

COMMUNICATIONS FROM THE OXFORD MINERALOGICAL  
LABORATORY. NO. VIII.*On the regular growth of soluble salts on each other.*

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PREVIOUS work on the regular growth of crystals of salts on those of Minerals belonging to the same isostructural series led the author<sup>1</sup> to the discovery that parallel deposition is conditioned by closeness, not of angle nor of axial ratios, but of molecular volume. Now although the substances previously examined resemble each other crystallographically, yet they exhibit such great differences in chemical properties, that reasonable doubt might be entertained whether conclusions drawn from them can be directly applied to isomorphous substances; and it therefore became advisable to extend the observations to a group of the latter.

The group selected should, from the nature of the problem, not only be numerous but should also exhibit great differences of molecular volume amongst its members. Now the largest isomorphous group known is that of the double sulphates and selenates, which has been so thoroughly investigated by Tutton; this group, however, like that of the alums, does not fulfil the second condition, for the range of molecular volume is comparatively small: this results from the high molecular weight associated with the relatively small amount of chemical substitution. A suitable group is met with in the chlorides, bromides, iodides, and cyanides of sodium, potassium, rubidium, caesium, and ammonium, which crystallize in the cubic system; further, the majority of the salts possess a perfect cubic cleavage, so that there is no difficulty in obtaining clean surfaces.

Of the above salts, rubidium and caesium cyanides have not been

<sup>1</sup> T. V. Barker, 'Contributions to the theory of isomorphism based on experiments on the regular growths of crystals of one substance on those of another.' Journ. Chem. Soc. Trans., 1906, vol. lxxxix, pp. 1120-1158.

previously described; but, although the published crystallographic data concerning the remaining salts leave little to be desired individually, yet great uncertainties exist with regard to their relationships as a whole. Thus, ammonium chloride and bromide cannot be obtained in cubes without the addition of other substances—especially urea—to their solutions, and the crystals so obtained exhibit only a very poor cleavage: the miscibility, again, of some of the pairs investigated is vanishingly small: finally, etching experiments point to a difference of symmetry. For the above reasons, strict isomorphism has been denied, and evidence for at least dimorphism has been adduced by Lehmann, Groth, and others.

It might therefore seem that a careful investigation of the group was imperative before carrying out experiments on parallel growths. But the latter have been taken in hand first, in order to see whether they can afford a new way of exploring the inter-relationships of the members of a group, concerning which most divergent opinions have been held.

### Experimental.

#### I. PREPARATION AND ANALYSES OF THE SALTS.

The chlorides, bromides, and iodides of rubidium and caesium were mostly purchased from Merck, small quantities of some of them being also made by double decomposition of the metallic sulphate and the halogen salt of barium. Potassium and barium cyanides were purchased from Kahlbaum, and, setting out from the latter, rubidium and caesium cyanides were made by double decomposition. The remaining salts were the chemically pure salts of commerce. Several attempts were made to bring ammonium cyanide into the scope of this inquiry, but were unsuccessful owing to the instability of this compound. The cyanides of caesium and sodium were prepared, but it was found impossible to use them, owing to the difficulties encountered in obtaining good crystals.

Sodium bromide and iodide crystallize with two molecules of water at ordinary temperatures in monoclinic plates, but at higher temperatures anhydrous cubes are formed. It was found possible to isolate cubes of sodium bromide of sufficient size above a temperature of 60° C., so the growths on these cubes were investigated. Anhydrous cubes of sodium iodide are more difficult to obtain, a higher temperature being necessary, and they are difficult to isolate owing to their great deliquescence; on this account it was found impossible to use them in the experiments on parallel growths. Sodium cyanide crystallizes at ordinary temperatures

in monoclinic plates—apparently isomorphous with the hydrated bromide and iodide—which are probably the compound  $\text{NaCN} \cdot 2\text{H}_2\text{O}$  obtained by Joannis<sup>1</sup> from an alcoholic solution. At slightly higher temperatures, anhydrous cubes are formed. Sodium chloride separates out in monoclinic plates with two molecules of water below  $-10^\circ\text{C}$ . (Mitscherlich). We therefore see that all the four sodium salts appear in two modifications, one anhydrous at higher temperatures, the other hydrated at lower temperatures; the transition temperatures approximately lie at  $-10^\circ\text{C}$ . for sodium chloride,  $50^\circ\text{C}$ . for sodium bromide,  $65^\circ\text{C}$ . for sodium iodide, and  $80^\circ\text{C}$ . for sodium cyanide.

The analysis of rubidium cyanide consisted in a cyanogen determination by precipitation with silver nitrate, the silver cyanide being dried and weighed—

0.4555 gram gave 0.4799 gram  $\text{AgCN}$ ;  $\text{CN} = 23.00$  per cent.  
( $\text{RbCN}$  requires 23.37 per cent.)

The specific gravities of potassium and rubidium cyanides were determined by the suspension method, the suspension fluid employed being a mixture of methylene iodide and benzene; only the clearest splinters were used.

Potassium cyanide: two determinations with independent material gave a mean value

$$\text{Sp. gr. } (17^\circ/4^\circ\text{C.}) = 1.578.$$

Rubidium cyanide: three determinations gave a mean value

$$\text{Sp. gr. } (21^\circ/4^\circ\text{C.}) = 2.295.$$

Determinations of the solubility of potassium cyanide and the specific gravity of the solution were made—

100 parts water dissolve 81.3 parts  $\text{KCN}$  at  $13^\circ\text{C}$ ., and the specific gravity of the saturated solution is

$$\text{Sp. gr. } (13^\circ/4^\circ\text{C.}) = 1.2220.$$

## II. CRYSTALLINE FORM AND HABIT OF THE SALTS.

Some of the salts yield fine, clear cubes from the pure aqueous solution, while others can only be obtained in clear crystals by the addition of other substances to the solution. The following is an account of the various salts:—

Sodium chloride.—Cubes of a sufficient size are difficult to obtain, so most of the experiments on parallel growths were made with rock-salt

<sup>1</sup> Ann. Chim. Phys. 1832, ser. 5, vol. xxvi, p. 484.

from Galicia. Retgers<sup>1</sup> obtained good cubes by the addition of various substances to the solution, e. g.,  $K_2CO_3$ ,  $HCl$ ,  $FeCl_3$ ,  $CuCl_2$ ,  $NaOH$ , &c.; the author found the last of these to give the best results.

