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The question of a relation between the Parallel Growths of Crystals and Isomorphous Miscibility, and the bearing of Parallel Growths on questions of Isomorphism.

(*With Plate II.*)

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I. THE QUESTION OF A RELATION BETWEEN THE PARALLEL GROWTHS OF CRYSTALS AND ISOMORPHOUS MISCIBILITY.

ONE of the most important and striking properties of isomorphous substances is their capacity for forming microscopically homogeneous mixed crystals, the physical properties of which are, as Retgers has especially shown, intermediate between the properties of the constituents. With the great majority of isomorphous substances the mixed crystals can be obtained in all proportions, but with others the miscibility is limited.

The first case of restricted miscibility was discovered by Retgers[1] in potassium phosphate (mol. vol.$=$58·25) and ammonium phosphate (64·17) crystallizing in the tetragonal system; he did not determine the exact proportions which each salt can take up of the other, but estimated them to be about 20 per cent. each way. Krickmeyer[2] found later that the miscibility is much more restricted, for the ammonium salt will only take up as much as 5·5 per cent. of the potassium salt. The two salts are in all other respects similar to each other, on which account they were still regarded by Retgers as isomorphous. Potassium phosphate and arsenate (62·82) form mixed crystals in all proportions, as was proved

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[1] Zeits. physik. Chem., 1889, vol. iii, p. 547.

[2] Zeits. physik. Chem., 1896, vol. xxi, p. 71.

by Muthmann and Kuntze.[1] The latter investigators also found that potassium permanganate (58·53) and rubidium permanganate (63·23) only mix in very restricted proportions, the miscibility scheme being: 1 per cent. $RbMnO_4$ . . . 8 per cent. $KMnO_4$; while the permanganate and perchlorate (54·91) of potassium are perfectly miscible. Again, although ammonium iodide (58·14) and potassium iodide (53·06) are miscible in all proportions,[2] and potassium chloride (37·49) and bromide (43·30) are nearly perfectly miscible,[3] sodium chloride (26·92) and potassium chloride on the other hand do not mix at all (Krickmeyer). Finally, potash alum (546·9) and thallium alum (566·6) are perfectly miscible, whereas sodium alum (549·9) and potash alum are quite immiscible (Krickmeyer).

Although in all the above cases, with the exception of sodium and potash alum, miscibility does seem to go hand in hand with closeness of molecular volume, the evidence would have remained very weak on account of the too small numerical differences, were it not for the more convincing work of Gossner and Wulff.

Gossner[4] observed that the isomorphous hexagonal salts $ZnSiF_6.6aq.$ (145·6) and $NiSiF_6.6aq.$ (144·6) mix in all proportions, while the former is quite immiscible with the isomorphous salt $ZnSnF_6.6aq.$ (166·0). The immiscibility is attributed by Gossner to the considerable difference of molecular volume. The justness of this view is greatly strengthened by the discovery of G. Wulff[5] that ammonium sulphate (74·63, Tutton) mixes completely to give perfect mixed crystals with rubidium sulphate (73·77) and also completely, though yielding somewhat less perfect crystals, with either potassium sulphate (65·33) or caesium sulphate (85·17); potassium and caesium sulphates, however, are totally immiscible, and Wulff points out that the inability to fit together so as to form mixed crystals must be due to the great difference of molecular volume.

Since miscibility and the formation of parallel growths are favoured by the same factor—closeness of molecular volume—it becomes of some importance to discover whether the two properties go absolutely hand in hand, and it was with a view to obtaining fresh evidence on this point that the following investigation was taken up.

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[1] Zeits. Kryst. Min., 1894, vol. xxiii, p. 368.

[2] Gossner, Zeits. Kryst. Min., 1905, vol. xl, p. 69.

[3] Fock, Zeits. Kryst. Min., 1897, vol. xxviii, p. 351.

[4] Zeits. Kryst. Min., 1906, vol. xlii, p. 475.

