XX.—*Anhydrous Sulphates of the Form $2M''SO_4.R'_2SO_4$; especially those of Isometric Crystallisation.*

By FREDERIC R. MALLET.

THE mineral known as langbeinite was so named by Zuckschwerdt, who published a description of specimens from near Halberstadt, in Prussian Saxony, in 1891 (*Zeit. angew. Chem.*, 1891, 356), his analyses of the substance being in close agreement with the formula $2MgSO_4.K_2SO_4$. Crystals of the mineral were first discovered in 1897, by Siebert, and examined by Luedecke, who showed that they belonged to the tetartohedral group of the isometric system (*Zeit. Kryst. Min.*, 1898, 29, 255). So far as I have been able to ascertain, the mineral constitutes the first known example, either natural or artificial, of an anhydrous sulphate with the composition expressed by $2M''SO_4.R'_2SO_4$, and, after some investigation into the literature of the subject, I have met with descriptions of only two other analogous salts; namely, $2CuSO_4.(NH_4)_2SO_4$, produced by Klobb in 1892 (*Compt. rend.*, 1892, 115, 230), and $2MnSO_4.(NH_4)_2SO_4$, formed by Lepierre in 1895 (*Compt. rend.*, 1895, 120, 924). The copper salt was prepared by melting one part of crystallised cupric sulphate with three parts of ammonium sulphate, and driving off the excess of the latter by gentle heat, the double salt remaining in "prisms." In obtaining the manganese compound, one part of crystallised manganese sulphate was fused with five parts of ammonium hydrogen sulphate, the excess of the latter decanted off, and the double salt, which forms isometric crystals, purified with boiling alcohol. Nickel and cobalt sulphates, treated like manganese sulphate, yielded salts of the composition $3M''SO_4.2(NH_4)_2SO_4$ (*Compt. rend.*, 1892, 115, 115).

During an examination of langbeinite, from the Mayo salt mines in the Punjab, a short account of which was read before the Mineralogical Society last April (*Min. Mag.*, 1899, 12, 159), I noticed that

the mineral, which fuses at a red heat, on cooling solidifies to a more or less distinctly crystallised mass. This observation naturally suggested that the salt might probably be artificially produced by the simple expedient of fusing magnesium sulphate and potassium sulphate together in the proper molecular proportion. On putting the question to the test, excellent results were obtained, the fused mixture solidifying to a highly crystalline mass, including, under favourable conditions, a large drusy cavity in the interior, lined by numerous well-formed octahedral crystals, often more than a millimetre in diameter.

As it seemed probable that other salts of similar constitution might be formed in the same way, I have spent some time lately in attempting their production, and a considerable number have been prepared; some of isometric crystallisation, like langbeinite, others in crystals with symmetry of lower grade.

The sulphates of the bivalent and of the univalent metals fuse together at temperatures which vary considerably in different cases. Thus, the mixed salts of zinc and potassium melt below redness; those of magnesium and potassium require a full red heat; a yellow heat is necessary with the sulphates of calcium and potassium, whilst for those of barium and potassium an incipient white heat is requisite. In all cases, the colourless mixtures fuse to a clear, transparent liquid. At the temperature of fusion, or not much above it, the mixed sulphates are in some cases nearly stable, scarcely any bubbles being given off, but, more commonly, such are eliminated, comparatively slowly in some instances, quite freely in others, a certain amount of sulphur trioxide being expelled, and a corresponding quantity of oxide of the bivalent metal disseminated through the product. If the temperature, however, is not raised unnecessarily high, and the material is allowed to cool as soon as fusion is complete, it dissolves in most cases so nearly perfectly in water that only a trifling residue—sometimes not more than an unweighable trace—of oxide is found in suspension.

The mixtures were generally dehydrated before fusion, in order to avoid the inconvenient intumescence which otherwise occurs. Except in the case of salts liable to partial reduction on heating, the fusions were made in a platinum crucible. If allowed to cool therein, the product can sometimes be shaken out, but, as a rule, the fused material was poured into a (subsequently covered) nickel crucible, to which it very rarely adheres when cold. Different salts require somewhat different treatment in obtaining the best results as to crystallisation. Thus, finer crystals of $2\text{MgSO}_4, \text{K}_2\text{SO}_4$ were obtained by heating the mould nearly to redness, before pouring in the fused mass, than when the latter was cooled either more quickly or more

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slowly. The corresponding rubidium salt, on the other hand, crystallised better when poured into a cool mould. As a general rule, the most favourable results were obtained when the salts were cast at the lowest possible temperature. There is generally a certain amount of crepitation during the cooling and crystallisation of the material, which is more marked in some cases than in others.