Potassium chloride.—This tends to form skeletal growths, but good crystals were obtained from solutions containing 1 per cent. of  $KOH$ .

Potassium bromide and iodide; ammonium iodide; rubidium chloride, bromide, and iodide; potassium and rubidium cyanides; sodium bromide (above  $60^\circ C.$ ).—The pure solutions of all these salts gave good cubes.

Ammonium chloride and bromide crystallize in skeletal forms, which are combinations of  $\{211\}$  and  $\{110\}$  (Tschermak, Slavík). Retgers (loc. cit.) showed that the presence of urea—which induces an octahedral habit in sodium chloride—favours the formation of simple cubes. These observations were repeated by Krickmeyer<sup>2</sup>, who failed to obtain good cubes of ammonium bromide. The author finds that far more urea is required with ammonium bromide than with ammonium chloride; in fact the solution must contain great excess of urea, and by this precaution large cubic crystals of a yellowish tinge are obtainable by slow evaporation over sulphuric acid. The cubes of ammonium chloride attain a considerable size—up to 3 cubic centimetres; the crystals of ammonium bromide are somewhat smaller. Analyses were made in order to see whether the crystals contain urea:—

0.1931 gram  $AmCl$  gave 0.5160 gram  $AgCl$ , corresponding  
to 99.75 per cent.  $AmCl$ .

0.2400 gram  $AmBr$  gave 0.4562 gram  $AgBr$ , corresponding  
to 99.18 per cent.  $AmBr$ .

Since the crystals contained many inclusions of the mother-liquor, the above analyses prove that the crystalline material is practically free from urea; the crystals are very tough and the cubic cleavage is very imperfectly developed.

Although Sprockhoff<sup>3</sup> obtained good crystals of the caesium salts, the author has not been able to get large enough crystals for the study of parallel growths, so that the caesium salts have only been used as solutes.

### III. VOLUME CONSTANTS.

The halogen salts have been repeatedly investigated, and quite recently they have been the subject of an elaborate research by Sprockhoff (loc.

<sup>1</sup> Zeits. physik. Chem., 1892, vol. ix, p. 267.

<sup>2</sup> Zeits. physik. Chem., 1896, vol. xxi, p. 71.

<sup>3</sup> Neues Jahrb. Min., 1904, Beilage-Band xvi, p. 121.

cit.), so that it was not necessary to make any specific gravity determinations. Below is a table giving the molecular weight, specific gravity, and molecular volume of all the substances used in this investigation. The sources of the values of the specific gravities are given in brackets, and the atomic weights are those recommended by the International Committee for 1906, O = 16.

*Table of Volume Constants.*

Salt.	Molec. wt.	Sp. gr.	Molec. vol.
NaCl	58.50	2.173 (Gossner) <sup>1</sup>	26.92
NaBr	103.01	3.198 (Favre and Valson) <sup>2</sup>	32.21
NaI	150.02	3.654 ( " " )	41.06
KCl	74.60	1.990 (Sprockhoff) <sup>3</sup>	37.49
KBr	119.11	2.751 ( " )	43.30
KI	166.12	3.131 ( " )	53.06
KCN	65.19	1.578 (Barker)	41.31
RbCl	120.95	2.806 (Sprockhoff)	43.10
RbBr	165.46	3.356 ( " )	49.30
RbI	212.47	3.564 ( " )	59.62
RbCN	111.54	2.295 (Barker)	48.60
CsCl	168.35	3.994 (Sprockhoff)	42.15
CsBr	212.86	4.452 ( " )	47.81
CsI	259.87	4.539 ( " )	57.25
AmCl	53.52	1.531 (Gossner)	34.96
AmBr	98.03	2.256 (Slavík) <sup>4</sup>	43.45
AmI	145.04	2.501 ( " )	58.14

The specific gravity determinations of the rubidium and caesium haloids made by Setterberg<sup>5</sup> agree well with the above values of Sprockhoff.

#### IV. EXPERIMENTS ON PARALLEL GROWTH.

The method of observation was extremely simple; a drop of a solution of one salt was placed on a fresh cleavage-piece of the other, which was viewed—on a glass-slide—under the microscope. Crystals of the solute appear as a rule in a few seconds, but the deposition is sometimes so rapid that the surface of the cleavage-flake becomes opaque instan-

<sup>1</sup> Gossner, *Zeits. Kryst. Min.*, 1903, vol. xl, p. 70.

<sup>2</sup> Favre and Valson, *Compt. rend. Acad. Sci. Paris*, 1873, vol. lxxvii, p. 579.

<sup>3</sup> Sprockhoff, *loc. cit.*

<sup>4</sup> Slavík, *Zeits. Kryst. Min.*, 1902, vol. xxxvi, p. 271.

<sup>5</sup> *Öfvers. k. Vet.-Akad. Förh. Stockholm*, 1882, vol. vi, p. 23.

taneously ; when this happened the solution was diluted a little, but even then, with certain pairs of salts, the deposition was so dense as to prevent the attainment of a positive result. Another difficulty also arises where the solubility is far greater for the crystal than for the solute, because the crystal then dissolves rapidly and the crystals deposited by the solute stream down the sides of the 'mother-crystal' and come to rest on the glass-slide.

Sometimes the cleavage-piece was heated while the deposition was going on. By varying the conditions of experiment, definite conclusions were finally arrived at with the great majority of the possible pairs of substances.

The following is a detailed account of the experiments :—

*Sodium Chloride.*—The material used was rock-salt from Galicia ; it contained many fluid-inclusions in the form of negative crystals.

KCl gave opaque cubes with somewhat imperfect outlines ; KBr, KI, and KCN crystallized out in cubes with sharp outlines ; RbCN in flowery cubes—the deposition of all these salts being parallel with the rock-salt. RbCl deposited crystals very similar to those of KCl, which were often parallel, but generally irregular<sup>1</sup> ; many attempts were made to decide one way or the other, but unsuccessfully. As the growths of sodium chloride on RbCl are parallel, it may be concluded that the deposition of RbCl on NaCl is really parallel. None of the remaining salts—except NaBr and NaI which are hereafter mentioned in a separate sub-section—gave a regularly orientated deposition : of these RbBr, RbI, AmI, AmCl, and AmBr, from solutions containing urea, gave well-defined cubes ; CsCl and CsBr gave petal-like forms ; CsI, AmCl, and AmBr, from their pure solutions, yielded rods.