[5] Zeits. Kryst. Min., 1906, vol. xlii, p. 558.

The Sulphate-chromate Group.

Although the miscibilities of the orthorhombic chromates of the alkali metals have not yet been determined, it seemed desirable to bring them into the scope of the experiments, so as to make the group serve not only to test the question concerning the connexion between miscibility and formation of parallel growths, but also to confirm, if possible, the author's previous results on parallel growths in general. The selenates could not be used on account of their high deliquescence. Good crystals of potassium, ammonium, and thallium sulphates are most difficult to obtain, but Dr. Tutton very courteously placed at the author's disposal excellent crystals of these salts, together with some pure caesium sulphate. The rubidium sulphate employed was purchased from Merck, and was part of the original stock used in the preparation of rubidium perchlorate and permanganate.

The chromates have not been so thoroughly investigated as the sulphates; the rubidium salt was measured by Piccard[1] and its optical properties and cleavage determined by Wyrouboff;[2] the specific gravity has not been previously determined. The caesium salt was measured by Fraprie,[3] who found it dimorphous, one of the forms being orthorhombic and isomorphous with the sulphate; the optical properties and the specific gravity were, however, not determined.

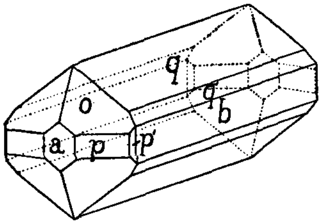

Fig. 1.—Rubidium chromate.

The rubidium and caesium chromates used in the present investigation were prepared by neutralizing rubidium hydroxide (Merck) and caesium carbonate (Merck) respectively with pure chromic acid. The salts were recrystallized.

Rubidium chromate.

System: Orthorhombic.

Ratios of the axes: $a:b:c = 0{\cdot}5666:1:0{\cdot}7490$ (Piccard).

Forms: $q = \{011\}$, $q' = \{021\}$, $b = \{010\}$, $o = \{111\}$, $a = \{100\}$, $p = \{110\}$, $p' = \{130\}$, and $o' = \{112\}$.

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[1] Jahrb. prakt. Chem., 1862, vol. lxxxvi, p. 455.

[2] Bull. Soc. Min. France, 1881, vol. iv, p. 129.

[3] Zeits. Kryst. Min., 1906, vol. xlii, p. 113.

The forms a and p' are new, whilst o' was not observed by the author; the habit of the crystals is shown in fig. 1.

Fundamental angles: (Piccard) $q' : q' = 021 : 0\bar{2}1 = 112° 33'$.
$o : o = 111 : 1\bar{1}\bar{1} = 86\ 43$.

Angles of new forms:

	Observed.	Calculated.
$p : p' = 110 : 130$	29° 58′	30° 0′
$a : o = 100 : 111$	43 26½	43 21½
$a : p = 100 : 110$	29 32	29 32

Cleavage: basal (Wyrouboff).

Specific gravity (16°/4° C.) = 3·518. Mol. vol. = 81·61.

Solubility: 100 parts of water dissolve 73·24 parts at 17·6° C. and the specific gravity of the solution, at 17·6°/4° C. = 1·4897.

Caesium chromate.

System: Orthorhombic.

Ratios of the axes: $a : b : c = 0{\cdot}5640 : 1 : 0{\cdot}7577$ (Fraprie).

Forms: a, b, c, o, p, q, and q'. The habit is very similar to that of the rubidium salt.

Fundamental angles: (Fraprie) $b : p = 010 : 110 = 60° 35'$.
$b : q = 010 : 011 = 52\ 51$.

Cleavage: perfect parallel to b {010}, imperfect parallel to c {001}.

Optics: axial plane parallel to b {010}; first positive mean line normal to a {100}; birefringence, fairly strong; axial angle narrow, $\rho > v$.

Specific gravity (16°/4° C.) = 4·237. Mol. vol. = 90·14.

