latter exhibiting a greater proportion of unsymmetrical figures than the former; rhodochrosite behaves in the same way, whilst calamine gives no definite results.

The author believes that, even if some slight difference of symmetry exist, the non-formation of parallel growths cannot be attributed to that alone; because several pairs of substances have been found by him to give parallel growths, although they do not possess the same symmetry. If, for example, a drop of an aqueous solution of potassium chloride be placed on a fresh cleavage surface of rock salt, cubes of potassium chloride immediately appear in parallel position. It is certain that the cubes deposited do consist of potassium chloride, for they appear immediately, before much solution of the rock salt can have taken place, and, secondly, the two salts in question do not form isomorphous mixtures. Since rock salt appears to belong to the holohedral, potassium chloride to the holoaxial, class of the cubic system, a difference of symmetry within the system does not prevent a parallel deposition. In spite of difference of symmetry, the two structures probably possess some similarity, for the two salts possess a perfect cubic cleavage. Similarly, all the rhombohedral carbonates belong to the same system and possess many properties in common, notably a good rhombohedral cleavage; the composition, again, is similar: it may therefore be concluded that the above analogy between them on the one hand and sodium chloride and potassium chloride on the other is a legitimate one.

It is conceivable that in the case of two "isostructural" substances the actual size of the structural unit may be of the greatest importance in determining whether or not parallel deposition shall take place. Now whatever the structural unit may be, it is probable that, in an isostructural series of substances, the structural units will bear the same relations to each other as the molecular volumes.

In the rhombohedral series of carbonates, the similarity of cleavage speaks for a similarity of structure. If, therefore, cleavage rhombohedra of the members of the group be taken of such sizes that their volumes are proportional to the molecular volumes of the substances, their edges may be taken to represent the intervals between the crystal units spaced along those directions, and are known as the topic axes. The latter are calculated from the formula

$$\chi = \psi = \omega = \frac{3\sqrt{V}}{\sin 60^\circ \sqrt{C}}.$$

In consequence of the similarity of cleavage and of other physical properties, sodium nitrate may be regarded as belonging to the same isostructural series, and it is therefore possible to compare the intervals in the structure of sodium nitrate with the corresponding intervals of the rhombohedral carbonates.

The values of the ratios $c:a$ in the following list are taken from Groth's *Physikalische Krystallographie*, 3rd edition; the molecular volumes are due to Tschermak (*loc. cit.*).

Table of Axial Ratios, Molecular Volumes, and Topic Axes of the Calcite Group.

	$r:r.$	$c:a.$	$v.$	$\chi.$
(Na,Ag)NO ₃	?	?	$\left\{ \begin{array}{l} 38.6 \\ 37.8 \end{array} \right\}$?
NaNO ₃	73°30'	0.8276	37.8	4.1276
Calcite	74 55	0.8543	36.8	4.0478
(Dolomite).....	73 45	0.8322	32.1	3.9015
Rhodochrosite	73 0	0.8183	31.0	3.8781
Chalybite	73 2	0.8191	30.2	3.8432
Calamine	72 19	0.8062	28.2	3.7763

It will be seen from the above table that sodium nitrate is more nearly related to calcite than to any other member of the series both as regards molecular volume and topic axes. It therefore seems to suggest that the requisite condition for a parallel deposition is a not too great disparity of molecular volume, and, hence, of topic axes. If the distances between the structural units of two isostructural substances be greatly different, it may be expected that the structure of one will not fit into the structure of the other, and the crystals of one substance, grown on a crystal of the other, may have no definite orientation.

The regular growths of sodium nitrate on forms of calcite other than the rhombohedron are, perhaps, of greater interest than those on the rhombohedron itself. In the latter case, the whole orientation of the crystals of sodium nitrate is, as far as the small differences of angle

allow, entirely congruent with the calcite. When we consider the parallel growths of rhombohedra of sodium nitrate on other forms of calcite, it is at once seen that the only possible congruence is that of a similar edge or zone axis, for the faces of contact are of necessity dissimilar.

In the case of the regular growths on the two forms $a\{1\bar{1}0\}$ and $v\{2\bar{1}0\}$, a rhombohedral zone axis was congruent, and the faces of the above two forms themselves lie in the rhombohedral zones. On the other hand, with the forms $b\{2\bar{1}1\}$ and $M\{3\bar{1}1\}$, the crystals of sodium nitrate were so orientated as to bring the edge $b:M$, the axis of the zone $[011]$, into congruence with the corresponding edge of the calcite.

Although the line, zone axis $[bM]$, is not itself present as a crystal edge on the rhombohedra of sodium nitrate, yet it exists as a line in the face.

The results show that a coincidence of edge with edge is, perhaps, of greater importance than a coincidence of plane with plane; this derives additional confirmation from the consideration that, although the parallel growths on cleavage surfaces of calcite have apparently a similar plane in congruence, yet only one similar edge in that plane can be absolutely congruent, since the plane angles of the faces are different. Further, as mentioned previously, the rhombohedra deposited on cleavage surfaces of calcite are often in twin position to the latter, and in that case it is certain that only one similar edge is congruent, namely, the twin axis.

The distances apart of the structural units in the directions of the rhombohedral edge are given by the above values for χ . Again, from the formula $\xi = 2\chi \sin \frac{\theta}{2}$, where θ is the plane rhombohedral angle, the distances apart along the edges $b:M$ may be calculated. These values for sodium nitrate and calcite are, respectively, 6.4506 and 6.2878, and it is seen that they are very close.

In the above experiments, regular growths of rhombohedra of sodium nitrate were ultimately obtained on all the forms of the calcite crystals, with the exception of the form $c\{110\}$, the faces of which were always corroded. The question arises whether regular growths could be obtained on any form of calcite whatsoever, provided, of course, the crystal be thoroughly cleansed, so as to lay bare the unimpaired structure. The answer may be in the affirmative, because a similar direction can always be found in the rhombohedral face and in the face of the form in question. This similar direction is, of course, given by the edge of intersection of the two planes.

(II) *The Potassium Perchlorate—Barytes Group.*

The experiments on sodium nitrate and the calcite group had led to the suspicion that in such a group the parallel growth is not conditioned by the similarity of axial ratios (or of the angular measurements) alone; since if this were so, the sodium nitrate would crystallise in parallel position with more facility on chalybite than on calcite, whereas we have seen that the converse holds. The group is somewhat unsatisfactory, for only the mineral, and not the substance deposited, can be varied. Attempts were made to find a group of minerals isostructural with a series of isomorphous salts and possessing, if possible, good cleavages. It was at last found that the perchlorate and permanganate of potassium are remarkably like the barytes group of minerals. Preliminary experiments having proved that the former salt is regularly deposited on barytes from aqueous solution, the author resolved to study the growth of all substances isomorphous with that salt on the minerals celestine and anglesite, which are strictly isomorphous with barytes, and, in addition, on anhydrite.

Crystallography of the Perchlorates and Permanganates.

The permanganates of potassium, rubidium, caesium, and ammonium have already been described by Muthmann (*Zeit. Kryst. Min.*, 1894, 22, 527), whilst of the perchlorates the potassium salt was previously measured by Groth (*Ann. Phys. Chem.*, 1868, 133, 193) and the ammonium salt by Mitscherlich (*Ann. Phys. Chem.*, 1832, 25, 300). Rubidium and caesium perchlorates have not previously been measured. The following is a brief account of the perchlorates and permanganates; a more complete description will appear shortly.

Preparation and Analysis of the Perchlorates.

The source of all the perchlorates was the commercially pure potassium salt, which was submitted to several recrystallisations; the operation is very effective with this salt owing to its slight solubility. The other salts were made by the double decomposition of solutions of barium perchlorate and the sulphate of the metal, the barium perchlorate itself being prepared from potassium perchlorate by the method given by Groth (*loc. cit.*). The sulphates of rubidium, caesium, and thallium were obtained from Merck. Perfect mutual decomposition of the metallic sulphate and the barium perchlorate was ensured by testing the solution on a glass slide viewed in a microscope. The high purity of the salts was shown by the analyses, which consisted in chlorine estimations by the Carius method. The heating

was done in two operations, each lasting four hours, the capillaries being opened at the end of the first operation in order to relieve the pressure of gas. The silver chloride was estimated gravimetrically.