*Sodium Bromide.*—Cubes were obtained from aqueous solution above 60° C.

KI, RbI, RbBr, and RbCl gave beautiful parallel cubes, as did also probably CsCl, but it is impossible to say with certainty owing to the rapidity of the deposition ; the character of the deposition of KCN, RbCN, AmI, and CsBr could not be made out for the same reason. Streams were immediately set up with NaCl, KCl, KBr, AmCl, and AmBr ; CsI gave irregular growths of cubes and dodecahedra.

*Potassium Chloride.*—The crystals were obtained from a solution containing a little potash.

<sup>1</sup> The term *irregular* does not mean that the outlines of the crystal were ill-defined, nor does it mean that the crystals do not belong to the regular system ; throughout this paper it is consistently used to denote *not parallel*.

NaCl gave cubes traversed by two diagonal bands: they are apparently made up of an immense number of small parallel cubes; KBr, RbCl, RbBr, KCN, and RbCN gave fine cubes: all the above were parallel. AmBr, with or without the addition of urea, gave a zonal growth or layer-crystal (Schichtkrystall): in other words the solution evaporates away without the formation of any separate, visible crystals in parallel position, but an even layer of crystalline material is spread over the whole cleavage-surface of the mother-crystal. (For a discussion of zonal growths see p. 252.) The remaining salts crystallized in the characteristic forms noted above under sodium chloride, but without any recognizable regularity.

*Potassium Bromide.*—Crystals were obtained from pure aqueous solution.

NaCl, KCl, and AmI immediately gave dense deposits of parallel cubes; the crystallization was slower with KI, RbBr, RbI, and RbCN, which yielded beautiful cubes in parallel position. But, in addition, AmCl and CsCl, which usually crystallize in rods or fronds, came down in parallel cubes. A zonal growth was afforded by KCN and RbCl, but on warming the latter slightly delicately fine, parallel cubes were obtained. The remaining salts were irregularly orientated: CsCl crystallized in petals; CsI in rods and dodecahedra.

*Potassium Iodide.*—Cubes were obtained from aqueous solution.

Parallel deposits of cubes were obtained with NaCl, RbCl, RbBr, AmCl, AmBr, KCN, KBr, and RbI, the two last salts coming down copiously. Nothing definite could be arrived at with KCl, owing to the rapid dissolution of the mother-crystal with subsequent streaming. AmI did not produce any separate crystals, but a zonal growth was formed. CsCl, CsBr, and CsI crystallized irregularly in rods.

*Potassium Cyanide.*—Obtained as cubes by slowly cooling a hot, aqueous solution.

KI and AmI gave parallel cubes; KCl gave a fine deposit, but parallel cubes grew out from the sides of the crystal, whilst RbCl formed a zonal growth. Dense deposits were immediately given by NaCl, KBr, AmCl, AmBr, CsCl, and CsBr, which excluded further investigation; RbCN gave some parallel cubes on heating. With RbBr the deposition, even with dilute solutions, was too rapid to enable one to judge whether it was parallel or no; finally CsI gave irregular rods.

*Rubidium Chloride.*—Obtained as cubes from aqueous solution.

Parallel deposits of cubes were afforded by CsBr and RbCN, and also, as a rule, by NaCl, whilst RbI and AmI gave cubes in irregular positions.

A zonal growth was formed with KBr and with KCN, but the latter gave a parallel deposition of cubes on heating; nothing could be deduced from the growth of KCl, KI, and RbBr owing to the rapid precipitation. AmCl and AmBr crystallized in irregular positions, in cubes or fronds, according as urea was present or absent; CsCl yielded irregular petals, and CsI, on heating, irregular rods.

*Rubidium Bromide.*—Obtained as cubes from aqueous solution.

Parallel cubes were deposited from solutions of KI, RbI, AmI, KCl, KBr, and RbCl, and the deposition of the three last salts was particularly dense; the cubes of NaCl, on the other hand, were irregular. The floral crystals of CsCl, and the rods of CsBr, CsI, and AmBr, together with the fronds of AmCl, had no definite orientation. A very finely divided deposit was given by KCN, but RbCN afforded a zonal growth.

*Rubidium Iodide.*—Obtained as cubes from aqueous solution.

Parallel cubes were obtained with KBr, RbBr, and with AmBr, even in absence of urea, whilst AmCl gave irregular growths; parallel deposits of a semi-zonal character were obtained with KI and AmI, but irregular rods were deposited from solutions of CsCl, CsBr, and CsI. Nothing could be made out with regard to NaCl, KCl, and RbCl, owing to the streaming set up. Copious precipitation immediately occurred on contact with solutions of KCN and RbCN, and of these it can only be said with certainty that the former salt was parallel.

*Rubidium Cyanide.*—Obtained as cubes from aqueous solution.

KCl, KBr, KI, RbCl, RbI, and AmI gave parallel cubes, the deposition as a rule being copious; RbBr gave a zonal growth, but, on heating, parallel cubes. The deposition was so rapid with NaCl, AmCl, AmBr, CsCl, and CsBr that its nature could not be made out; CsI gave irregular rods, and, finally, streaming occurred with KCN.

*Ammonium Chloride.*—Cubes were obtained from an aqueous solution containing urea.

The following salts gave irregular deposits of cubes: NaCl, KCl, KBr, KI, KCN, RbCl, RbBr, RbI, AmI, and (probably) RbCN; whilst parallel deposits of cubes ensued with AmBr (with or without urea), CsCl, and CsBr. CsI, on the other hand, gave irregularly orientated rods.

*Ammonium Bromide.*—Cubes were obtained from an aqueous solution containing great excess of urea.

Floral cubes in irregular positions were obtained from solutions of KBr, KI, KCN, RbCl, RbBr, RbI, RbCN, and AmI; whilst NaCl, KCl, and AmCl yielded parallel cubes. Parallel depositions, taking the form of 4-petal groups, were derived from CsCl and CsBr; a very finely divided



deposit was afforded by CsI, the character of which could not be made out.