Solubility: 100 parts of water dissolve 71·35 parts at 13° C., and the specific gravity of the saturated solution, at 13°/4° C. = 1·5027.

Ammonium chromate crystallizes in the monoclinic system, and is isomorphous with the selenate, not with the sulphate.

The following are the molecular volumes of the salts used: the values for the sulphates are due to Tutton, and for the chromate of potassium to Gossner.[1]

	Sulphate.	Chromate.
Potassium	65·33	70·39
Rubidium	73·77	81·61
Thallium	73·98	?
Ammonium	74·63	(81·1)
Caesium	85·17	90·14.

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[1] Groth's 'Einleitung in die chem. Krystallographie', p. 46.

The author's usual method of observation was employed; fresh cleavages or sometimes crystals fresh from their solutions were taken, and on them were placed drops of the solutions of the other salts, the whole being observed under the microscope. To give the details of each experiment would be superfluous; the results are incorporated in the following diagram, which is constructed in exactly the same way as the one given in a former memoir [1] on the halogen salts of the alkalis. No decisive result could be obtained with the pairs denoted by a note of interrogation, owing either to the too rapid deposition of the solute or dissolution of the crystal. (See plate II, and explanation on p. 53.)

Results of Experiments on Parallel Growth.

Solutions.

Crystals.

Mol. Vol.	65·33	70·39	73·77	73·98	74·63	81·61	85·17	90·14
	$_2SO_4$	K_2CrO_4	Rb_2SO_4	Tl_2SO_4	Am_2SO_4	Rb_2CrO_4	Cs_2SO_4	Cs_2CrO_4
K_2SO_4		P	P	P	P	P	Ir	Ir
K_2CrO_4	P		P	?	P	P	P	Ir
Rb_2SO_4	?	P		?	Z	P	P	P
Tl_2SO_4	P	P	P		P	?	P	?
Am_2SO_4	P	P	?	P		?	P	Ir
Rb_2CrO_4	?	P	P	?	P			P
Cs_2SO_4	?	P	P	?	P	P		P (Z)
Cs_2CrO_4	?	Ir	P	?	Ir	P	P	

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[1] T. V. Barker, Min. Mag., 1907, vol. xiv, p. 235.

A glance at the table shows that the irregular growths occur in the squares *at the top right-hand and the bottom left-hand parts of the* diagram: that is, in positions expressing greatest differences of molecular volume. The general results are, then, in accordance with the previous observations on parallel growths.

With respect to the connexion between miscibility and the formation of parallel growths, it is seen that among the sulphates the only case of irregular growth is with potassium and caesium sulphates (plate II, fig. 6), which are precisely the only pair (as yet investigated) which do not yield mixed crystals. In this group the limiting difference of molecular volume for parallel growths does happen to fall with that for miscibility, but this is probably only a coincidence, as will be seen from the results obtained with other non- or partially-miscible pairs of isomorphous substances.

Caesium chromate forms irregular growths on both potassium sulphate and chromate: this is in accordance with expectations. Whether caesium and potassium chromates are miscible or no, is a question the author hopes to examine experimentally.

Other immiscible Pairs of Substances.

Potassium and ammonium phosphates readily give beautiful parallel growths; and, since the solubilities are sensibly equal, the growths may be obtained in either direction—using either substance as crystal or as solute. The growths are so perfect as to be almost of a zonal character, and are formed equally readily on natural faces of the prism or pyramid forms.

Whether rubidium and potassium permanganates form parallel growths on each other has not been decided, owing to the opacity of the crystals; numerous attempts were made to illuminate the slide from above but without success. Potassium perchlorate and caesium permanganate, however, do form parallel growths, and, as the difference of molecular volume is here much greater than with the former pair, it may be safely assumed that the growths are in reality parallel.

Of the remaining pairs mentioned, sodium and potassium chlorides, potassium chloride and bromide have been previously proved to form parallel growths[1]; sodium and potassium alum probably form zoned crystals. The growths of zinc silico- and stanno-fluorides have not been investigated for want of material.