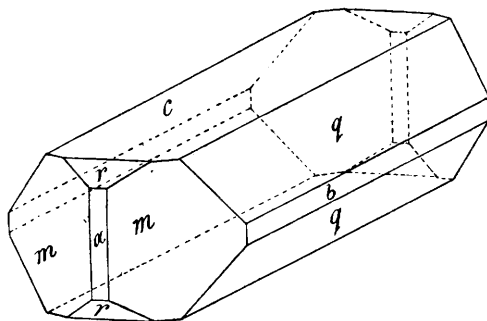
Rubidium perchlorate : 0.1611 gave 0.1264 AgCl. Cl = 19.40.
 RbClO_4 requires 19.18 per cent.

Cæsium perchlorate : 0.2810 gave 0.1749 AgCl. Cl = 15.39.
 CsClO_4 requires 15.26 per cent.

The isomorphous perchlorates and permanganates dealt with crystallise in the orthorhombic system and possess two very good sets of cleavage-directions, namely, parallel to the basal plane, and the prism. The indices allotted to the forms throughout the whole of this paper are those usually given to the barytes group, where the cleavage prism is $\{110\}$ and the brachydome $\{011\}$. The reasons for this were twofold : first, the salts greatly resemble the members of the barytes group of minerals, and, secondly, this orientation leads to a simplification of indices. The indices adopted by Muthmann for the permanganates lead to a value for the ratio $c:b$ which is one-half that adopted by the author.

Potassium Perchlorate.—Sixteen crystals obtained from two crops were measured. The habit was of two kinds : (1) prismatic, elongated along the axis- a (shown in Fig. 4), (2) tabular, parallel to c - $\{001\}$. The forms present were $c = \{001\}$, $q = \{011\}$, $m = \{110\}$, $r = \{102\}$, $b = \{010\}$, $s = \{111\}$, and $a = \{100\}$.

FIG. 4.

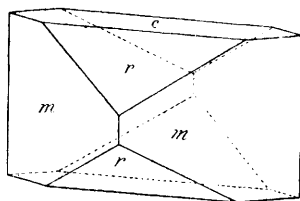


Rubidium Perchlorate.—This salt was first prepared by Longuine (*Ann. Chem. Pharm.*, 1862, 121, 123). It is less soluble than potassium perchlorate, but very good crystals were obtained by slowly cooling hot saturated solutions ; of these, nineteen crystals selected from three crops were measured. The habit of the crystals was very

like that of the caesium salt, which is shown in Fig. 5. The forms present were $m = \{110\}$, $c = \{001\}$, $r = \{102\}$, $s = \{111\}$ and $b = \{010\}$.

Cæsium perchlorate was first prepared by Setterberg (*Öfver. K. Vet. Akad. Förh.*, 1882, 6, 23). Fifteen crystals obtained from one crop were measured. The larger crystals were of the habit shown in Fig. 5, whilst the smaller ones were more elongated along the axis- b

FIG. 5.



and more tabular parallel to $c\text{-}\{001\}$. The following forms were observed: $m = \{110\}$, $r = \{102\}$, $c = \{001\}$, $s = \{111\}$ and $q = \{011\}$; s and q were rarely present.

Ammonium Perchlorate.—Several fruitless attempts to get good crystals were made, but at last a fairly good crop was obtained from a hot solution; twelve crystals were measured. The habit was slightly prismatic owing to an elongation along the axis- c . Of the forms present— $m = \{110\}$, $c = \{001\}$, $r = \{102\}$, $a = \{100\}$ and $q = \{011\}$ — m and c preponderated, r being generally small; q was only once observed.

Thallium Perchlorate.—This salt was first prepared and also measured by Roscoe (*Trans.*, 1866, 19, 504). As the author did not succeed in obtaining crystals good enough to warrant a re-measurement, the values of Roscoe are used in this paper. The crystals were slightly elongated along the axis- b , rarely the axis- c , and the forms $c = \{001\}$, $r = \{102\}$, and $m = \{110\}$ were present.

The specific gravities were determined by the method due to Retgers (*Zeit. physikal. Chem.*, 1889, 3, 289 and 497), which has been lately used by Tutton (*Trans.*, 1905, 87, 1130), and the directions given by Tutton were all observed. Methylene iodide and benzene were the liquids used. The weighings were corrected for displaced air, but the specific gravities were not reduced to a standard temperature, since the temperatures were so close to those at which Muthmann worked that a correction would only amount to one unit in the third place of decimals. Three to six determinations were made for each salt, fresh, carefully selected crystals being used each time. A single determination of the specific gravity of potassium perchlorate was

made, but the value obtained was so close to that determined by Muthmann that his number was adopted.

Following is a table of some of the more important crystallographic constants of the perchlorates and permanganates. The atomic weights used for the perchlorates were taken from the International Table for 1904, $O=16$. The data for the permanganates were taken directly from Muthmann's memoir. A table of the axial ratios is given on p. 1139.

Crystallographic Constants of the Perchlorates and Permanganates.

	$m : m.$	$c : q.$	$c : r.$	Mol. wt.	Sp. gr.	Mol. vol.
KClO ₄	76° 1'	52° 1'	39°19 $\frac{1}{2}$ '	138.60	2.524	54.91
RbClO ₄ ...	77 5	—	38 57	184.85	3.014	61.33
CsClO ₄	78 31	52 23	38 27	232.35	3.317	70.05
AmClO ₄ ...	76 50 $\frac{1}{2}$	52 1	38 55	117.49	1.952	60.19
TlClO ₄	77 10	—	38.57	303.55	4.844	62.66
KMnO ₄	77 8	52 24	39 9	158.226	2.7035	58.526
RbMnO ₄ ...	79 28	53 7	38 43	204.530	3.2248	63.228
CsMnO ₄ ...	81 56	53 53	38 17	251.97	3.5974	70.042
AmMnO ₄ ..	78 28	52 47	38 53	137.144	2.2076	62.126

It is seen from the above table that all the constants of rubidium perchlorate are intermediate between those of potassium perchlorate and caesium perchlorate; again, the angles and molecular volumes of ammonium perchlorate and thallium perchlorate are very close to those of rubidium perchlorate, although the molecular weight of ammonium perchlorate is very low, whilst that of thallium perchlorate is very high. Further, since Tutton has shown that the angles of all the ammonium salts which he has investigated are very close to those of the corresponding rubidium compounds, it seems to follow that in an isomorphous series molecular weight alone does not determine the angles. The relations between the perchlorates are also seen to hold good for the permanganates. A comparison of the molecular volumes of the perchlorates and permanganates shows that the replacement of a chlorine by a manganese atom is accompanied by an increase of molecular volume in the potassium and rubidium salts and a decrease in the caesium and ammonium salts; the amount of change is greatest with the potassium and smallest with the caesium salts; this is in accordance with the fact that the relative change in the molecule is greatest with the salt possessing the lowest molecular weight.

A perusal of the tables of axial ratios given on page 1139 will prove that in both series—the perchlorates and permanganates—there is apparently a regular increase in the relative length of the axes a and c with regard to b , and also of the ratio of a to c , on replacing potassium by the heavier atom rubidium, and the latter by the still heavier atom caesium; in other words, there is a regular progression

of the ratios of the axes with molecular weight : but the values of the ammonium salts lie between those for the potassium and rubidium salt, and approximate more closely to the latter than the former. Again, the values for thallium perchlorate are almost identical with those for rubidium perchlorate. Finally, the ratios $a:b$ and $c:b$ of any permanganate are greater than those of the corresponding perchlorate.

Structure and Topic Axes.