*Ammonium Iodide*.—Obtained as cubes from aqueous solution.

CsCl, CsBr, and AmBr gave rods; NaCl and AmCl (with urea), cubes; CsI, petals—all irregularly orientated. KCN gave a very thick deposit, which was finally made out to consist of parallel cubes. The precipitation of the other salts—KCl, KBr, KI, RbCl, RbBr, RbI, and RbCN—was too dense for the determination of the nature of the growth.

#### V. BEHAVIOUR OF SOLUTIONS OF SODIUM BROMIDE AND IODIDE.

Sodium bromide is deposited from its aqueous solution on rock-salt in the monoclinic form— $\text{NaBr} \cdot 2\text{H}_2\text{O}$ —in irregular position, but, on heating, anhydrous parallel cubes come out. Parallel deposits of isotropic cubes (presumably anhydrous) are also immediately formed even in the cold on crystals of KCl, RbCl, KI, and RbI; and a very copious precipitate obtains with AmI and AmCl (parallel?), whilst with KBr, RbBr, and AmBr no cubic crystals seem to come out (it is of course possible that a zonal growth is partly formed, though not to be expected); but on allowing to stand in a desiccator, birefringent crystals (hydrated) are deposited. If, however, the temperature is above  $50^\circ\text{C}$ . parallel growths of isotropic cubes are obtained. The character of the growths on KCN and RbCN could not be made out, a thick deposit being immediately formed.

It will be observed from the above that isotropic cubes only appear immediately, where there are four variables or ions: e.g., NaBr on KCl; whilst no cubes—but in time hydrated salts—appear, where three variables are present: e.g., NaBr on NaCl. The same inexplicable behaviour is met with on turning to sodium iodide: here, parallel growths of isotropic cubes are immediately obtained on crystals of KBr, RbBr, KCl, and KCN; the deposition is too rapid with RbCl, but with AmCl and AmBr the cubes deposited are irregular. No cubic crystals have been observed to appear on crystals of NaCl, KI, RbI, and AmI—where there are only three variables; but, on heating, isotropic cubes, apparently parallel, are obtained on KI, RbI, and AmI. The nature of the growth of NaI on RbCN could not be made out.

#### Theoretical.

##### I. DISCUSSION OF THE INTER-RELATIONSHIPS OF THE SALTS.

Although all the seventeen salts used in the above experiments crystallize in the same system and are of analogous chemical composition,

there is, nevertheless, considerable doubt whether they can be regarded as isomorphous in the strictest sense of the term. At the outset, sodium salts are rarely, if ever, isomorphous with the corresponding potassium, rubidium, and caesium salts, except in very complex molecules, where it is also generally found that substitution even by hydrogen does not alter the crystalline form; moreover, much evidence has been accumulated by different observers indicating that it is not permissible to regard the remaining salts as constituting a single isostructural group: upon this point, all authors are in agreement. But, how the group is to be subdivided, and what are the relationships of these sub-groups to each other, are questions difficult to decide and conducive to much controversy. It would be superfluous to give an historical summary of the views hitherto held. The following are the author's views: and it is only just to say that they are almost wholly based on the work and opinions of others.

The group must be divided into two sub-groups, which are hereafter called *A* and *B* respectively: the members of each sub-group are at least isostructural and possibly isomorphous in the strictest sense. Groups *A* and *B*, on the other hand, are not isostructural with each other; but a salt belonging to group *A* may mix with a salt of group *B* in restricted proportions, each salt taking up a little of the other, the salt taken up assuming the (labile) structure of the other: in other words the two sub-groups are isodimorphous. The classification is as follows:—

Group *A*.—NaCl, NaBr, NaI, KCl, KBr, KI, KCN, RbCl, RbBr, RbI, RbCN, AmI (and probably NaCN).

Group *B*.—AmCl, AmBr, CsCl, CsBr, CsI (and probably CsCN).

The following are the reasons for this classification:—

### 1. *Considerations of Molecular Volume.*

It has been shown by Tutton, as also by Muthmann and others, that the replacement of an atom of potassium by one of rubidium, or the latter by one of caesium, is accompanied by a fairly regular increase in molecular volume: this holds for all the salts investigated by Tutton (with the exception of ammonium selenate), namely, the simple and double sulphates and selenates, also for the permanganates (Muthmann) and the perchlorates; moreover, the molecular volumes of the ammonium salts approximate very closely to those of the rubidium salts—sometimes they are a little greater, sometimes a little less.

Now in the above cubic group of salts, the increase in molecular

volume in passing from a potassium to the corresponding rubidium salt regularly amounts to about 5-6 units; but on turning from a rubidium to a caesium salt one actually finds a decrease in molecular volume. Again the molecular volumes of ammonium chloride and bromide are abnormally low—even less than those of potassium chloride and bromide, whilst ammonium iodide has a normal value, being nearly equal to that of rubidium iodide.

The above irregularities disappear if the group is split up into two parts—groups *A* and *B*—the members of group *A* having relatively greater molecular volumes.

*Division into groups A and B.*

Group <i>A</i> .—NaCl, 26.92	(NaCN, ? )	NaBr, 32.21	NaI, 41.06
KCl, 37.49	KCN, 41.31	KBr, 43.30	KI, 53.06
RbCl, 43.10	RbCN, 48.60	RbBr, 49.30	RbI, 59.62
Group <i>B</i> .—AmCl, 34.96	(AmCN, ? )	AmBr, 43.45	AmI, 58.14
CsCl, 42.15	(CsCN, ? )	CsBr, 47.81	CsI, 57.25

A glance at the above table is sufficient to show that each sub-group exhibits regularities in molecular volumes comparable with those met with in the groups investigated by Tutton.

The sodium salts are placed in group *A* because they possess lower molecular volumes than the potassium salts; this would be expected from the position of sodium in the periodic classification, provided all the salts belong to the same isostructural group.<sup>1</sup>

That the sodium salts all belong to one group, in contradistinction to the ammonium salts, is conclusively proved by the absence of any sudden jump in passing from one to another.