The first question which suggests itself in respect to the products, is whether they are homogeneous, in other words, whether they are composed of one salt, or more than one; and, in this connection, whether the crystals lining the drusy cavities have the same composition as the rest of the material. In so far as the products displaying isometric characters are concerned, there is conclusive evidence that but one salt is present in each.

(1) The crystallisation is the same throughout, although the crystals in the cavities, which are frequently attached on one side only, are naturally the most perfectly developed, the whole of the upper (free) surface of the mass is generally covered by crystalline facets of the same kind, and the fractured surfaces of the material throughout display crystals, or at least crystal faces, similar to those in the cavities.

(2) When fragments,* whether from the cavities or elsewhere, are examined under the microscope in parallel polarised light, all are isotropic.†

(3) Fragments of the highly-coloured products containing nickel or cobalt, when examined with the microscope, show no indication, by difference in colour, of two salts being present.

(4) In view of the above, it would be unnecessary labour to analyse the crystals in the cavities and the general mass of the substance separately, in the case of each salt. This has, however, been done in respect to the magnesium potassium sulphate, which may be regarded as the type of the series, and it has been found, as shown by the analyses given below, that the least crystalline part of the fusion, that nearest to the mould, which cooled most rapidly, and the crystals in the cavities, have the same composition.

* Preferably mounted in Canada balsam.

† Sometimes a few scattered birefringent specks, forming a quite insignificant portion of the whole material, are included in the isotropic fragments; in other cases none are visible. Where present, they are probably due to the original mixture of sulphates not having been in perfect molecular proportion, or to the proportion being slightly altered, during fusion, by the elimination of sulphur trioxide, previously alluded to, whereby a minute excess of R'_2SO_4 is induced.

I. ISOMETRIC SALTS.

Magnesium Potassium Sulphate, $2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$.

The mixed salts fuse at a full red heat, and during the cooling of the mass there is usually considerable intumescence, some of the material from the still liquid interior erupting through the surface crust. On breaking the solidified mass, a drusy cavity is found in the interior, which is of large size when the conditions of cooling have been most favourable. The walls of the cavity are thickly covered by crystals, which are, geometrically, octahedrons, the eight faces being approximately equally developed. The faces are most commonly smooth and lustrous, but are often more or less cavernous, the edges of the hollows being parallel to those of the crystal faces. In many cases, the octahedral edges are replaced by faces of the rhombic dodecahedron. The crystals show a very strong tendency to group themselves with parallel orientation, as one result of which columns composed of interpenetrant octahedrons, with their vertical axes in line, are of frequent occurrence. Measurements of the crystal angles with a reflecting goniometer are given below.

	Measured.	Calculated.
$111 \wedge 1\bar{1}1$	$70^\circ 33'$	$70^\circ 32'$
$111 \wedge 110$	$35 \quad 16$	$35 \quad 16$

In accordance with Luedecke's determination of the natural crystals from Bernburg (*loc. cit.*) as belonging to the tetartohedral group, it would seem that the octahedral faces on the artificial ones should be regarded as those of two tetrahedrons of opposite sign, and in this connection it is noteworthy that a tetrahedron is the predominant, or only, form in the corresponding salts of zinc, manganese, and cobalt. Attempts to settle the point by etching the crystals were not very decisive. When exposed to water, or damp air, for some time, the faces of one set seem to become dull more quickly than those of the other, but the difference is not very sharply marked. The loss of lustre is due to the surfaces becoming pitted by numerous triangular hollows of the same character as the larger ones which produce the cavernous crystals.

The crystals obtained by fusion, on which only the forms mentioned above have been noticed, are simpler than the natural ones examined by Luedecke, which were presumably formed from solution, and on which he discovered eight or nine different kinds of faces.

Employing material from the same fusion, well-developed crystals from the interior, and a portion from the least crystalline part (nearest the mould), were analysed separately, with the following results:

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	Crystals	Exterior.	Calculated.
SO ₃	57·83	57·92	57·89
MgO.....	19·29	19·28	19·41
K ₂ O	[22·88]	[22·80]	22·70
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

A portion of the salt, exposed in powder to the air until it ceased to gain in weight, was found to have increased 56·26 per cent.,* an increase of 56·44 per cent. being equivalent to 13H₂O. Decomposition by hydration, therefore, evidently takes place in accordance with the equation :

or, in the case of the natural alteration of the mineral, one molecule of langbeinite is converted into one molecule of picromerite, and one of epsomite (*Min. Mag.*, 1899, 12, 163).

Zinc Potassium Sulphate, 2ZnSO₄.K₂SO₄.

This salt fuses below a red heat, or at a lower temperature than any of the other potassium double salts examined. None of them (2ZnSO₄.K₂SO₄ included) intumesces on cooling as much as the magnesium salt just described ; the masses obtained do not include equally large cavities, and although well-developed crystals are to be found in the latter, they do not occur in such profusion.