The axial ratios of a series of isomorphous salts like the perchlorates and permanganates are not strictly comparable, since they only express, for each salt, the relative lengths of the axes- a and $-c$ with regard to the axis- b ; the ratio to each other of the b -axes of any two salts, however, is unknown. Now, by cleaving a crystal of any member of the group along the planes c and m , a parallelepipedon could be obtained such that its height and diagonals are proportional to the lengths of the crystallographic axes- c , $-a$, and $-b$ respectively. Moreover, if cleavage parallelepipeds of the perchlorates and permanganates, derived as above, be taken of such sizes that their volumes are proportional to the molecular volumes of the substances, they may be taken to represent the elementary cells at whose corners eight crystal-units are situated, whilst no such units are contained within the cells; their edges may, therefore, be taken to represent the intervals between the crystal-units measured along those directions, and are the topic axes. A table of the topic axes of the perchlorates and permanganates is given on page 1142, from which it is evident that the values of the topic axes of each rubidium salt lie between the corresponding values of the potassium and cesium salt, whilst the thallium and ammonium salts are very close to the rubidium salts. The replacement of the chlorine by the manganese atom generally effects an increase in the values of the topic axes.

It is obvious from the above that the degree of isomorphism between the perchlorates and permanganates is very close and quite comparable with that exhibited by, say, the metallic sulphates and selenates. Now, perhaps the chief evidence in favour of placing the element manganese in the seventh group of the periodic classification is derived from the close relationship of the permanganates and the perchlorates; and not the least important conclusion of the above work is, that this evidence, so far as it goes, is of the strongest possible kind. It may be added that the perchlorates and permanganates exhibit two other important properties possessed by isomorphous substances : namely, the formation of parallel growths and of mixed crystals.

Experiments on the Deposition of Potassium Perchlorate and Potassium Permanganate on the Barytes-minerals.

As mentioned above, the first regularity in growth noticed was that crystals of potassium perchlorate are deposited from aqueous solutions on barytes in regularly orientated positions. The deposition is regular on both cleavages, namely, parallel to c and m .

The following points are worthy of notice. On the c -cleavage, the small crystals of potassium perchlorate are bounded by the pinacoids a and b , the prism- m being but slightly developed when not entirely absent; in the case of the macroscopic crystals of potassium perchlorate measured, on the other hand, the prism is the dominant form in the zone $[001]$. The face of contact is $c\{001\}$, as was subsequently proved by the goniometrical measurement of large crystals grown on the basal cleavage of barytes. The edges ca , cb of the crystals of potassium perchlorate were parallel to the extinction directions of the barytes, and therefore bisected the prism angles of the latter.

The microscopic crystals deposited on prism-cleavages of barytes had each a prism face in contact; the boundaries of the crystals were the traces of the form c , a pair of prism faces, and $s\{111\}$; the edges $c:m$ were congruent. The crystals of potassium perchlorate, therefore, are entirely parallel with the crystals of barytes, in so far as the small differences of angles will allow.

The same was found to be true for cleavage-pieces of celestine; good cleavages of anglesite were not available.

Potassium permanganate also gave regularly orientated crystals on the basal and prismatic cleavages of barytes. The crystals appeared to be combinations of $a\{100\}$, $m\{110\}$ and $c\{001\}$, and were generally elongated along the axis- b ; by illuminating the slide from above, however, it was seen that the crystals are really combinations of the above forms together with $r\{102\}$. The edges $c:m$ were always parallel to the corresponding edges $C:M$ of the barytes.

The progress of growth on the prism-cleavage was very interesting: the potassium permanganate began to crystallise in small isosceles triangles, the bases of which were all parallel to the edge $M:M$ of the barytes. The mean value for the interior vertical angle was 51° ; the triangles grew in the direction of the base, and, in general, developed three new sides, thus becoming elongated, six-sided crystals. The orientation here is identical with that of the barytes, for the above interior angle, calculated on the supposition that the faces are r and c —the crystal lying on m —is $53^\circ 49'$, which is sufficiently close to the microscope-reading.

In two or three cases it has been observed that two crystals,

joined together, have, on further growth, given rise to one of the above-mentioned isosceles triangles. Such pairs of crystals would seem to be twinned on the face $C\{001\}$ (if C is really not a plane of symmetry), but their opacity renders optical experiments impossible, and prevents a further examination; on the other hand, no macroscopic twin-crystals of the perchlorates or permanganates have been observed.

The growths of potassium permanganate are also parallel on basal cleavages of celestine. The prism-cleavage of the latter mineral is not so good as that of barytes, and it was found that the growths of potassium permanganate on this cleavage are generally irregular; whether this is due to the rough surface, or to another cause hereafter mentioned, has not been settled.

Drops of solutions of the perchlorates of rubidium, caesium, ammonium, and thallium, and permanganates of rubidium, caesium, ammonium, and barium were then allowed to evaporate on cleavage flakes of barytes and celestine, and a parallel growth of ammonium permanganate was once observed on a basal cleavage of barytes; in none of the other cases was a definite orientation noticeable.

An account of the forms noticed on the crystals of the various salts is given below.

RbClO_4 :—Generally simple combinations of the basal plane and the prism, a microscope-reading of the prism-angle gave 79° ; a few crystals were elongated like the crystals of potassium permanganate along the axis- b .

CsClO_4 :—Often feathery aggregates, but a very few thin plates were measureable, and gave a reading of 80° for the prism-angle.

TlClO_4 :—Exhibited the forms c , r , m , and rarely q ? $m : m = 77\frac{1}{2}^\circ$.

AmClO_4 :—Very similar to thallium perchlorate.

RbMnO_4 :—Very similar to potassium permanganate.

CsMnO_4 :—Some crystals were obviously lying on the c -face, $m : m = 82^\circ$; r and s were also noticed.

AmMnO_4 :—The habit was the same as that of potassium permanganate; the growths observed on m - and c -cleavages of celestine, and on the m -cleavage of barytes, were never parallel; this was generally true of the c -cleavage of barytes also. In one case of the latter, however, eight small crystals, near to each other, were found to be parallel; all the remaining crystals (above 100 in number) were totally irregular. Further attempts to obtain a parallel growth on many other cleavage-pieces were fruitless.

$\text{Ba}(\text{MnO}_4)_2$:—Was also irregular (orthorhombic "cubes").

Solutions in all proportions of potassium perchlorate and permanganate deposited regularly orientated mixed-crystals on barytes without exception.

Further attempts were made to obtain parallel growths by immersing cleavage-pieces of the barytes-minerals in hot saturated solutions of the various salts, and allowing to cool slowly. Beautiful, large crystals of potassium perchlorate have thus been obtained, grown on the *c*- and *m*-cleavages of barytes and celestine, and on natural crystals of anglesite and barytes. The crystals of potassium perchlorate were always parallel to the mineral on which they were deposited. The natural crystal of barytes employed was two inches long in the direction of the *b*-axis, and exhibited the forms *r*, *m*, and *c*; and the crystals of potassium perchlorate, deposited on all these forms, had the same orientation as the barytes, the faces of contact being *r*, *m* and *c* respectively. The crystal of anglesite was not so good, but measurement on the two-circle goniometer proved that the crystals grown on it were parallel with itself.

The perchlorates of rubidium, cæsium, ammonium, and thallium and permanganates of rubidium and cæsium all failed to give definitely orientated growths. In the case of the permanganates, the cleavage-pieces were found to be covered with a scum, possibly manganese dioxide.

Growths on Anhydrite.

Anhydrite, CaSO_4 , possesses three good cleavages parallel to the three pinacoids; it is therefore not isostructural with the permanganates and perchlorates of the alkalis. Nevertheless, attempts were made to obtain regular growths on all three cleavages. The salts used with the drop method were ammonium perchlorate and the permanganates of potassium, rubidium, cæsium, and ammonium; with the cooling method, the perchlorates of potassium, rubidium, cæsium, and ammonium. No regular growths were obtained by either method.

Discussion of Results of Experiments on the Barytes Group.