The cyanides of potassium and rubidium are placed in group *A*, though it might seem arbitrarily. Considerable difficulties have been met with in the investigation of caesium cyanide, and this is unfortunate, for a

<sup>1</sup> It is worthy of note that the difference in molecular volume of the sodium and potassium salts is about twice the corresponding difference between the potassium and rubidium salts, and it may possibly be argued from this that the sodium salts ought to form a further sub-section of group *A*; still another argument in favour of this is found in the total non-miscibility of sodium chloride and potassium chloride (Krickmeyer, loc cit.). On the other hand, since the molecular volumes of the sodium salts are so low, it might be inferred that they ought to belong to group *B*; but, as will be seen later, the good cubic cleavage and, more especially, the experiments on parallel growth effectually negative this alternative.

knowledge of the molecular volume of caesium cyanide—if it proved to be lower than that of rubidium cyanide—would furnish fairly conclusive evidence for placing rubidium and potassium cyanides in group *A*, and caesium cyanide itself in group *B*. But, as will be seen later, the results of the experiments on parallel growths furnish evidence of a trustworthy character for the correctness of the above position. The elusive nature of ammonium cyanide prevented its employment in this research. It is a remarkable fact that the volume occupied by the cyanogen radical—consisting of two atoms—is about equal to the volume occupied by an atom of bromine, but less than that of an atom of iodine. This is a similar result to that derived by Tutton with respect to the volume of the ammonium radical—consisting of five atoms—compared with the volumes of the metallic atoms, rubidium and caesium. One of the contributory causes is, of course, the low molecular weight of these two radicals.

### 2. *Considerations of Form and Cleavage.*

The characteristic crystalline form of the members of group *A* is without exception the simple cube (sometimes octahedral facets are present); moreover, there is a perfect cubic cleavage with all the members. The cube, however, is quite a subordinate form with salts in group *B*: ammonium chloride and bromide crystallize in feathery groups which are probably combinations of {211} and {110}; caesium chloride, generally in the same form, but also in dodecahedra and cubes; caesium bromide, in dodecahedra which are as a rule elongated along a trigonal axis (Sprockhoff); and caesium iodide, in dodecahedra.

As mentioned above, ammonium chloride and bromide can be obtained in large cubes by the addition of urea to the solution, but the cubic cleavage is very imperfectly developed. The caesium haloid salts nevertheless, according to Sprockhoff, exhibit a good cubic cleavage.

### 3. *Considerations of Miscibility.*

The evidence derived from the degree of miscibility of pairs of salts is generally in favour of the above classification: the members of group *A* mix better with each other than do those of *A* with those of *B*. The miscibility of members of group *B* with each other has, unfortunately, not been investigated.

Below is given a list of those miscibilities which have been hitherto determined:—

- (i) Members of group *A* with each other.  
 AmI and KI in all proportions (Gossner)<sup>1</sup>.  
 KCl and KBr almost totally miscible (Fock)<sup>2</sup>.  
 KI takes up 30 per cent. KBr (Fock). [(Gossner).  
 KCl with KI, there is a gap, not determined quantitatively
- (ii) Members of group *A* with group *B*.  
 18 per cent. AmCl—3 per cent. KCl (Fock).  
 40 „ „ AmBr—1½ „ „ KBr (Fock).  
 AmCl with AmI, large gap (Gossner).  
 NaCl and AmCl do not mix at all (Krickmeyer).

Perhaps the force of this evidence is weakened by the fact that sodium chloride and potassium chloride do not mix at all, although they both belong to group *A* (see footnote on p. 245).

#### 4. Considerations of Parallel Growth.

The results of the experiments on parallel growth decidedly point to the above classification: as a rule, members of group *A* form parallel growths on each other, and the same holds for members of group *B* *inter se*; while members of group *A* on group *B* (or group *B* on group *A*) almost always yield growths which are irregular.

It must be stated that the evidence derived from etching is not in agreement with the above classification: thus, AmCl (Tschermak); KCl (Brauns); KBr, RbCl, RbBr, and CsBr (Sprockhoff) all belong to the tesseral-holoaxial or gyrohedric-hemihedral class of the cubic system. But KI, CsCl, and CsI (Sprockhoff) as well as NaCl (Brauns) belong to the holohedral class.<sup>3</sup> It will thus be seen that a classification based on symmetry, as derived by etching, only succeeds in separating salts which otherwise resemble each other, just as well as it brings together salts which have the least analogies of all.

The author believes that the above considerations are strongly in favour of the classification here adopted. Whether each sub-group is further divisible or no can only be decided when evidence, much more

<sup>1</sup> Zeits. Kryst. Min., 1905, vol. xl, p. 69.

<sup>2</sup> Zeits. Kryst. Min., 1897, vol. xxviii, p. 351.

<sup>3</sup> The symmetry of a crystal, as derived from etching figures, does not necessarily give the real symmetry; for the latter, although it cannot be higher, may nevertheless be lower than the former. Hence, it is not absolutely excluded that the real symmetry of the above compounds is the same, and possibly even lower than the symmetry exemplified by the tesseral-holoaxial class.

than is at present available, has been accumulated. The experiments on parallel growth do not furnish any evidence, for or against, in this direction.

It is interesting to note that direct evidence for the isodimorphism of ammonium chloride has been produced by Lehmann<sup>1</sup>, who observed that feathery cubes separate from hot solutions which, on contact with the ordinary rod-modification, were transformed into the latter. Again, from an aqueous solution containing a little cadmium chloride, rounded cubes were obtained which on standing 'explode' into skeletal crystals.

More reliable evidence would be obtainable from a careful determination of the specific gravities of the isomorphous mixtures given by ammonium and potassium bromides, for if the specific gravity of the labile modification of ammonium bromide, taken up by the potassium bromide, were found different from (and probably less than) the specific gravity of the ordinary modification, we should have direct and conclusive evidence of isodimorphism.

## II. CONNEXION BETWEEN PARALLEL GROWTH AND MOLECULAR VOLUME.

The results of the experiments on parallel growths are collected in the accompanying table in which the members of group *A* are followed by those of group *B*; the salts in each group are arranged in order of molecular volume. The table is divided up by means of heavy lines into four areas corresponding to the growths of the following salts:— (1) *A* on *A*, (2) *B* on *A*, (3) *A* on *B*, and (4) *B* on *B*.