The salt crystallises in unmodified tetrahedrons, the faces of which are generally striated parallel to the edges. The crystals are frequently more or less cavernous. Owing to the concavity of the faces, the angles are ill-adapted for measurement by the reflecting goniometer, but measurement by contact showed no indication of divergence from the calculated (actual) angle of 70°32'.

On analysis :

SO₃ found = 48·29 ; calculated = 48·31 per cent.

When the salt was exposed to the air until the weight no longer increased, the absorption amounted to 46·74 per cent., 13H₂O requiring 47·10 ; the salt therefore decomposes in the same way as the previous one.

* In weather of rather less than medium humidity. The absorption varies, to some extent, with the humidity of the air, and the products of hydration cannot be dried by H₂SO₄, as efflorescence then takes place. The same remark applies to the salts described in the sequel.

Manganese Potassium Sulphate, $2\text{MnSO}_4, \text{K}_2\text{SO}_4$.

The salt forms pale reddish, unmodified tetrahedrons, with faces which are generally smooth and lustrous, but sometimes cavernous.

	Measured.	Calculated.
$111 \wedge 111$	$109^\circ 28'$.	$109^\circ 28'$.

The crystals show a tendency to group themselves with parallel orientation, and sometimes form columns composed of interpenetrant tetrahedrons in parallel position.

On analysis :

SO_3 found = 50.46 ; calculated = 50.42 per cent.

After exposure to the air until no further increase of weight took place, the absorption amounted to between 0.26 and 0.86 per cent. (according to the weather), which was evidently due to hygroscopic moisture only. In its stability, under the circumstances, the manganese potassium salt differs from the corresponding sulphates of magnesium, zinc, nickel, and cobalt ; and its non-decomposition by hydration, in accordance with an equation similar to that given for $2\text{MgSO}_4, \text{K}_2\text{SO}_4$, is in agreement with the experience of Tutton and others, who have been unsuccessful in all attempts to produce the salt $\text{MnSO}_4, \text{K}_2\text{SO}_4, 6\text{H}_2\text{O}$ (Trans., 1893, 63, 342 ; 1896, 69, 399).

Nickel Potassium Sulphate, $2\text{NiSO}_4, \text{K}_2\text{SO}_4$.

The brownish-yellow crystals of this salt are, geometrically, octahedrons, but sometimes there is a certain amount of inequality in size between the two sets of planes, suggestive of + and - tetrahedrons. The solid angles of the octahedrons are occasionally truncated by minute faces of the cube.

	Measured.	Calculated.
$111 \wedge \bar{1}\bar{1}\bar{1}$	$= 70^\circ 33'$	$70^\circ 32'$
$111 \wedge 100$	$= 54\ 47$	$54\ 44$

The crystals tend to group themselves with parallel orientation.

A slight, but quite weighable, residue of nickel oxide was left on dissolving the salt in water, indicating loss of sulphur trioxide during fusion.

On analysis :

SO_3 found = 49.52 ; calculated = 49.65 per cent.

On exposure to the atmosphere, the salt absorbs a large amount of water, but the exact proportion is difficult to estimate, on account of

efflorescence in air of medium humidity, and deliquescence when the air is damp. Results varying from $43\frac{1}{2}$ to 53 per cent., and more, were obtained, $13H_2O$ requiring 48.41.

Cobalt Potassium Sulphate, $2CoSO_4, K_2SO_4$.

The salt is violet when hot and purplish-crimson after cooling, the crystals, as a rule, being somewhat more complex than those previously described. The predominant form is a tetrahedron, of which the trihedral solid angles are truncated by the faces of the tetrahedron of opposite sign, whilst the edges are frequently truncated by faces of the cube. The edges, again, between the + and - tetrahedrons are sometimes replaced by very minute planes, which are, apparently, those of the rhombic dodecahedron, as they seem to make equal angles with the tetrahedral faces. Some crystals, also, are met with showing the faces of an unmodified tetrahedron only. Not unfrequently, the crystals are distorted by elongation parallel to one edge of the predominant tetrahedron.

	Measured.	Calculated.
$111 \wedge 1\bar{1}\bar{1}.....$	$108^\circ 53'$	$109^\circ 28'$
$111 \wedge 1\bar{1}1.....$	70 14	70 32
$111 \wedge 100.....$	54 27	54 44

The crystals are minute, but excellently developed, with smooth faces which have a considerable lustre when the mass of salt is first broken up. As this brilliancy is quickly lost on exposure to the air, the crystals measured were dipped in a dilute solution of Canada balsam in benzene, but even so the reflections were unsatisfactory. Hence, doubtless, the discrepancy between the measured and calculated angles. The crystals show a strong tendency to arrange themselves with parallel orientation.

A slight, but quite weighable, residue of cobalt oxide was left on dissolving the salt in water, indicating loss of sulphur trioxide during fusion.