The axial ratios of the minerals in the barytes group are:

Anglesite	$a : b : c = 0.7852 : 1 : 1.2894$
Celestine	$a : b : c = 0.7811 : 1 : 1.2830$
Barytes	$a : b : c = 0.8152 : 1 : 1.3136$

Whilst those of the salts investigated are:

	a	b	c		a	b	c
KClO_4	0.7815	1	1.2805	AmMnO_4	0.8164	1	1.3168
AmClO_4	0.7932	1	1.2808	CsClO_4	0.8172	1	1.2976
RbClO_4	0.7967	1	1.2882	RbMnO_4	0.8311	1	1.3323
KMnO_4	0.7972	1	1.2982	CsMnO_4	0.8533	1	1.3705
TiClO_4	0.7978	1	1.2898				

It is therefore evident that similarity of axial ratios, and the attendant similarity of angles, is not the favouring factor for a parallel deposition. Following is a table of the prism angles :

Celestine	75°58'	TlClO ₄	77°10'
KClO ₄	76 1	Barytes	78 23
Anglesite	76 17	AmMnO ₄	78 27½
AmClO ₄	76 50½	CsClO ₄	78 31
RbClO ₄	77 5½	RbMnO ₄	79 2½
KMnO ₄	77 8	CsMnO ₄	81 56

Now we have seen that potassium perchlorate will grow in parallel position on either celestine or barytes, the difference in prism angle being +0°3' and -2°22' respectively ; whereas rubidium perchlorate will not grow regularly on either, the corresponding differences being +1°7' and -1°17'. Again, the difference between $m:m$ for barytes and caesium perchlorate is -8' only, and yet no regular deposition takes place.

On turning to the molecular volumes, however, we find a most remarkable connection between the similarity of the values of this constant and the formation of parallel growths.

The molecular volumes are in the following order :

Celestine, 46·8 ; anglesite, 48·2 ; barytes, 52·0 ; KClO₄, 54·915 ; KMnO₄, 58·498 ; AmClO₄, 60·19 ; RbClO₄, 61·33 ; AmMnO₄, 62·076 ; TlClO₄, 62·66 ; RbMnO₄, 63·415 ; CsMnO₄, 70·023 ; CsClO₄, 70·05 ; and one sees at once that in those cases in which parallel depositions have been observed there is a closeness in the values of the molecular volumes ; for example, no salt having a greater molecular volume than that of potassium permanganate (with the exception of the isolated observation with ammonium permanganate) has offered any parallel growths on any of the minerals of the barytes group. As mentioned above, the difficulty of obtaining parallel growths of potassium permanganate on the m -cleavage of celestine may be partly due to the somewhat inferior cleavage ; but it is worthy of notice that celestine has a lower molecular volume than barytes. Again, ammonium permanganate was only once obtained on barytes, never on celestine.

Hence, in the above series, it is similarity of molecular volume which determines whether there shall or shall not be parallel growth, whereas conclusions drawn from a similarity of angle alone (or of axial ratios) would be erroneous.

The conception of topic axes, suggested by Becke and employed so successfully by Muthmann and Tutton in their work on isomorphous series, embodies the relationships both of molecular volumes and axial ratios as described above under calcite ; by their use, one can compare isostructural substances with each other, and draw conclusions regard-

ing the relative distances apart of the structural units, and hence the reticular densities in all planes can be calculated; further, such densities and distances apart are comparable for all isostructural members. The merit of this method especially lies in the last statement: for Bravais long ago showed how to calculate the relative distances apart of the structural units, and also the reticular densities, of an individual salt; the values so obtained for an individual salt, however, are not comparable with each other, since a different arbitrary unit—namely, axis $b = 1$ —is taken for each salt.

In order to make justifiable comparisons, one must be certain that the structure of the salts to be compared is similar. Now the extraordinary similarity of angles, cleavage, molecular volume, and, in addition, the formation of similarly orientated overgrowths, argue for a similarity of structure in the barytes group and the isomorphous series of the permanganates and perchlorates; we are therefore justified in making comparisons between the various members of these three groups; comparisons between such groups have not previously been made.

The structure of all the above substances is probably founded on the orthorhombic-prism space-lattice, for a maximum reticular density in the cleavage directions c and m is thereby obtained.

Just as the topic axes of the rhombohedral group were calculated from the cleavage rhombohedra, so in the barytes-perchlorate-permanganate series, topic axes can be calculated from the cleavage parallelepipeda formed by the forms c and m , and they enable us to compare corresponding lengths along their edges.

In the following table, ω and ξ represent corresponding lengths along the edges $m:m$ and $m:c$ respectively of the elementary parallelepiped; χ and ψ are their diagonals: so that χ , ψ , ω , and ξ represent distances between contiguous crystal-units.

The values of χ , ψ , ω , and ξ are obtained from the formulæ:

$$\chi = \sqrt{\frac{3}{2} \frac{V a^2}{c}}; \psi = \sqrt{\frac{3}{2} \frac{V}{ac}}; \omega = \sqrt{\frac{3}{2} \frac{V c^2}{a}}; \text{ and } \xi = \sqrt{\frac{1}{\chi^2 + \psi^2}},$$

where V is the molecular volume, a and c the axial ratios.

Since the topic axes are simple functions of the molecular volume and the axial ratios, and since the axial ratios betray far less differences than the molecular volumes, it is not surprising that the topic axes, when arranged in order of magnitude, follow, in general, the same sequence as the molecular volumes.

Topic Axes of the Potassium Perchlorate—Barytes Group.

	χ .	ψ .	ω .	ξ .
Celestine	3·5349	4·5931	5·7649	2·8980
Anglesite	3·5743	4·5520	5·8694	2·8938
Barytes	3·6509	4·7899	5·9472	3·0113
KClO ₄	3·7360	4·7878	6·1307	3·0365
KMnO ₄	3·8555	4·8360	6·2779	3·0924
AmClO ₄	3·8959	4·9117	6·2909	3·1346
RbClO ₄	3·9244	4·9264	6·3447	3·1492
AmMnO ₄	3·9757	4·8698	6·4126	3·1433
TlClO ₄	3·9964	5·0093	6·2606	3·2040
RbMnO ₄	4·0362	4·8565	6·4704	3·1574
CsClO ₄	4·1625	5·0929	6·6086	3·2888
CsMnO ₄	4·2551	4·9005	6·7161	3·2450

It is seen from the table that all the topic axes of potassium perchlorate and potassium permanganate are closer to those of the three minerals than are the topic axes of the remaining salts, which all failed to give parallel growths. Therefore, in these three groups of compounds—perchlorates, permanganates, and sulphates—as in the two rhombohedral groups studied above, a consideration of the topic axes enables one to predict which crystals are capable of growing in parallel position on each other. The result may be stated, then, as follows. In an isostructural series, those structures which are most nearly congruent, as indicated by similarity of molecular volume or of topic axes, are the structures which yield parallel growths. If this be true, then it is possible that salts such as rubidium permanganate, caesium permanganate, &c., which fail to give parallel growths on barytes, may grow in parallel position on potassium perchlorate or permanganate. Experiments fully confirming this prediction are described on page 1152.

We are now in a position to account for the insignificant part played by similarity of axial ratios (with the attendant similarity of angles) in conditioning a parallel growth; these ratios simply determine the solid and plane angles and the ratios of the lengths of the edges of the elementary parallelepipedal cell; they do not determine the volume of the same, nor do they give us the distances between contiguous crystal-units; as seen above, the latter depend rather on the molecular volumes. It follows, then, that the difference between the spacing of the crystal-units of two isostructural substances like barium sulphate and caesium perchlorate is not necessarily small, although the angles are almost identical. On the other hand, two substances like potassium perchlorate and barium sulphate may exhibit great differences in angles, and yet the spacing of their crystal-units may be almost identical.

Following is a list of mesh-areas, formed by four contiguous crystal-

units in the two planes $c\{001\}$ and $m\{110\}$ —the planes on which attempts were made to obtain parallel growths; these areas are inversely proportional to the reticular densities. The area in the plane $c\{001\}$ is equal to the product $\frac{1}{2}\chi\psi$, the value in the plane $m\{110\}$ being $\xi\omega$.

List of Mesh-areas.

	$c\{001\}$.	$m\{110\}$.		$c\{001\}$.	$m\{110\}$.
Celestine	8·1181	16·706	RbClO ₄	9·6664	19·980
Anglesite	8·1351	16·985	AmMnO ₄	9·6804	20·157
Barytes	8·7437	17·909	TlClO ₄	10·010	20·059
KClO ₄	8·9437	18·616	RbMnO ₄	9·8003	20·429
KMnO ₄	9·3225	19·414	CsClO ₄	10·600	21·734
AmClO ₄	9·5678	19·720	CsMnO ₄	10·426	21·794

The far less mesh-area in the plane $c\{001\}$ than in the plane $m\{110\}$ is in harmony with the fact that the basal cleavage is better than the prismatic.