The method of construction of the table is best illustrated by taking an example. In the vertical column headed by KBr and horizontally opposite to RbCN there is a letter P; this denotes that the growth of crystals (deposited from a solution) of KBr on a crystal of RbCN is parallel; similarly, under the column headed RbCN and horizontally opposite to KBr the letter P again denotes that the growth of crystals (deposited from a solution) of RbCN on a crystal of KBr is parallel. Ir denotes that a growth was irregular (not parallel), and Z that a (parallel) zonal growth is obtained. For the signification of the letters placed in brackets see below, under 'Members of group *A* on each other'. From the method of construction of this table, it is obvious that, the less the difference between the molecular volumes of two

<sup>1</sup> Zeits. Kryst. Min., 1885, vol. x, p. 321.

salts, the closer will the squares, which represent the growths in the table, approximate to the diagonal line drawn from the top left hand to the bottom right hand corner.

RESULTS OF EXPERIMENTS ON PARALLEL GROWTH.

Members of Group A on each other.

Group B on Group A.

Mol. Vol.	26-92	32-21	37-49	41-06	41-81	43-10	43-30	43-60	49-30	58-06	58-14	59-62	84-06	42-15	43-45	47-81	57-25
	NaCl	NaBr	KCl	NaI	KCN	RbCl	KBr	RbCN	RbBr	KI	AmI	RbI	AmCl	CsCl	AmBr	CsBr	CaI
NaCl		P	P	P?	P	P	P	P	Ir	P	Ir	Ir	Ir	Ir	Ir	Ir	Ir
NaBr	(P)		(P)	P	?	P	(P)	?	P	P	?	P	?	P?	?	?	Ir
KCl	P	P		P	P	P	P	P	P	Ir	Ir	Ir	Ir	Ir	P	Ir	Ir
NaI	(P)	(P)	(P)		(P)	(P)	(P)	?	(P)	(P)	(P)	?	?	?	?	?	?
KCN	(P)	?	P	P		Z	Z	P	?	P	P	(P)	?	?	?	?	Ir
RbCl	P	P	(P)	P?	Z		Z	P	(P)	(P)	Ir	Ir	Ir	Ir	Ir	Ir	Ir
KBr	P	P	P	P	Z	Z		P	P	P	P	P	P	P	P	Ir	Ir
RbCN	(P)	?	P	?	(P)	P	P		Z	P	P	P	?	?	?	?	Ir
RbBr	Ir	P	P	P	?	P	P	Z		P	P	P	Ir	Ir	Ir	Ir	Ir
KI	P	P	Ir	P	P	P	P	P	P		Z	P	P	Ir	P	Ir	Ir
AmI	Ir	?	(Ir)	P	P	(Ir)	(P)	(P)	(P)	(Z)		Z	Ir	Ir	Ir	Ir	Ir
RbI	Ir	P	Ir	?	P	Ir	P	(P)	P	Z?	Z		Ir	Ir	P	Ir	Ir
AmCl	Ir	?	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir		P	P	P	Ir
CsCl	P	P	?	?	?	?	?	?	?	?	?	?	(P)		(P)	?	?
AmBr	P	P	P	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir	Ir	P	P		P	?

Group A on Group B.

Group B on each other.

(P = parallel growth; Ir = irregular (non-parallel) growth; Z = zonal growth.)

The discussion may be conveniently divided into three parts corresponding respectively to growths where

- (1) both salts belong to group A,
- (2) both salts belong to group B, and
- (3) one salt belongs to A and the other to B.

### 1. *Members of group A on each other.*

It is obvious that with each pair of substances we have two cases, namely, salt (1) on salt (2), and salt (2) on salt (1); and whenever it was possible to come to a definite conclusion, it was always found that the growths were either both parallel or both irregular: e. g., both KCl on NaCl, and NaCl on KCl gave parallel growths, but RbBr on NaCl and NaCl on RbBr both afforded irregular deposits. This is, of course, what one would expect.

Now, as mentioned above, with certain pairs of salts it was only possible to determine the character of the growth in one direction: e. g., RbCl on RbBr was made out to be parallel, but the deposition of RbBr on RbCl was too rapid to enable one to decide whether it was parallel or no. The fact that a parallel growth is obtained one way is strong evidence for believing that the same is really obtained the other way, and, in order to make the table as complete as possible, the letter P is placed in brackets; the same remarks hold for (Ir). Finally, in a few instances, the nature of the parallel growth could not be determined either way, and notes of interrogation are then placed in the table.

This isostructural group is big enough, and only just big enough, to show that parallel growths are conditioned by a similarity of molecular volume, or perhaps it were better to say that irregular growths are only met with where the molecular volumes differ considerably.

It is seen from the table that the irregular growths are all grouped in the top right hand and the bottom left hand parts of the diagram, and the line of demarcation is essentially, though not perfectly, indicated by the double line: the parts thereby cut off are chiefly occupied by irregular growths and the rest of the field is wholly taken up with the parallel growths.

The parallel growths met with in the two 'irregular regions' are those in which the salts NaBr and NaI are concerned, and it was pointed out in the experimental part of this memoir that the behaviour of these salts is in many other respects of an equally inexplicable character, so that a further investigation is desirable. For a discussion of zonal growths see p. 252.

### 2. *Members of group B on each other.*

Owing to the difficulties encountered in obtaining crystals of a sufficient size of the salts CsCl, CsBr, and CsI, we are here restricted to the



growths on cubes of AmCl and AmBr crystallized from solutions containing urea. But the results, as far as they admit of interpretation, point in no less degree to the importance of similarity of molecular volume in conditioning a parallel growth; this is immediately seen from the fact that, of the four salts AmBr, CsCl, CsBr, and CsI, the last is the only one to give irregular growths on crystals of AmCl. Unfortunately, the character of the growth of CsI on AmBr could not be definitely determined owing to the fineness of the deposit: the latter may be possibly consequent on the formation of a parallel growth, but this, of course, is by no means necessary.