On analysis :

SO_3 found = 49.34 ; calculated = 49.59 per cent.

On exposing the salt to the air until no further gain in weight took place, the increase amounted to 46.53 per cent., equivalent to about $12\frac{1}{2}H_2O$, $13H_2O$ requiring 48.35 per cent. The deficiency is probably due to the tendency of $CoSO_4, 7H_2O$ to effloresce.

Ferrous Potassium Sulphate, $2FeSO_4, K_2SO_4$ (1).

As ferrous iron is associated with the preceding five bivalent metals in more than one series of isomorphous salts, it would, perhaps,

not be surprising if the compound $2\text{FeSO}_4, \text{K}_2\text{SO}_4$ were found to crystallise in the isometric system. Whatever the possibilities of producing the salt in the wet way may be, it does not seem feasible to prepare it by fusion on account of the facility with which the ferrous sulphate decomposes and ferric oxide is produced. As the oxidation may take place by means of oxygen present in the sulphate, it cannot be prevented by effecting the fusion in a current of hydrogen.

Magnesium Rubidium Sulphate, $2\text{MgSO}_4, \text{Rb}_2\text{SO}_4$

Magnesium rubidium sulphate crystallises almost as freely as the corresponding salt of potassium. The crystals are, geometrically, octahedral, with the edges often replaced by narrow faces of the rhombic dodecahedron.

	Measured.	Calculated.
$111 \wedge 111 = 70^\circ 29'$		$70^\circ 32'$
$111 \wedge 110 = 35\ 15$		$35\ 16$

The crystals display a strong tendency to group themselves with parallel orientation. As one result of this, crystals resembling tetragonal prisms, with pyramidal terminations, are very common; they are made up of numerous interpenetrant octahedrons, having their vertical axes in line, and their centres so close together that, on each side of the pseudo-prism, the lateral dodecahedral faces are united into one plane without striations. Very frequently one pair of octahedral faces, for example, 111 and $\bar{1}\bar{1}\bar{1}$, are comparatively large and cavernous, whilst the adjoining pair, $1\bar{1}1$ and $\bar{1}1\bar{1}$, are rather smaller and smooth, and, where many crystals are in parallel position, those faces which are similarly oriented are respectively cavernous or smooth. It is difficult to isolate crystals showing all eight octahedral faces so as to determine more decisively whether those of the positive and negative octants are differentiated in the way just indicated.

On analysis :

SO_3 found = 47.42 ; calculated = 47.32 per cent.

On exposure to the air until the weight no longer increased, the salt absorbed 45.71 per cent. of water, $13\text{H}_2\text{O}$ requiring 46.14 .

Mixed Crystals.

The preceding include all the isometric double salts which have been prepared (rubidium and caesium sulphates yielding, with the one exception just described, birefringent crystals when fused with those of the preceding bivalent metals). Some mixed crystals, however, such as $\text{MgSO}_4, \text{MnSO}_4, \text{K}_2\text{SO}_4$; $\text{MgSO}_4, \text{NiSO}_4, \text{K}_2\text{SO}_4$;

$\text{MgSO}_4, \text{CoSO}_4, \text{K}_2\text{SO}_4$; $\text{ZnSO}_4, \text{CoSO}_4, \text{K}_2\text{SO}_4$; and $2\text{MgSO}_4, \text{KRbSO}_4$, have been prepared, all of which are octahedral or tetrahedral in form. With the exception of the last, which much resembles the magnesium potassium, and magnesium rubidium, salts in the freedom with which it crystallises, such mixed salts do not crystallise as well as those containing two metals only. Doubtless many other such mixed crystals might likewise be produced.

II.—ANISOTROPIC SALTS.

The following sulphates have been fused together in the same molecular proportion as the preceding:

(1) Potassium sulphate, with the sulphates of beryllium, cadmium, copper, calcium, strontium, barium, and lead, respectively.

(2) Rubidium sulphate, with the sulphates of zinc, manganese, nickel, and cobalt, respectively.

(3) Cæsium sulphate, with the sulphates of magnesium, zinc, manganese, nickel, and cobalt, respectively.

(4) Magnesium sulphate, with thallium, lithium, sodium, and silver sulphates, respectively.

The resulting products are all of non-isometric crystallisation, as shown, in most cases by their external characters, and in all by their birefringence.* While they have not, as yet, been examined in detail, it may be said that many of them afford no obvious indication of the two sulphates being otherwise than in uniform combination. More than one of the coloured products, however, show, by differences in colour, that they are not homogeneous, a fact which is not only pertinent to these particular cases, but also suggests caution in forming conclusions as to those in which absence of colour would make the recognition of two intercrystallised birefringent salts more difficult.

I propose experimenting further, with a view to the production of other double salts of the same general type.