The above two large groups of substances supplement each other admirably, for in the calcite—sodium nitrate group we have only one salt to five or six minerals, whereas in the potassium perchlorate—barytes group we have three minerals and nine salts. The results obtained from both groups are identical, and especially show the importance of molecular volumes. Topic axes, which are the axial ratios interpreted in terms of molecular volume, not only emphasise the important part played by molecular volumes, but also the comparative insignificance of similarity of angle in determining parallel depositions of isostructural substances on each other.

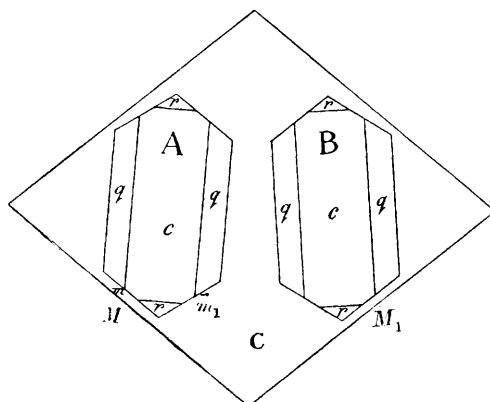
Exact Orientation of the Crystals on each other.

The crystals of the above salts cannot be absolutely congruent with the crystal of the mineral on which they are deposited, since the crystal elements are not identical. It is, therefore, of considerable interest to know what the exact orientation really is. Granted that the faces of contact lie in a plane, it still remains to determine which edges, if any, are parallel. The pair of substances chosen for the elucidation of this point was potassium perchlorate and barytes, for they exhibit the greatest difference of angle. Several fresh cleavage plates were immersed in hot saturated solutions of the former salt, which were allowed to cool slowly. The crystals were carefully dried, avoiding as far as possible any pressure which might slightly alter the orientation of the super-imposed crystals. Sometimes the crystals of potassium perchlorate were not dried by actual contact with filter-paper, but the latter was placed in contact with the barytes and the solution thus absorbed. The growths were measured on the two-circle goniometer, which is invaluable for such work.

Consider, first, the case of a crystal of potassium perchlorate growing on barytes with two prism faces in contact; then, if an edge $m:c$ of the one is parallel to an edge $M:C$ of the other, the edges $m:m$, $M:M$ must be parallel, since in both substances the angle $c:m$ is 90° . The angles between the planes of contact m and M , and the other faces, m_1 and M_1 , respectively, however, will not be the same, since $m:m_1$ and $M:M_1$ differ by $2^\circ 22'$.

The results obtained, although pointing to the above as the ideal position, showed slight variations therefrom. The angle between the faces of contact—which ideally should be 0° —was never greater than $20'$, and generally was a few minutes only. It was also found that

FIG. 6.



the edge $c:m$ is parallel to the edge $C:M$, and the angle $m_1:M_1$ always approximated to the theoretical angle $2^\circ 22'$.

Now consider the growths on the basal cleavages of barytes; granted that the contact-faces are parallel, the question arises whether an edge $c:m$ of the potassium perchlorate is parallel to an edge $C:M$ of the barytes, the other edge $c:m_1$ consequently making an angle of $2^\circ 22'$ with the edge $C:M_1$, or whether the crystallographic axes are parallel instead of these pairs of edges. Now, if the first alternative be correct, there is no reason why one pair of edges $C:M$, $c:m$ should be preferred to the other pair, and when several crystals of potassium perchlorate are grown on one crystal of barytes, there is no reason why the former, *inter se*, should be exactly congruent; if, however, the crystallographic axes be parallel, it follows necessarily that all the crystals of potassium perchlorate will be congruent.

The goniometrical results showed that the contact-faces were coplanar (subject to variations of a few minutes); they proved, too, that although the positions of various crystals on the same piece of barytes varied by $2\frac{1}{2}^\circ$, they yet tended to be such that either the edges $m : c$, $M : C$ or the edges $m_1 : c$, $M_1 : C$ were parallel. It will be seen from Fig. 6 that the position of crystal *B* can be derived from that of crystal *A* by a counter-clock-wise rotation of $2^\circ 22'$; rarely was a crystal orientated in a position derivable from that of *A* by a small clock-wise, or from that of *B* by a small counter-clock-wise, rotation, in which cases no prism edges would be parallel. Thus, so far as could be made out, it is the prism edges which are congruent. Now, parallel growths may be regarded as the result of the fitting together of two similar and almost identical structures; hence, it might follow that, in a parallel growth, those similar edges of the two substances would be absolutely congruent along which the crystal-units are most nearly equally spaced. The topic axes of potassium perchlorate and barytes are:

	χ .	ψ .	ω .	ξ .
KClO ₄	3.7360	4.7878	6.1307	3.0365
BaSO ₄	3.6509	4.7899	5.9472	3.0113
Difference ...	0.0851	-0.0021	0.1835	0.0252

Now the edges of the potassium perchlorate developed in contact with the barytes were $c : q$, $c : r$, and $c : m$, and the distances between contiguous crystal-units along these three directions are given by χ , ψ , and ξ respectively. Since the ψ -axes are almost identical, it would appear at first sight that the edges $c : r$ (the ψ -axes) should be parallel. But in this case (since the angle between the zones cr and cq is 90° in both substances) the edges $c : q$ would necessarily be parallel also: but these edges exhibit the greatest difference of spacing, and would not be expected to fit (compare the values of χ). On the other hand, the difference between the ξ -values is fairly small, and, moreover, the ξ -values themselves are the smallest; that is to say, the particles along the edge $c : m$ are the most densely packed, and also the most similar in the two crystals. This may account for the observed fact that a pair of edges $c : m$ is parallel.

(III) *Are Substances like Sodium Nitrate and Calcite, Barytes and Potassium Perchlorate, Isomorphous?*

The later definition of isomorphism by Mitscherlich was: "Substances possessing an analogous composition, which crystallise in the same form (or in similar forms), and which are capable of mixing in any proportions, are isomorphous"; but the terms of this definition are unsatisfactory for three reasons:

(1) Analogous chemical composition must be held to imply that dissimilar groups can replace each other, for example :

NaSi and CaAl in the feldspars.

CaSi and 2Al in the pyroxenes.

TiF₂, NbOF and WO₂ in the compounds described by Marignac.

(2) Similarity of form and angle are found with substances which probably differ in symmetry, for instance, KLiSO₄ and NaLiSO₄ ; NaCl and KCl.

(3) The formation of mixed crystals is not limited to substances of analogous composition, thus, ammonium chloride forms mixed crystals with ferrous chloride, ferric chloride, and manganic chloride ; further, the miscibility of some "isomorphous" substances is very limited indeed.

Now calcite and sodium nitrate possess certain similarities of chemical composition, in fact, they resemble each other in much the same way as do albite and anorthite, for example :

		Valencies.
{ Albite, NaAlSi ₃ O ₈	= NaSi(AlSi ₂ O ₈).	Na + Si = V. }
{ Anorthite, CaAl ₂ Si ₂ O ₈	= CaAl(AlSi ₂ O ₈).	Ca + Al = V. }
{ Sodium nitrate, NaNO ₃	= NaN(O ₃).	Na + N = VI. }
{ Calcite, CaCO ₃	= CaC(O ₃).	Ca + C = VI. }
{ Potassium perchlorate, KClO ₄	= KCl(O ₄).	K + Cl = VIII. }
{ Barytes, BaSO ₄	= BaS(O ₄).	Ba + S = VIII. }

They also possess similar forms and angles ; moreover, they exhibit the following physical properties :

Comparison of Physical Properties of Calcite and Sodium Nitrate.

