

XXXVII.—*On the Composition of the Hyposulphites.*

By E. A. LETTS, Daniell Scholar of King's College,
London.

THOUGH the salts of hyposulphurous acid have been comparatively well studied, much difference of opinion exists as to their chemical constitution. Rose (*Traité de Chimie Analytique*, p. 1475) states that an atom of water is retained by all the hyposulphites, which is essential to their composition, and can only be expelled when the salts themselves are decomposed. On the other hand, Pape (Jahresb. für 1864, p. 57), Kessler (Pogg. lxxxiv), and some other chemists, maintain that most, if not all the hyposulphites can be obtained in the anhydrous condition. Dr. Schorlemmer (Chem. News, May 28, 1869) thus quotes Pape's view:—"Pape (Pogg., Ann. cxvii, 408) found all the hydrogen present in the form of water of crystallisation, which, with care, could be expelled without the salt being decomposed, but the last portion of water is driven off at a temperature only a few degrees below that at which decomposition begins. By heating the sodium, barium, and potassium salts to 215° C., they can be obtained anhydrous, while at 5° higher they decompose; the lead salt is anhydrous at 100° C., but at a few degrees higher it blackens."

The discrepancies in the above statements may perhaps be accounted for in the following manner:—

First, the determination of sulphur in these salts is sometimes a matter of considerable uncertainty, and though many experiments were performed to ascertain where the difficulty lay, no really satisfactory conclusion was arrived at.

Moreover it has been found impossible to fix definitely the decomposing point of many hyposulphites; thence perhaps Pape's assertions may have arisen. Take for example the sodium salt; this salt, if *rapidly* heated, will bear a temperature of 233° C., without apparent decomposition, but if heat be applied more gradually, the salt actually decomposes at 100° C.

The following experiments were undertaken, with a view to ascertain whether hydrogen was to be regarded as an essential constituent of the hyposulphites.

The salts submitted to experiment were the sodium, barium, strontium, magnesium, lead, nickel, and cobalt hyposulphites.

A specimen of pure crystallised hyposulphite of sodium was first analysed.

The sodium in the crystallised salt was estimated as sulphate. Strong sulphuric acid was poured upon a weighed quantity of the salt in a porcelain crucible, the cover being inverted in the crucible. In this state when the action (which at first was very violent) had subsided, the crucible was cautiously heated. Sulphur and sulphurous anhydride, together with a considerable quantity of sulphuretted hydrogen, were evolved. When these had ceased to come off, the excess of sulphuric acid was expelled, and the remaining salt, after being repeatedly heated with carbonate of ammonia, weighed.

As a mean of three experiments, 18.46 per cent. were obtained, 18.5 per cent. being the theoretical quantity ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$).

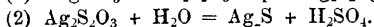
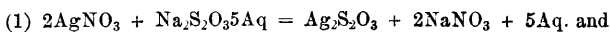
The estimation of sulphur as already stated, was a matter of considerable difficulty.

The following methods were tried :—

- (1.) Oxidation with red fuming nitric acid.
- (2.) Oxidation with aqua regia.
- (3.) Oxidation with chlorate of potass and nitric acid.
- (4.) Oxidation with permanganate of potass (both volumetrically and gravimetrically).
- (5.) Oxidation with bichromate of potass.
- (6.) Rose's nitrate of silver method.*
- (7.) Another plan suggested itself, based on the reaction of the hyposulphites with nascent hydrogen. Here they are decomposed, their sulphur uniting with the hydrogen, to form sulphuretted hydrogen.

In applying this method the hyposulphite dissolved in a little water, and some granulated zinc were placed in a flask fitted with a cork, through which passed two tubes, one for introducing hydrochloric acid, the other for conducting the sulphuretted

* To the hyposulphite dissolved in water (in cold solution) excess of nitrate of silver is added. This occasions the precipitation of hyposulphite of silver, which, as it is well known, is decomposed almost directly it is produced, into sulphide of silver. This, when weighed, represents half of the sulphur. The remaining half existing in the solution as sulphuric acid is precipitated in the ordinary manner with a barium salt, and weighed.



hydrogen produced by the reaction, mixed with excess of hydrogen, into a set of Mitscherlich's bulbs, containing a solution of potass, which absorbed the sulphuretted hydrogen. The escaping gas was afterwards passed into a solution of acetate of lead, so that no sulphuretted hydrogen escaped.

On the whole the best general results were obtained by employing the red fuming nitric acid. The practical details are as follows:—

The salt to be experimented upon is placed in a tube, and lowered into the acid contained in a plain retort. The action is usually violent, though not explosive. When this somewhat moderates, the sulphur separates in yellow flakes, and the retort placed vertically is very gradually heated in a water-bath, starting with cold water, and gradually raising the temperature to boiling; in this way all the sulphur is oxidized. The contents of the retort are next washed into a beaker, and the solution evaporated as far as possible over a water-bath, then diluted, boiled, and whilst boiling, the sulphuric acid produced by the oxidation is precipitated with chloride of barium. If the excess of nitric acid is not evaporated off, a couple of days may be required for the complete separation of the sulphate of barium.*

The water in the crystallised salt was determined by placing a quantity (4·913 grms.) in vacuo over sulphuric acid, and weighing at intervals. In about two months, 1·790 grm. had been lost, the remainder, when heated to 100° C., lost only 0·005 grm. more. The total loss was therefore 1·795; this represents 36·5 per cent; according to the formula, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, five molecules of water equal 36·3 per cent. It is therefore perfectly evident that the whole of the water contained in this salt is expelled, either in vacuo over sulphuric acid, or at 100° C. In order to verify this, another experiment was made in the same manner. In this latter 36·3 (being exactly the five molecules) was lost.

