

Reviews and Notices.

CRYSTALLOGENETIC OBSERVATIONS BY THE LATE CHEVALIER CHARLES
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Crystals from Solutions of mixed isomorphous combinations.

TWO series of crystalline mixed substances must be distinguished among these crystals. In the *first* place, the mixed solution may be composed of substances possessing in their isolated condition a similar chemical constitution and crystalline form, being thus *a priori* isomorphous.

Such isomorphous combinations are known to crystallize together in relatively very variable proportions. However, in many cases, narrow limits are traced by the different solubility of the component salts. Crystals deposited from a solution of two isomorphous combinations, and allowed to grow for some time, are not of homogeneous composition, if the components are notably different as to their solubility. The less soluble salt predominates in the interior of the crystal, the more soluble one in the superficial portion. If the less soluble component be coloured, the interior will be intensely coloured, the tint gradually vanishing towards the external layers. *Vohl's* so-called "paired double salts" of the Magnium* (sic) group, in their assumed equal-molecule constitution, can be only partly formed in so far as the relations of solubility allow. An obvious exception is that a mixture of isomorphous combinations cannot be brought to crystallize, when the salts, whose solutions are to be mixed, are so composed that their contact must give rise to mutual chemical action.

* "Magnium" was a term used by the author for Magnesium. It is thought better to retain it throughout whenever it appears in the German original.—Ed.

The specific crystalline form of the salts, belonging to the same isomorphous group, is known occasionally to be very different. In crystallizing any such mixture, either some one salt acts with a certain prevalence, impressing its form on the mixed crystals, or these take a form different from any of the components when crystallising by themselves. In this last case, the mixed crystals exhibit generally less complicated forms than those of their components. Thus, the mixed crystals exhibit constant variations from the forms of their components, together with frequent irregularities, which, by their continuous repetition, give them a distinctive character. In many cases, the relative quantities of the salts in a mixed solution may determine the form of the crystals.

The differences of solubility being such as to make it impossible in many cases to establish any desired predominance of one of the component salts, experiments in this direction are necessarily limited. All therefore that as been said before relates to crystals deposited from a solution of more than two isomorphous salts.

Experiments have been made on the crystallizations out of mixed solutions of ferrid and cobaltid-cyanide of potassium, the double nitrates of cerium with nickel and manganese, and the double oxalates of iron, chromium, and aluminium, with ammonium, potassium or sodium. The individual members of each of these groups of isomorphous combinations, when isolatedly crystallized, form a group as well defined as the group of the alums, and similarly exhibit certain aberrations from symmetry and slight irregularities. Other subjects of investigation were solutions of double sulphates of the magnium group and potassium, in which variable quantities of sulphuric acid were replaced by chromic acid. The crystals from these solutions, which are isomorphous with the first of these salts, exhibit constantly a "habitus" quite different from that of the double sulphate of magnesia and potash, provided chromic acid has been added in sufficient proportion. The rhombic prisms of this monoclinic salt, in this last case, appear notably shortened, and the terminal surfaces are unusually extended, the crystals assuming thus a tabular form. If chromic acid, instead of sulphuric acid, is introduced into the sulphate of magnesia-ammonia, the crystals undergo no perceptible change.

The cobaltid-cyanide of potassium, like the analogous iron compound, appears invariably in twin crystals, like those formed from a mixture of both these combinations, which Mr. Kopp pronounces to be monoclinic, and Messrs. Schabas and Rammelsberg consider as rhombic.

The crystals from a mixture of cero-manganese and cero-nickel nitrates exhibit a hexagonal tabular form with two extra faces on the edges, like those of their components, the nickel salt showing frequently

truncated edges and angles. These crystals are nearly uncoloured, when the manganese salt prevails; in the opposite case they are light-green, diaphanous, and will easily grow to a considerable size. Their hexagonal character is not yet duly ascertained.

The oxalates of chromium and ammonium or potassium and iron-ammonium deposit out of their mixed solutions bluish-green crystals, which may be allowed to grow large without impairing the perfection of their form. They are exactly identical in form with those of their components. Their transparency is secured by carefully arranging the predominance of the iron salt in the mixture. They are somewhat less sensitive to the action of light than those of the isolated iron salt.