	Calcite.	NaNO ₃ .
Cleavage.	{100}	{100}
$c : a$	0.8543	0.8276
$r : r$	74°55'	73°30'
Molecular volume	36.8	37.8
Topic axis ($\chi = \psi = \omega$)	4.0478	4.1276

Optical properties :—

Birefringence.	Negative.	Difference.	Negative.
Refractive indices... ω	B 1.6531	0.074	1.579
	D 1.6585	0.071	1.587
	E 1.6636	0.070	1.594
	H 1.6833	0.057	1.626
Refractive indices... ϵ	B 1.4839	0.149	1.335
	D 1.4863	0.150	1.336
	E 1.4887	0.142	1.337
	H 1.4978	0.154	1.344
$(\omega - \epsilon)$ B	0.1692	—	0.244
$(\omega - \epsilon)$ H	0.1855	—	0.282

Induced magnetism.	Diamagnetic.	Diamagnetic.
Magnetic character.	Positive.	Positive.
Artificial twinning: twin pl.	{110}	{110}
Thermal conductivity (Jannettaz).	Greater axis of ellipsoid parallel to principal axis.	

In view of the above remarkable resemblances, the question arises whether calcite and sodium nitrate should not be called isomorphous, in spite of the fact that they do not form mixed crystals.

Now there are two other properties which have been long advanced as characteristic of isomorphous substances: (1) the formation of parallel growths, (2) the relief of supersaturation of a solution by a crystal of a substance isomorphous with the solute. It has been shown that the first property is possessed by calcite and sodium nitrate; further, Professor Miers and M. Chevalier have found that calcite does relieve supersaturation in a metastable solution of sodium nitrate, and this the present author has confirmed.

The parallel growth of sodium nitrate and calcite has long been known, and it has led many mineralogists, especially Tschermak, to entertain the view that the two substances are isomorphous; yet little significance has been attributed to it by many others, partly because the case was regarded as unique. The views of Groth and Retgers may be given here, since they were most prominent in denying the isomorphism. Groth says, "Zweierlei Molecüle von sehr verschiedener Moleculargrösse können wohl, jeder Art für sich, zu einen Aufbau von übereinstimmender Struktur sich vereinigen, aber niemals können sie mit einander gemischt einen homogenen Krystall liefern. Hierin dürfte wohl die einfache Erklärung für die Tatsache liegen, das gewisse chemisch nicht analoge Körper, welche sehr ähnliche Krystallstruktur besitzen, wie Natronsalpeter und Kalkspath, zwar im Stande sind, der eine auf den Krystallen des anderen als regelmässige Fortwachsung zu krystallisieren, niemals aber isomorphe Mischungen zu liefern."

It may be pointed out that, although of different molecular weight, calcite and sodium nitrate are really not of different molecular size, for their molecular volumes are almost identical.

Retgers asserted that parallel growth may not be taken as a criterion for isomorphism. He says of parallel growth: "Das Phänomen ist nicht beschränkt auf isomorphe, sondern erstreckt sich auch auf morphotrope Körper. . . . Die ganze Erscheinung hat also nicht den geringsten Werth für chemische Schlussfolgerungen. Es ist weiter nichts als ein Influcenciren auf die Richtung bei der Ausscheidung aus dem flüssigen in den festen Zustand und sehr gut vergleichbar dem sich parallel Orientiren von Eisenstäbchen in der Nähe eines starken Magnetes." Now Retgers here confused the two terms, parallel and regular growths: although it is true that regular growths of morphotropic substances (or of substances which are apparently not even morphotropic) are known, yet parallel growths as exhibited by calcite and sodium nitrate, potassium perchlorate and barytes—that is, where the substances are isostructural and the whole orientation is congruent

—such parallel growths are not found among morphotropic substances (the feldspars being held to be isomorphous). Further, there is only a superficial analogy between parallel growths and the action of a magnet on iron-filings; because, although the magnet does orientate the filings in a definite manner, yet the position taken up by the molecules or the crystal-units of the filings is not, necessarily, congruent with the position of the molecules of the orientator—the magnet.

Retgers has proposed another definition of isomorphism: "Two substances are really only isomorphous when the physical properties of their mixed crystals are continuous functions of the chemical composition." If this definition be accepted, substances which do not, or cannot, form mixed crystals are rigidly excluded; moreover, complete investigations of the physical properties of mixed crystals have been made very seldom. Retgers, however, was not consistent, for, in ridiculing a proposal (made by Arzruni) that a similar degree of solubility may be taken as characteristic of isomorphous compounds, he said " CaF_2 and CaCl_2 are both cubic, the former being nearly insoluble, the latter extraordinarily deliquescent. Mixed crystals, therefore, cannot be formed from an aqueous solution; yet the two compounds are isomorphous. It is possible that a common solvent might exist, from which mixed crystals would be obtainable; or the latter might be obtained from the fused mixture." No mixed crystals, no parallel growths, no relief of supersaturation had been observed; therefore the only reason for asserting that these two substances are isomorphous was that both are cubic, coupled with the fact that chlorine and fluorine sometimes replace each other isomorphously. The remarks of Retgers concerning calcium chloride and calcium fluoride are really applicable to sodium nitrate and calcium carbonate.

It has been shown above that in an isostructural series the formation of parallel growths depends on a similarity of molecular volume. The question arises whether the miscibility of isomorphous salts also depends on this, but an examination of the investigated cases, especially of those with limited miscibility, has failed to lead to the recognition of the existence of any connection between molecular volume and miscibility.

In spite of this difference, however, the author does not see why the parallel growths should not be taken as evidence in favour of isomorphism in lieu of the formation of mixed crystals. It may be concluded, then, that the isostructural substances, sodium nitrate and calcite, are really isomorphous.

Reliable results would probably not be obtainable from experiments on the relief of supersaturation of potassium perchlorate or permanganate by barytes, celestine, or anglesite; in the former case, owing to the slight solubility of the salt, in the latter because of the opacity

of the solution. But the analogies which have been made out, for example, composition, form, angle, molecular volume, and the formation of parallel growths, point to the isomorphism of these substances.

The author hopes to make an investigation of the physical properties of the perchlorates and permanganates, in order to see whether the two groups, calcium carbonate—sodium nitrate, potassium perchlorate—barium sulphate, are completely analogous.

(IV) *Other Experiments with Solutions on Minerals.*

Growths on Mica.

In the course of the present investigation, the author also studied the growths on mica, first obtained by Frankenheim, whose results were, in general, confirmed, and the following additional interesting facts were observed. In the case of potassium iodide, part came down in cubes which were totally irregular (Frankenheim asserted that they are regular); besides these, skeletal, triangular-shaped masses—often twinned—were present and were regularly arranged, one side of the triangle being parallel to the plane of symmetry of the mica. Potassium bromide gave similar results, but here in some rare cases cubes standing on a face $\{111\}$ were observed, and they possessed the same orientation as the triangles. Potassium chloride gave skeletal growths which were quite irregular. Sodium bromide and iodide crystallise in monoclinic forms containing two molecules of water of crystallisation; the deposition is irregular. Finally, sodium chloride gave irregularly orientated cubes. Sodium nitrate generally comes down in rhombohedra which have no definite orientation; sometimes, however, triangular-shaped masses are met with, which possess the same orientation as the above salts. Moreover, rhombohedra standing on $\{\bar{1}\bar{1}\bar{1}\}$ have been obtained in the same orientation as the triangular crystals; rarely is the face $\{111\}$ developed, and it is always pitted, and generally disappears on the further growth of the crystal. In some cases a negative rhombohedron was observed.

The above regular growths do not meet with so ready an explanation as the isostructural substances previously studied, for the molecular volume of the mica is certainly far greater than those of the substances deposited. It is worthy of remark, however, that the structure of the haloid compounds may not be greatly different from that of sodium nitrate, for the cleavage is very similar. Further, the orientation of the regularly deposited crystals of all the above substances was the same, as were also the forms. Is it merely a coincidence that the above crystals were so orientated that a trigonal axis is parallel to the pseudo-trigonal axis of the mica?

Since mica causes substances so diverse as the above to crystallise

on it in regular position, it was resolved to study the crystallisation of other salts on mica and on other minerals possessing good cleavages.