### 3. *Members of group A on those of group B, and vice versa.*

It will be seen from the table that as a rule the growths are here irregular, which is an indication that these pairs of salts are not isostructural. But in some nine cases (possibly ten) parallel growths are obtained and they are tabulated below:—

{ KCl, 37.49	{ CsCl, 42.15	{ CsCl, 42.15	{ NaBr, 32.21
{ AmBr, 43.45	{ KBr, 43.80	{ NaBr, 32.21 } †	{ AmBr, 43.45
{ KBr, 43.80	{ KI, 53.06	{ RbI, 59.62	{ NaCl, 26.92
{ AmCl, 34.96	{ AmBr, 43.45	{ AmBr, 43.45	{ AmBr, 43.45
	{ KBr, 43.80	{ KI, 53.06	
	{ AmBr, 43.45	{ AmCl, 34.96	

With the first pair, parallel growths of a semi-zonal character are obtained, no matter which salt is the solute; the next three pairs could only be investigated in one direction: the second and third with the salt of group *B*, the fourth with the salt of group *A*, as solute. But the remaining six pairs only yielded parallel growths when the salt of group *A* was used as the crystal, the salt of group *B* being the solute; if crystals of group *B* were taken, and solutes of group *A*, then the growths obtained were irregular. This can hardly be caused by the roughness of the surface (owing to the imperfect cleavage) in the salts of group *B*, for, as mentioned above, KCl does give a parallel growth on AmBr.

It will be noted that the difference between the molecular volumes in certain of these pairs is considerable, while many other pairs, which fail to give parallel growths, exhibit far closer molecular volumes. Is it possible that the cubes of AmCl and AmBr, deposited in parallel position on the salts of group *A*, are crystals of the labile (group *A*) forms of AmCl and AmBr †; for the molecular volumes of labile AmCl

and AmBr would be about 42 and 48 respectively, and the differences between these numbers and the molecular volumes of the salts on which they were deposited would be very small, and therefore parallel growths would be expected (the crystals being isostructural). On the other hand, a crystal of AmCl or AmBr may not be able to force a salt of group *A* to take up the labile (group *B*) form; and hence parallel growths may not be formed. This is a hypothesis which can be proved or disproved by a study of parallel growths of isodimorphous pairs of substances, which crystallize in two different systems: and the author hopes to attack this problem in the near future.

#### 4. Zonal Growths.

With some of the pairs of substances investigated, separate discernible crystals of the solute are not formed on the mother-crystal, but, as the solution evaporates away, the solute is evenly deposited on the whole of the surface; a zonal growth (Schichtkrystall) is thereby formed. Under a high magnification, a fine network of lines is often visible parallel to the cube-edges. It was previously shown by the author (*loc. cit.*) that this behaviour is characteristic of isostructural substances, the molecular volumes of which are practically identical; and it is satisfactory to note that the present work is in complete accord with that generalization.

It is seen from the table that the zonal growths lie close to the long diagonal running from the top left hand to the bottom right hand corner, which is the line expressing equality of molecular volume.

Now, as pointed out on p. 243, no separate crystals appear when, say, a drop of a solution of NaBr is placed on a crystal of RbBr, and yet the molecular volumes of these salts are greatly different. But on forcing the crystallization by heating, a most beautiful and copious formation of parallel cubes obtains. On the other hand, with the true zonal growths very few, if any, separate cubes (in parallel position) appear: the solute is deposited, partly in an even manner on the whole of the surface, and partly in ridges which often have crystallographic outlines parallel to those of the mother-crystal. This behaviour was especially observed with the alums, which possess almost identical molecular volumes, and with solutions of ammonium or thallium perchlorate on crystals of rubidium perchlorate. When a crystal of potash-alum and a solution of ammonia-alum are employed, a ridge, hexagonal or triangular in outline, is gradually formed round the edges of the upper surface of the crystal, and many drops of solution may be successively

added and evaporated away by heat, without the separation of separate octahedra. Again, with rubidium perchlorate, the polarization-tint gradually alters owing to the thickening of the crystal by the even deposition of a layer of thallium or ammonium perchlorate.

### III. INTERPRETATION OF PARALLEL GROWTHS IN TERMS OF TOPIC AXES.

The simplest assumption one can make with regard to parallel growths is that they are brought about by a fitting together of similar structures. And it has been shown that in the above two isostructural sub-groups, as well as in the two isostructural groups previously studied by the author (the calcite-sodium-nitrate and the barytes-perchlorate groups), parallel growths are conditioned by similarity of molecular volume. Now, by combining the molecular volume with the axial ratios in a simple way, the distances between adjacent particles of the crystal structure may be calculated; these distances are known as topic axes. Hence, if parallel growths result from the close fitting of two similar structures, it would follow that the topic axes of those pairs of substances which yield such growths should be very close. This was found to be the case with the groups previously studied, and the present investigation affords additional confirmation.

With the salts of group *A*, the similarity of cleavage speaks for a similarity of structure. If, therefore, cleavage cubes 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, in fact, the topic axes.

The latter are calculated from the formulae,  $\chi = \psi = \omega = \sqrt[3]{V}$ , where  $V$  = the molecular volume.

#### *Topic Axes of salts of group A.*

NaCl, 1.3911	NaBr, 1.4768	KCl, 1.5534	NaI, 1.6013
KCN, 1.6045	RbCl, 1.6274	KBr, 1.6299	RbCN, 1.6939
RbBr, 1.7020	KI, 1.7741	AmI, 1.7981	RbI, 1.8132

Similarly, the different compounds in group *B* can be compared with each other with regard to topic axes, but the topic axes of group *B* cannot be compared with those of group *A*.

#### *Topic Axes of salts of group B.*

AmCl, 1.5177	CsCl, 1.6154	AmBr, 1.6318
CsBr, 1.6846	CsI, 1.7889	

Now, a comparison of the collected results, given in the large table on p. 249, with the above topic axes, will show that, within each isostructural group, irregular growths are only afforded by those pairs of salts the topic axes of which betray considerable differences. In other words, a fitting of the one structure into the other cannot take place when the distances apart of the crystal-units, as given by topic axes, differ greatly.