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[1] Min. Mag., 1907, vol. xiv, p. 235.

The present experiments prove that there is no direct connexion between formation of parallel growths and of mixed crystals, although these two properties are favoured by the same factor—similarity of molecular volume; for the necessary closeness of the molecular volume, or of the topic axes, is much greater for miscibility than for parallel growth. The experiments therefore shed some light on the much debated question of the constitution of a mixed crystal. The two views held are: (1) a mixed crystal is a parallel growth of layers (or an intercalation of crystalline pieces) of the two constituents, the fragments coming together without any complete continuity of the same space-lattice mesh across the boundaries between the different constituents; (2) the mixing is of a more intimate nature, one or more atoms of one constituent being replaced, here and there, at some of the nodes of the same space-lattice by a corresponding atom or atoms of the other; so that atoms or radicals common to the constituents are continuously disposed, to form a single set of congruent space-lattices extending throughout the single mixed crystal. Although the optical properties of mixed crystals were formerly expected to throw some light on the subject, yet Pockels[1] finds the present optical data to be insufficient to discriminate between the alternative views, i.e. whether one atom replaces another, or whether crystalline pieces are grown together in parallel position.

The evidence afforded by the present experiments is decidedly against the validity of regarding mixed crystals as parallel growths in the ordinary sense, for if they were, substances which do not mix at all or only partially should not be capable of giving parallel growths, whereas in reality they are.

Another essential difference between mixed crystals and parallel growths is found in the gradual change in the values of the angles of mixed crystals with the composition. When one substance grows in parallel position on another, the values of the angles of the crystals deposited do not tend to approximate to those of the mother-crystal: this was conclusively proved during the investigation of the growths of crystals of potassium perchlorate on barytes.[2] But when mixed crystals are formed the structures accommodate themselves to each other, the result being a structure with intermediate angles. This give and take must be greatly facilitated by the circumstance that the substances come together in the liquid condition, and the accommo-

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[1] Neues Jahrb. Min., 1893, Beilage-Band viii, p. 117.

[2] T. V. Barker, Journ. Chem. Soc., 1906, vol. lxxxix, p. 1143.

dation takes place before, or at least during, solidification; but in the formation of a parallel growth, one of the surfaces is already in the solid condition and cannot therefore alter its dimensions to become absolutely congruent with the liquid substance, nor is it found to induce congruence in the latter. In spite of this, since the structures are similar and nearly congruent, the crystal has sufficient influence on the liquid substance to bring at least one line of particles of very small extent into congruence with a similar line in itself, and, when once this has been effected, the tiny crystals proceed to grow on their own account, just as they would on an amorphous surface, and therefore with the preservation of their own particular angles.

II. The bearing of Parallel Growths on questions of Isomorphism.

The later definition of isomorphism by Mitscherlich was: 'Substances possessing an analogous composition, which crystallize in the same form (or in similar forms), and which are capable of mixing in all proportions, are isomorphous.' This definition, though very useful at the time it was enunciated, is now arbitrary and unsatisfactory for the following reasons:—

(1) The term 'analogous' must not be interpreted too closely, for many compounds are universally admitted to be isomorphous, although the replacing elements or groups are dissimilar. Thus, the ammonium salts are held to be strictly isomorphous with the alkali salts; the cyanides with the haloids; the groups NaSi and CaAl replace each other isomorphously in the felspars; CaSi and 2Al in the pyroxenes; and TiF_2, NbOF, and WO_2 in the compounds described by Marignac.

(2) Similarity of form and angle are found with substances which probably differ in symmetry, e.g., $KLiSO_4$ and $NaLiSO_4$, and it is very difficult to decide whether such compounds ought to be regarded as isomorphous. Again, all cubic substances necessarily possess the same angles.

(3) The researches of Retgers, Krickmeyer, Fock, Gossner, Wulff, and others have shown that many substances, which in all other respects exhibit the properties characteristic of isomorphous substances, do not form mixed crystals in all proportions.