Potassium nitrate gave three kinds of crystals on mica :

- (1) Ordinary orthorhombic prisms which were irregular,
- (2) Equilateral-triangular, and
- (3) Skeletal-hexagonal masses, which were both orientated in the same regular manner as the crystals of potassium iodide.

Attempts to detach these crystals in order to investigate their optical properties were without success owing to their extreme tenuity. Crystallisation on the thinnest piece of mica obtainable by cleavage was also tried, but the interference figure of the mica was still predominant. The triangular- and hexagonal-crystals with the above orientation remained dark when the nicols were rotated, but a few crystals not in the above orientation polarised in bright colours, and are therefore strongly birefringent.

Potassium nitrate, crystallised on glass, gave the orthorhombic crystals only.

Hydroquinone on Calcite.

It was found that two kinds of crystals of hydroquinone are deposited on calcite from a warm aqueous solution : (1) long prisms irregularly arranged, and (2) stouter plates which were orientated regularly with one side parallel to the longer diagonal of the calcite-rhomb. The extinction of the prism-modification is straight and the birefringence weak ; this is, therefore, probably the hexagonal modification (hydroquinone is dimorphous) ; they were too small to be measured, but crystals of a similar habit obtained in a test-tube were, on measurement, found to be hexagonal.

The second regularly-orientated modification was also obtained by allowing a solution to crystallise on glass, and was found to be strongly birefringent ; the quartz wedge compensates across the prism, and examination in convergent polarised light shows the first mean line is normal to the section. The axial angle is very wide and the plane of the optic axes is parallel to the direction of compensation ; hence the birefringence is positive. The extinction is straight. This modification may be the monoclinic one.

Experiments with other Minerals and Salts.

The majority of the experiments made with other minerals and salts gave negative results, so the details of each case are not gone into ; the following is a list of the substances tried which all gave irregularly orientated deposits. Only fresh cleavage surfaces of the mineral were used,

Calcite.—Potassium iodide, bromide, and chloride.

Mica.—Ammonium alum, barium nitrate, ammonium nitrate, potassium fluoride and perchlorate, and sodium chlorate.

Gypsum.—Sodium nitrate (Frankenheim says regular); potassium chromate, iodide, perchlorate, and permanganate; sodium chloride and barium nitrate.

Rock Salt.—Potassium bromate, chromate, perchlorate, and sulphate; sodium chlorate.

Barytes.—Potassium chromate, nitrate, and sulphate.

Cubic Substances on Cubic Minerals.

The following failed to yield regular growths :

On blende, $V = 23.75$.

	<i>V</i> .
Ammonium alum	552.2
Barium nitrate	81.0
Lead nitrate	73.3
Sodium chloride	27.2
Potassium chloride.....	37.4
Sodium chlorate	46.5
Sodium bromate	45.2
Potassium iodide	53.24
Potassium cyanide	?

On fluor-spar $\frac{V}{24.5}$

All the above salts, and also ammonium chloride and silver chloride (from ammoniacal solution), failed to give any regular growths on fluor-spar.

The Aragonite Group.

It has been asserted by v. Hauer (*Sitzungsber. K. Akad. Wien.*, 1860, 39, 612) that de Senarmont obtained an overgrowth, in parallel position, of potassium nitrate on aragonite; but neither Arzruni nor the author has been able to find an account of this in de Senarmont's published papers.

It was decided to investigate this point, since the crystallographic relationships of potassium nitrate and aragonite are much the same as those of calcite and sodium nitrate. Crystals of aragonite, from Bilin, possessing bright faces, were cleansed by means of a saturated solution of potassium nitrate, and the two methods previously used—the drop and the cooling method—were applied in the attempt to obtain regular depositions; but no trace of regularity could be found

in the crystals of potassium nitrate deposited. Cleavage faces, too, were tried, but all to no purpose. Crystals of cerussite, exhibiting the forms $m\{110\}$, $v\{120\}$, $q\{011\}$, $\{021\}$, and $\{010\}$ were also tried; but here, again, no regular growths were obtained. Twin-crystals of witherite (the only ones available) with very rough faces also afforded no regular growths.

(V) *Parallel Growths of Isomorphous Salts on each other.*

Investigations were then made in order to find whether similarity of molecular volume is as necessary for the formation on each other of parallel growths in the case of isomorphous salts which do form mixed crystals as is apparently the case with substances like potassium perchlorate and barytes, which do not; for, if isomorphous salts were found capable of giving parallel growths, no matter how great the difference of molecular volume, this property would distinguish them from merely isostructural substances. It has, of course, long been known that isomorphous substances are capable of giving zone-crystals, but this property has, hitherto, not been systematically studied, and the simple drop method does not seem to have been used in its investigation. In order to test this point, the series of isomorphous salts selected should show great differences of molecular volume amongst its members, and this condition is most likely to be fulfilled in groups containing isomorphously replaceable acidic—as well as basic—radicles. The only such groups which have been worked out with regard to volume properties, as well as geometrical, are:

- (1) Sulphates and selenates of the alkalis (Tutton),
- (2) Double sulphates and selenates of the form $R_2SO_4 \cdot MSO_4 \cdot 6H_2O$ (Tutton),
- (3) The alums (Pettersson),
- (4) The haloid salts of the alkalis (Sprockhoff), and
- (5) The permanganates and the perchlorates of the alkalis.

Parallel Growths of the Perchlorates and Permanganates on each other.

Freshly-prepared basal and prismatic cleavage-pieces of the salts were used, and drops of a saturated solution of another salt were placed on them and the crystallisation watched. The rapidity with which crystals appeared on the mother-crystal varied with the individual pairs of salts. The growths always appeared more quickly, however, than with calcite and sodium nitrate; in some cases they appeared as soon as the drop touched the crystal. All possible pairs of substances were not taken, but all the salts were used, either as crystals or in solution, and all gave parallel growths. This is no

doubt to be accounted for by the fact that, as shown on p. 1135, they do not differ greatly in molecular volume.

Following is a list of the experiments :

KMnO ₄ aq.	on crystals of	KClO ₄ , RbClO ₄ , and CsClO ₄ .
RbMnO ₄ aq.	„	KClO ₄ .
AmClO ₄ aq.	„	KClO ₄ .
TlClO ₄ aq.	„	KClO ₄ .
KClO ₄ aq.	„	CsClO ₄ .
CsMnO ₄ aq.	„	KClO ₄ .

Cæsium permanganate is very slightly soluble in water, so the crystals deposited on a crystal of potassium perchlorate were extremely small ; there was no doubt, however, concerning the regularity of the deposition. Since cæsium and potassium perchlorates possess, respectively, the highest and lowest molecular volumes of all the salts in the series, and since all the other pairs tried gave parallel growths, it is very probable that all possible pairs would also give parallel growths.

The results go far to prove that there is no inherent difference between the salts which form parallel growths on barytes, potassium perchlorate and permanganate, on the one hand, and those which do not, on the other ; moreover, they confirm the view that only a too great dissimilarity of molecular volume renders parallel growths impossible.

The investigation of the halogen salts of the alkalis is now in progress.

Growth of Two Salts possessing almost identical Molecular Volumes.

It was observed in the course of the above work that a drop of solution of a salt, placed on a crystal of the solute itself, does not on evaporation give rise to visible parallel crystals, but a few irregularly orientated crystals are formed ; a closer study showed, however, that the crystals which are formed really fall from the surface of the drop and are not formed in contact with the large crystal. Further, very often separate crystals are not formed at all, but the large crystal grows as a whole.

The examination of several pairs of isomorphous salts, selected at random, finally disclosed the fact that a drop of sodium bromate solution behaves in exactly the same manner when placed on a crystal of sodium chlorate—the solution evaporates without the formation of separate crystals. Now the molecular volumes of these two salts are almost identical, namely, 45·2 and 46·5 respectively. It therefore appeared likely that the property might be common to all pairs of isomorphous salts which possess nearly identical molecular volumes.