*Addendum.*—An important contribution to the theory of crystal-structure has recently been made by Barlow and Pope (Journ. Chem. Soc. Trans., 1906, vol. lxxxix, p. 1675), which seems to point to the possibility of correlating dissimilar structures. In this memoir the authors advance the idea that a crystalline medium results from the close-packing of identical groups of spheres; each group represents a chemical molecule, and is made up of as many spheres as there are atoms in the molecule; further, the volume of each sphere is approximately proportional to the valency of the atom it represents. It must be noted that the absolute volume of an atom of any given element is not necessarily the same in different compounds of that element, but that a dilatation may occur in passing from one compound to another. The sum of the valencies of the constituent atoms is known as the valency volume.

Now, topic axes result from the combination of axial ratios with molecular volumes; if, however, valency volumes are substituted for molecular volumes, a new set of constants, which Barlow and Pope term equivalence parameters, are obtained.

From the above conceptions and by the use of the equivalence parameters, the authors have been able to explain why certain regularities—hitherto unexplained—subsist between the members of a morphotropic group such as that of the humite minerals; and what is even more important, from a consideration of valency volume, they have constructed assemblages of spheres, derived from each other in a simple way, which account for the crystalline form of many aromatic derivatives.

But in their memoir the authors certainly seem to suggest that equivalence parameters possess some advantages over topic axes—even within an isomorphous or, more generally, an isostructural series—and can be employed in place of them.

The writer would remark on this that although valency volumes may be invaluable for certain purposes, yet topic axes are not the less important when comparisons have to be made among the members of an isostructural group. For, although the crystalline structure may be

deducible from the chemical constitution by means of valency volumes, yet it is only by means of molecular volumes, and therefore of topic axes, that one can compare the relative dilatation of the valency volumes when they unite to form different structures. It is obvious, then, that equivalence parameters do not give the relative magnitudes of the crystal-units of two isostructural substances unless they be further combined with the molecular volumes. Now, since the valency volumes of members of an isostructural group are generally identical, the valency volume may be neglected for purposes of comparison within such a group, and the magnitudes of the crystal-units on Barlow and Pope's theory, or the relative distances between adjacent particles (supposed infinitely small) on the generally received theory, are in reality simply given by the topic axes.

That the consideration of topic axes is indispensable, at any rate within an isostructural group, is proved by the writer's investigations, all of which lead to the conclusion that the possibility of parallel growths can be predicted from a comparison of the topic axes; on the other hand, the following table (p. 256) serves to show that such predictions could not be made from equivalence parameters. The table refers to the isostructural barytes-perchlorate-permanganate group, previously studied by the writer (*loc. cit.*). Of all the nine soluble salts enumerated, only potassium perchlorate and permanganate form parallel growths on the barytes minerals.

It is seen from the table that, with the exception of the ammonium salts, the equivalence parameters do not show great differences; nor can they be arranged in order of magnitude, for it will be seen that some salts possess a very close  $x$ -value to those of the minerals, while others exhibit almost identical  $y$ -values. And it would be impossible to foretell from the table which salts should yield parallel growths. A perusal of the topic axes, however (*loc. cit.*), will show that there is a remarkable relation between similarity of topic axes and formation of parallel growths.

The valency volumes of the halogen salts all possess the same value (namely, 2), with the exception of the ammonium salts, which, together with the cyanides, have the value 8. In the cubic system the equivalence parameters are given by the cube roots of the valency volumes: the equivalence parameters, then, have the values  $\sqrt[3]{2}$  or  $\sqrt[3]{8} = 1.2599$  and 2 respectively, and a consideration of equivalence parameters would lead to erroneous expectations with regard to the formation of parallel growths.

*Equivalence Parameters of the Barytes-Perchlorate-Permanganate Group.*

	Val. vol. <sup>1</sup>	<i>x</i>	<i>y</i>	<i>z</i>
Celestine ...	12	2.2457	2.9180	3.6624
Anglesite ...	12	2.2485	2.8636	3.6924
Barytes ...	12	2.2394	2.9381	3.6478
KClO <sub>4</sub> ...	10	2.1176	2.7138	3.4749
KMnO <sub>4</sub> ...	10	2.1394	2.6835	3.4836
AmClO <sub>4</sub> ...	16	2.5050	3.1581	4.0449
RbClO <sub>4</sub> ...	10	2.1439	2.6913	3.4662
AmMnO <sub>4</sub> ...	16	2.5301	3.0992	4.0810
TlClO <sub>4</sub> ...	10	2.1677	2.7171	3.3958
RbMnO <sub>4</sub> ...	10	2.1806	2.6238	3.4957
CsClO <sub>4</sub> ...	10	2.1776	2.6644	3.4574
CsMnO <sub>4</sub> ...	10	2.2242	2.5615	3.5105

*Conclusions.*

The above work, taken in conjunction with the author's previous investigations, proves that in an isostructural group of substances, irregular growths are only obtained where the molecular volumes differ considerably; and this holds good no matter whether the group consists partly of insoluble minerals and partly of soluble salts, or wholly of soluble salts. But the present memoir especially emphasizes that these conclusions only hold for isostructural substances, and a study of parallel growths will therefore serve to discover whether all the members of a given group are really isostructural.

The investigation of the groups already made does not enable one to predict whether the members of any other isostructural group will all yield parallel growths, because for each group there is a 'crucial difference of molecular volume', which will vary with the group taken; but, when this crucial difference has been determined by a limited number

<sup>1</sup> The values of the valency volumes were derived from the following considerations. Barlow and Pope take S and O as divalent; N, trivalent; and H, Cl, K, Rb, Cs, and Tl monovalent. The writer considers that Ba, Pb, and Sr must be divalent, and has deduced the valency volumes of the permanganates and perchlorates from that of the sulphates by Barlow and Pope's second principle: the replacement of Ba by K necessarily requires a decrease by one in the valency volume of the remaining complex. The valency volume of KMnO<sub>4</sub> is therefore 10, and this agrees with the valency volume of KClO<sub>4</sub> which must necessarily be 10 since Cl is monovalent. If manganese be taken as divalent (KMnO<sub>4</sub> = 11), results are obtained in the equivalence parameters which are at a still greater variance than in the given table.

of observations, it can confidently be expected that pairs of substances exhibiting a less difference of molecular volume will afford parallel growths.

It is obvious from the present investigation that the crucial difference of molecular volume is a very great one, so that it will not be surprising if no other isostructural group of soluble salts can be found of such a size as to render possible the attainment of *irregular* growths.

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