Two other properties have been long advanced as characteristic of isomorphous substances:—(1) the formation of parallel growths; (2) the relief of supersaturation of a solution by inoculation with a substance isomorphous with the solute.

It would be very difficult to offer a definition free from objection. The cause of this is to be found in the fact that the degree of similarity between pairs of isomorphous substances is by no means always the same: nor could this be expected; for, to take an example, even if, as in the cubic system, the angles remain constant, yet each compound has its own molecular volume, which is quite different from those of the isomorphous compounds, and it has been recently proved that those very properties which are used as tests for isomorphism, depend greatly on the value of the molecular volumes. Again, if the miscibility be considered, it will be found that some substances mix in all proportions, whilst other compounds do not, although in all other respects they may be just as similar to each other as the former.

Although isomorphism is difficult to define, there is no doubt that its cause is to be sought in a similarity of structure, by which one means that the points at which the chemical atoms or molecules are situated, are distributed in space in a similar manner. Since any particular form of assemblage must be an equilibrium arrangement due solely to the interaction of forces between the constituent atoms or molecules, it follows that the forces obtaining in compounds built up on the same chemical type will favour similar structures. Compounds of the same type are generally obtained by replacement of elements by others belonging to the same group of the periodic system, whereby the chemical structure (distribution of valencies) remains the same, and of late years Mitscherlich's term 'analogous chemical composition' has been narrowed down to connote this type of replacement alone. This limitation is quite arbitrary: the types of the compounds $NaNO_3$ and $CaCO_3$, $KClO_4$ and $BaSO_4$ are just as analogous as those of the compounds K_2SO_4 and Rb_2SO_4, and much more so than those of the compounds $(NH_4)_2SO_4$ and K_2SO_4.

Similarity of structure gives rise to similarity of physical properties, and it is by means of the latter that the former can be detected. The three chief properties used in the determination of crystal structure are: (1) cohesion (cleavage and elasticity relationships), (2) formation of parallel growths, and (3) the formation of mixed crystals.

(1) The cleavage-directions are of great value in the determination of crystal structure; all the members of a well-defined isostructural group exhibit the same cleavage-directions, although the degree of perfection is, of course, not always the same.

(2) When a regular growth of any kind takes place there is undeniable evidence of some similarity of structure, for the only conceivable cause is a fitting together of two similar structures. The fitting may be possible only along a particular line or plane, as in most of the regular growths met with in the mineral kingdom, e.g., rutile on haematite, or as in some artificially obtained regular growths, e.g., potassium iodide on mica. In other cases, however, the fitting can take place along any line or plane, which proves that to each and every line or plane in one structure, there is a similar line or plane in the other: in other words the whole structures are similar and the two substances are isostructural. When parallel growths of this nature can be obtained, there is overwhelming evidence for regarding the substances in question as possessing absolutely similar structures.

The usefulness of parallel growths in determining whether two substances are isostructural or not, is somewhat weakened by the fact that to obtain them it is not only necessary to have similar structures, i.e., structures possessing the same point-systems, but the distances between the points (topic-axes) must be sensibly equal. This drawback disappears when we are dealing with large groups of substances, for the differences between the topic-axes of consecutive members is generally small. Thus the fact that rubidium sulphate forms parallel growths on either potassium or caesium sulphate, no matter which crystalline form be used, proves that it is isostructural with both, and, hence, that the latter are themselves isostructural.

(3) The formation of mixed crystals was considered by Retgers to be the most important property of isostructural substances. But, just as with parallel growths, the absence of formation of mixed crystals cannot be taken as decisive evidence against the presence of similarity of structure. An additional drawback is also found in the formation of mixed crystals by substances which are certainly not isostructural.