The crystallisation of various alums on each other, and of a solution of zinc sulphate on crystals of the less soluble magnesium sulphate, was studied. The molecular volumes of the latter salts are, respectively, 146.72 and 147.096, and the topic axes calculated from Dufet's measurements are :

	χ .	ψ .	ω .
ZnSO ₄ 7 aq.	6.28650	6.41955	3.63561
MgSO ₄ 7 aq.	6.31895	6.38361	3.64661
Differences	0.03245	0.03594	0.01100

In most cases no separate crystals were formed, but the solution evaporates, leaving a zonal growth of ZnSO₄, 7aq. on MgSO₄, 7aq.

The same behaviour has been found with solutions of chrome and ammonium alum on crystals of potassium alum, and with a solution of ammonium alum on crystals of chrome alum. Sometimes a few crystals were formed, but they were never parallel.

The molecular volumes of these alums are :

Chrome alum.....	542.2	} Otto Petterssen.
Potassium alum	541.6	
Ammonium alum	552.2	

There is therefore apparently a remarkable connection between the character of parallel growths and the amount of the difference of molecular volumes.

It is significant that the most beautiful examples of zonal-growths (Schichtkrystalle) recorded have been obtained from pairs of salts possessing almost identical molecular volumes ; for example, by the immersion of crystals of zinc sulphate, nickel sulphate, or cobalt sulphate in a solution of magnesium sulphate ; or, again, the various alums on each other (described by von Hauer). An explanation of the common occurrence of zonal structure in the feldspars may be found in the extraordinary similarity of molecular volume of the individual members of the group. The molecular volumes of the two extreme members, albite and anorthite, are respectively 100.13 and 101.49.

Complications which ensue owing to the Common Solubility of Two Salts in the same Solvent.

The deposition of a salt on crystals of an isomorphous salt which is soluble in the solution of the former is not a simple process due to evaporation alone ; this follows from the observation that even if the solution of the former is not quite "saturated," crystals are still immediately deposited on the isomorphous salt. Further, on placing a

small fragment of the solute in the solution, it begins to dissolve, although apparently the same substance is simultaneously separating out on the crystal of the isomorphous salt. Again, if the solution (not saturated) is of a suitable concentration, a crystal of an isomorphous salt, when introduced, becomes covered with small crystals (generally in parallel position), but itself begins to dissolve; if the crystals introduced be very small and more soluble than the solute, it dissolves completely, and then the crystals of the solute, which have separated out, begin to dissolve themselves, and may totally disappear.

Suitable solutions of ammonium chloride, potassium iodide, and potassium chloride were prepared by slightly diluting the saturated solutions, and small cleavage-pieces of rock salt were pushed into drops of them; in all cases, crystals appeared on the rock salt, and the latter began to dissolve. Further, on adding a small crystal of the solute to the drop, it also began to dissolve; if, however, this crystal was placed on the rock salt, it did not dissolve. This shows that the concentration and composition of the solution vary greatly in different parts of the drop; the solution in contact with the rock salt is saturated with regard to the solute, whereas the rest of the solution is unsaturated. Crystals of ammonium perchlorate behave in the same way when immersed in a nearly saturated solution of thallium perchlorate. In the case of suitably diluted solutions of potassium bromide and potassium iodide, rock salt causes an immediate liberation of cubes in parallel position, whilst the rock salt itself dissolves away; finally, the cubes of potassium bromide and iodide dissolve.

Crystals of caesium chloride on immersion in potassium iodide solution dissolved rapidly, but in a remarkable manner; the sides of the crystals alternately grew and dissolved several times, until finally all had disappeared. Similarly, crystals of ammonium perchlorate cause a liberation of crystals of potassium perchlorate (in parallel position) from a nearly saturated solution of the latter salt, but dissolve rapidly themselves; finally, the crystals of potassium perchlorate themselves disappear.

We have seen that crystals of sodium chloride cause an immediate liberation of crystals of potassium iodide from a solution of the latter; now a crystal of potassium iodide also liberates crystals of sodium chloride from its aqueous solution, and if the solution of the latter be not quite saturated, the crystals of sodium chloride which have separated on the crystal of potassium iodide dissolve again completely after the solution of the potassium iodide.

The liberation of crystals of the solute in all the above cases is probably preceded by the dissolution of a small portion of the crystal of the isomorphous salt; this follows from a consideration of the fact that the solution was in many cases not saturated in the absence of the crystal

introduced. This, together with the variations of concentration which it causes in different parts of the solution, is sufficient to explain the above observations. It follows from Roozeboom's thermodynamic deduction of the laws of equilibrium between isomorphous salts and a common solvent that a salt cannot be in equilibrium with a pure saturated solution of another salt; an interchange of salt and solute will take place in general, with the formation of mixed crystals. Now it is extremely unlikely that the mixed crystals first formed will have the same composition as the mixed crystals which are finally in equilibrium with the solution, for the equilibrium is only gradually reached and not *per saltum*; the composition of the solution, therefore, is continually changing, and mixed crystals of varying concentrations will be formed during the process, which will all in turn dissolve again. The best example of this phenomenon noticed by the author was found with crystals of caesium chloride and a solution of potassium iodide. It follows from the above considerations that the crystals deposited on a crystal of an isomorphous salt are not pure crystals of the solute, but mixed crystals; nevertheless, the percentage of the solute will be very high, and hence the molecular volume of the mixed crystals deposited will not be greatly different from the molecular volume of the pure solute.

Summary of Conclusions.

(1) The parallel deposition of sodium nitrate on fresh cleavage surfaces of calcite is independent of the habit or variety of the latter, so long as a good cleavage surface is obtainable.

(2) Isomorphous mixtures of sodium and silver nitrate, and sodium and potassium nitrate, behave like pure sodium nitrate.

(3) An essential condition for parallel growths is a clean surface: in the experiments described, contact with the unimpaired crystalline material was found to be absolutely necessary.

(4) Artificial twinning over the glide-plane, $e\{110\}$, does not prevent the parallel deposition of crystals.

(5) The orientation of the crystals deposited is not affected by crystallisation in a magnetic field.

(6) Sodium nitrate is deposited in regular position on certain other forms of calcite besides the cleavage surface; in all cases congruent edges of the calcite and sodium nitrate are parallel.

(7) Sodium nitrate does not form parallel growths on the other minerals of the calcite group—chalybite, calamine, dolomite, rhodochrosite, breunnerite, and diallogite—nor on barytocalcite.

(8) The necessary condition for parallel (and regular) growth is

closeness of molecular volume rather than similarity of angle (or of axial ratios).

(9) Parallel growths have been discovered amongst the members of another, and far more numerous, group of isostructural minerals and salts. Potassium perchlorate and potassium permanganate form parallel growths on the minerals, barytes, anglesite, and celestine, whereas the perchlorates of rubidium, caesium, ammonium, and thallium, and the permanganates of rubidium, caesium, and ammonium, do not. Here, again, closeness of molecular volume—and, hence, of topic axes—is necessary for parallel growth.

(10) The above isomorphous salts do not form parallel growths on anhydrite; the latter is, however, not isostructural with the former, for it has a different cleavage.

(11) The parallel growths and, in addition, the extraordinary similarities—crystallographic and physical—of sodium nitrate and calcite (and also of potassium perchlorate and barytes, &c.), is strong evidence for regarding them as isomorphous. This view is in harmony with the observations regarding the action of calcite on a metastable solution of sodium nitrate.

(12) Regular growths of potassium bromide, potassium iodide, sodium, and potassium nitrate can be obtained on mica; also of hydroquinone on calcite.

(13) No parallel growths of cubic salts on cubic minerals were obtained.

(14) No parallel growths were obtained in the potassium nitrate-aragonite group.

(15) All the members of the perchlorate-permanganate group form parallel growths on each other; this is the first investigation of the parallel growths of substances which form mixed crystals.

(16) Pairs of isomorphous salts, the molecular volumes of which are almost identical, form zonal-growths (*Schichtkrystalle*) rather than parallel growths of distinct crystals.

(17) The perchlorates of potassium, rubidium, caesium, ammonium, and thallium, and the permanganates of the first four metals, form an isomorphous group. The crystallographic relationship between the perchlorates and permanganates is the same as that between the sulphates and selenates; the crystallographic evidence for placing manganese in the seventh group of the periodic classification is therefore the same as holds for placing selenium in the sixth group.

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