Chemical literature offers but scanty details concerning the double combinations of oxalate of alumina with ammonia, potash, and soda. C. Gerhardt, in his "Treatise of Organic Chemistry," says "The solution of alumina in binoxalate of potash, when slowly evaporated, and especially when a stratum of spirit of wine is spread over it, produces thin lamellæ." These salts are obtained in well formed, transparent, colourless crystals, an inch long, by repeated solution and crystallization. When hydrate of alumina is dissolved in a solution of binoxalate of potash under the action of heat, then evaporated and left to cool, nothing is obtained but crystalline crusts and bubbles, which are aggregations of thin lamellæ. If a notable proportion of the simple alkaline oxalate be added to this solution, it at once produces crystals on concentration. The original solution has always a yellow tint; the crystals, purified by repeated solution and crystallization, give a colourless solution. Good crystals are easily obtained by moderate artificial, or by natural, evaporation,—the use of alcohol is not absolutely necessary.

The re-crystallization of the oxalates here in question does not require another addition of alkaline oxalate, as is the case with the other double salts, which cannot be re-crystallized without decomposition, except in presence of an excess of one of their components. It may thus be supposed that the double oxalates of alumina differ in composition from those of the sesquioxides of iron and chromium. However, both are undoubtedly of similar crystalline form, and their crystalline equivalence is proved by the fact that the double oxalates of alumina, when mixed with those of iron and chromium, yield crystals of the same form as those of the last-named oxalates.

According to Baron Foullon's investigations, the double oxalates of iron and chromium have not yet been accurately investigated. Mixtures of oxalates of iron with those of alumina produce light yellowish-green crystals. Exceedingly beautiful crystals are obtained by dissolving

together one of the alumina compounds together with the chrome salt. According to the mutual proportion of the ingredients these crystals, which may be obtained in very large size, are more or less intensely violet, reflecting rays of ruby-red light.

Another series of crystals from mixtures of isomorphous combinations arises from mechanical mixtures of salts, which, when crystallized separately are either not similar in chemical composition, or identical in crystalline form, or are even dissimilar in both respects, not being isomorphous *a priori*, and only becoming so when crystallizing out of a mixed solution. The sulphates of magnium and cobalt, mixed in very various proportions, are crystallizable in the form of sulphate of magnesium. Both these sulphates are of a similar chemical composition, as they both crystallize with 7 atoms of water; however, the sulphate of magnium is *rhombic*, and the sulphate of cobalt is *monoclinic*, in the form of green vitriol. In a mixture of both, however, the sulphate of cobalt becomes a crystalline equivalent to the sulphate of magnium, and is thus proved to be dimorphous.

The crystallization of the double sulphate of potassium and manganese offers a striking instance of the way in which a combination mixed with another may change its chemical constitution and crystalline form, and thus become a crystalline equivalent to the latter combination. This double sulphate crystallizes with 4 atoms of water, and in a form quite different from that of the double sulphates of the magnium group.

The existence of a double sulphate of potassium and manganese with 6 atoms of water, as mentioned by several chemists, seems to rest on mere supposition. It may be, indeed, worth notice, that among the numerous series of isomorphous double sulphates of the magnium group, the non-existence of this single combination constitutes a "hiatus." This exception is the more remarkable, as there exists a double sulphate of potassium and ammonium with 6 atoms of water.

A solution of the potassium salt mixed with another of the magnium group, gives rise to crystals isomorphous in composition and form to those of this group. A dimorphism of the double sulphate of potassium and magnium is out of question in this case, as the combination, passing into a new form, changes its chemical constitution. The experiments of Professor Rammelsberg, on crystallizations out of mixed solutions of sulphates of copper and iron, of sulphates of iron and magnium, &c., have proved that in such cases, when a mixture of two isomorphous salts crystallizes isomorphously with one of them, the relative quantity of this salt determines the mode of crystalline metamorphosis.

It appears from what has been said, that the comparative chemical and crystallographical examination of two salts in itself, does not always show how far they are isomorphous, or rather crystallographically equivalent, or may become so. The question must be decided by way of experiment. A notable difference exists between the dimorphism of a substance, manifested by its appearance in a pure state in two different crystalline forms, and the other dimorphism in which, only mixed with another substance, it assumes a crystalline form other than the one peculiar to it. The first form of dimorphism may be called "primary," the other "secondary." No doubt many substances will prove dimorphous in the latter way; this, however, can only be ascertained by empirical experiments. The more instances are known, in which a substance with unchanged composition is able to adopt different crystalline forms, the more difficult becomes the question concerning the connexion between chemical constitution and crystalline form.