Besides the above three principal methods of exploring crystal structure, a general comparison of the physical properties may be of use, but this method must be used with some caution, for although isostructural substances will necessarily possess similar angles, forms, optical properties, &c., some of these may nevertheless be exhibited by quite dissimilar substances; thus, all cubic substances must exhibit much the same forms, and the angles between them are, of necessity, constant. It is in such cases as these that a study of parallel growths is especially useful.

The ready formation of parallel growths has led some investigators, and notably Tschermak, to the conviction that sodium nitrate and calcite are to be regarded as isomorphous, but little significance has been attributed to this wonderful property by others, partly no doubt because the case was unique. Retgers asserted that parallel growths may not be taken as a criterion for isomorphism. He said of parallel growths: 'Das Phänomen ist nicht beschränkt auf isomorphe, sondern erstreckt sich auch auf morphotrope Körper. . . . Die ganze Erscheinung hat also nicht den geringsten Wert für chemische Schlussfolgerungen. Es ist weiter nichts als ein Influenzieren auf die Richtung bei der Ausscheidung aus dem flüssigen in den festen Zustand und sehr gut vergleichbar dem sich parallel Orientieren von Eisenstäbchen in der Nähe eines starken Magnetes.'[1] Now, although regular growths of morphotropic substances (or even of substances which are not morphotropic) are known, yet parallel growths as exhibited by sodium nitrate and calcite, potassium perchlorate and barytes—i. e. where the substances are isostructural and the whole orientation is congruent—such parallel growths are never found among morphotropic substances (the felspars being held isomorphous). Further, there is only a very 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 crystal-units of the filings is not necessarily congruent with the position of the molecules of the orientating magnet.

The author's investigations prove that the case of sodium nitrate and calcite is by no means so uncommon, for the perchlorate-permanganate group stands in the same relation to the barytes group. In both groups an equal number of atoms have arranged themselves in space to form similar structures: that the structures are similar follows from the similarity of cleavage-directions, form, angles, general physical properties, relief of supersaturation, and the formation of parallel growths. Whether these isostructural substances are to be regarded as isomorphous is a matter of definition. The composition is just as analogous as that of $(NH_4)_2SO_4$ and K_2SO_4, or KCN and KCl, $(NH_4)_2Al_2(SO_4)_4.24H_2O$ and $(C_6H_{11}NH_3)_2Al_2(SO_4)_4.24H_2O$, or $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$. Like all isomorphous substances possessing similar molecular volumes, they form parallel growths; they cannot be made to mix because a suitable solvent cannot be found, and if found double decomposition would set in to form substances with quite

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[1] Zeits. physik. Chem., 1890, vol. v, p. 460.

different crystal structures. On the other hand, caesium and potassium sulphates do not mix, nor do they form parallel growths, because of the great difference of molecular volume. If the latter salts are still regarded as isomorphous, so must also sodium nitrate and calcite, potassium perchlorate and barytes, if one would be consistent.

The author has recently found that the periodates of silver, lithium, sodium, ammonium, potassium, and rubidium form an isomorphous group crystallizing in the tetragonal system with similar angles to the scheelite group. Using the monomolecular formula for the periodates the similarity of composition becomes obvious: RIO_4 and $CaWO_4$. The growths of the periodates on these minerals will be investigated when suitable mineral specimens have been obtained.

The author's thanks are due to Mr. W. Barlow, for valuable advice on the constitution of a mixed crystal; and also to Professor H. A. Miers, in whose laboratory the above work was carried out.