Episomorphous Crystals. The successive deposition, in one and the same crystal, of compounds, frequently very different in quality, colour, and even in specific form and number of surfaces, has a particular interest. While in naturally crystallized minerals such occurrences are but rare, crystals produced in laboratories offer them frequently in the most conspicuous variations and in the highest perfection of form. The superposition of two compounds is the surest criterion of the crystalline affinity, and more to be relied upon than identity of form or similitude of chemical composition.

The Museum of the Imperial Geological Institute numbers several hundred specimens of varied episomorphous crystals, conspicuous by their size and perfection. The groups of episomorphous combinations, among whose terms superpositions have succeeded, are: (1) the alums; (2) the vitriols; (3) the mixtures of sulphate of magnium with other sulphates; (4) the sulphates and chromates; (5) the double combinations of oxalic acid; (6) the double nitrates of cerous oxide; (7) the ferrid—and cobaltid—cyanides of potassium; (8) the chlorate and bromate of soda.

It results from what has been said before about crystallizations of mixed isomorphous combinations, that superpositions of isolated salts can only take place among the terms of the first series of isomorphous combinations, each term of two isomorphous salts of the second series being a mixture of this term with another salt. The mere introduction of a crystal of one salt into a solution of another will not produce a change of form, although if the two salts be mixed *in solution* the former will be modified by the latter. Thus, a crystal of sulphate of iron cannot grow in a solution of sulphate of magnium, although, in a mixed

solution of both these sulphates, a crystalline mass, isomorphous with green vitriol, is deposited.

Of course, the order, according to which the superposition of salts of an isomorphous group takes place, depends on their relative solubility. However, if the solubility of two combinations is not very different, a superposition of the less soluble salt over a crystal of the more soluble one is possible. In this case the saturated solution of the second salt should be mixed with a small proportion of the more soluble one, then the crystal should be introduced into solutions gradually containing less and less proportions of the more soluble salt, and at last into the pure solution of the less soluble one. This operation is promoted by keeping the vessel, in which the crystallization goes on, at a temperature somewhat inferior to that at which the solutions have been prepared. In this way beautiful crystals of potassium-magnium-chromate-sulphate, with superposition of potassium-magnium-sulphate, have been obtained.

Crystals of simple and mixed salts from an isomorphous group may be superposed in any order by mixtures of salts of the same group, when as much of the most soluble salt as they are able to take up is added to the solutions. If the process of superposition is sufficiently continued, the specific "habitus" of the superposed substance, which it shows when isolated, comes out. Such observations tend to prove clearly what is variable in the special form of such crystals, and what is a fundamental crystallographical character of the substance in question.

The degrees of solubility of the double oxalates in question are represented by the following series:—chrome, iron, aluminium. Crystals have been obtained, in which all these three compounds are superposed on each other. An addition of the double oxalate of alumina and ammonia serves for the saturation of the solutions for all these crystals. The superposed substances are separated from each other by very distinct stratification. Crystals of salts of chromium, and of chromium and aluminium, on which the oxalate of aluminium is superposed, are particularly beautiful.

Chrome alum is somewhat more soluble than common potash alum. A good method of obtaining a superposition of this last alum over the first one, is to leave at first crystals of chrome alum in a solution of cubic alum (alumina alum with an addition of ammonia) in which they are not soluble, and when a stratum of cubic alum is deposited on them, to immerge them in a solution of common alum. The cubic surfaces formed at first, disappear again in the second solution.

The crystals of ferrid-cyanide of potassium increase with extreme rapidity along the axis of the prisms, while the diameter of the latter

increases very slowly. The same is the case with the cobaltid-cyanide of potassium. If crystals of the ferrid-cyanide are left to increase in a solution of cobaltid-cyanide, the ends of the crystal will, in a short time, show prolongations of the yellow cobaltid-cyanide, scarcely any superposition being apparent on the prismatic surfaces. The ferrid-cyanide is somewhat more soluble than the cobaltid-cyanide; however, by arranging the temperature, the superposition may be effected.

The double nitrates of cerium and nickel and of cerium and manganese are not materially different as to their solubility. Their superposition proceeds far more rapidly along the edges of the hexagonal tabular crystals than on their surfaces. At first, green tabular crystals with a broad red margin (or the reverse) are obtained, the superposition over the whole of the crystals progressing very slowly. Chloride of sodium being added to the mixture of both these double salts, crystals are obtained out of the solution, which are neither cubes nor tetrahedrons, but present a new form, resembling those of nitrate of lead.