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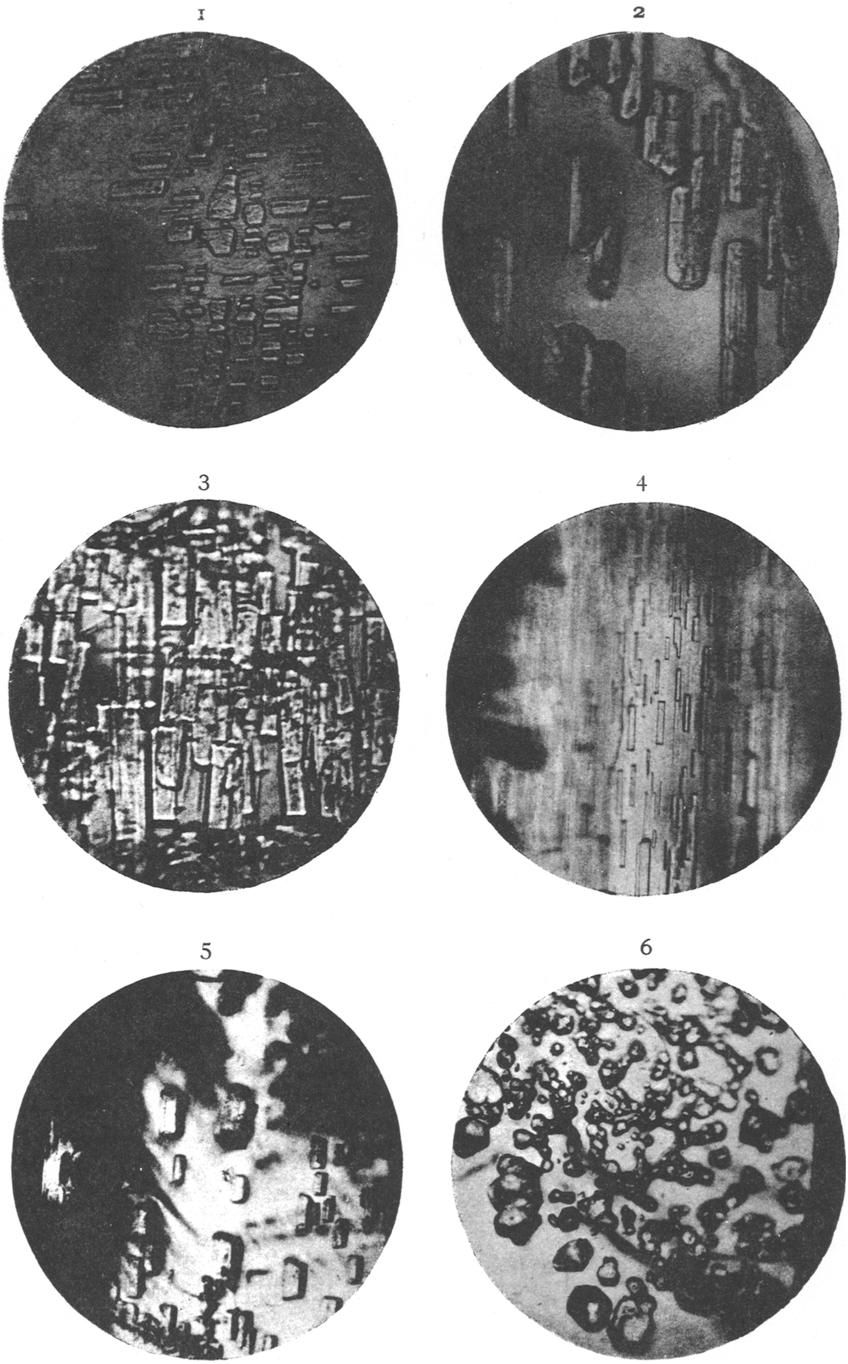
Explanation of Plate II.

Parallel (and irregular, fig. 6) growths of crystals of soluble salts on each other:

Fig. 1.—Rubidium chromate on rubidium sulphate (×100).
„ 2. „ „ on potassium sulphate (×100).
„ 3. „ „ on caesium sulphate (×25).
„ 4. „ „ on caesium chromate (×100).
„ 5.—Caesium sulphate on rubidium sulphate (×25).
„ 6.—Irregular growth of caesium sulphate on potassium sulphate (×25).

(From photographs by Mr. A. Robinson.)



T. V. BARKER: REGULAR GROWTH OF SOLUBLE SALTS ON EACH OTHER.