Hyposulphite of Sodium dried at 100° C., gave on analysis 28·8 per cent. sodium (estimated as sulphate), and 40·2 (the mean of five experiments) of sulphur. The formula of the anhydrous hyposulphite requires 40·5 per cent. sulphur, and 29·1 per cent. of sodium.

* Tetrathionate of barium is soluble in nitric acid, but gradually decomposes into sulphate.

The results may be thus compared :—

	Found.	Calculated $\text{Na}_2\text{S}_2\text{O}_3$.
Sodium	28·8	29·1
Sulphur	40·2	40·5
Water expelled at 100°C.	36·3	36·5($5\text{H}_2\text{O}$)

Hyposulphite of Barium was the next salt experimented upon. It was prepared by mixing hot and tolerably strong solutions of chloride of barium and hyposulphite of sodium, and allowing the mixture to cool. Under these circumstances brilliant white laminae were precipitated of a beautiful silvery appearance, which were washed several times with distilled water, and dried upon blotting paper.

The barium was estimated as sulphate. Four determinations gave—

I.	II.	III.	IV.
51·1	51·0	50·9	50·9 per cent. Ba.

In the formula $\text{BaS}_2\text{O}_3\cdot\text{H}_2\text{O}$, the barium amounts to 51·3 per cent.

The sulphur was estimated in the same manner as that already detailed for the sodium salt. But as the sulphate of barium formed by the oxidation of this salt is insoluble, and the proportion of barium present is to the sulphur as 1 to 2, the BaSO_4 , when weighed, represented half the sulphur. The other half was precipitated separately with chloride of barium.

The barium and sulphur thus estimated may be compared with the theoretical quantities, thus :—

	Found.	Calculated $\text{BaS}_2\text{O}_3\cdot\text{H}_2\text{O}$.
Barium	51·0	51·3
Sulphur	23·9	23·9

From these estimations it is evident that the salt was pure hyposulphite of barium, containing one molecule of water. In order to determine whether this water could be expelled, 0·5 gramme of the salt was left in vacuo over sulphuric acid for three or four days, and then heated to 100° C. in a water oven; the salt had then lost ·039 grm. This represents 6·7 per cent. of water. In another experiment, 3·397 grm. being taken, 0·228 was lost; this also represents 6·7 per cent.

The one molecule in $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ also equals 6·7 per cent. It is therefore evident that the salt loses all its water at 100°C .

The results obtained by the analysis of the hyposulphite of barium dried at 100°C . were—

	Found.	Calculated BaS_2O_3 .
Barium.....	54·9	55·0
Sulphur	25·5	25·5
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Water expelled at 100°C .	6·7	6·7(H_2O)

Hyposulphite of Lead.—To a tolerably concentrated solution of pure hyposulphite of soda, a solution of acetate of lead was added (at a temperature of 60°C .), till the precipitate first formed ceased to be redissolved. The mixture was then rapidly filtered, and cooled in a vessel containing cold water. Abundant starry masses of pure white crystals* were gradually formed and precipitated. They were washed in cold water and dried on blotting paper. The lead in this salt was determined as sulphate; 64·2 per cent. and 64·6 per cent. were thus obtained. The formula PbS_2O_3 requires 64·8. The sulphur was estimated in the same manner as in the barium salt, the sulphate of lead, the result of the oxidation of the salt, representing half the sulphur. The other half was estimated separately in the filtrate from the sulphate of lead.

The following are the results:—

	Found.	Calculated PbS_2O_3 .
Lead.....	64·4	64·8
Sulphur	19·9	20·0

It is therefore evident that hyposulphite of lead crystallises as an anhydrous salt.

Hyposulphite of Strontium was prepared by mixing equivalent quantities of solutions of hyposulphite of sodium and chloride of strontium; on cooling, large hexagonal crystals were formed. The strontium in these was estimated as sulphate, 30·4 per cent. of strontium being thus obtained. The formula $\text{SrS}_2\text{O}_3 \cdot 5\text{Aq}$ requires 30·3.

The sulphur was determined as in the lead and barium salts, the sulphate of strontium formed representing one half of the

* If these conditions be not strictly observed, it is possible the hyposulphite will not be quite white. It was after many experiments on its preparation that a good method was obtained.

sulphur. Two experiments were made; they both gave 22·0 per cent.; 22·1 is the quantity required by theory. For the water, 0·5 gramme of the salt was heated in a water-oven. It lost 1·239, representing 24·7 per cent., the formula of the crystallised salt being $\text{SrS}_2\text{O}_3\cdot 5\text{H}_2\text{O}$. Four out of the five molecules H_2O equal 24·9. It thus appears that only four out of the five molecules are expelled at 100°C .; but as it was thought possible that the remaining molecule H_2O might be expelled at a somewhat higher temperature, an experiment was made to ascertain this fact. For this purpose a quantity of the dried salt was placed in a Liebig's drying tube, and heated in a bath of fused paraffin, whilst a current of dry air was drawn over it by an aspirator, the water being collected in a weighed chloride of calcium tube.

10·235 grms. of the salt, dried at 100°C ., was placed in the drying tube, and the paraffin-bath very gradually heated. At each rise of about 10° the Liebig's tube and chloride of calcium tube were disconnected and weighed. When the temperature reached 200°C ., 0·421 gm. had been lost. This loss equals 4·1 per cent. Now 8·2 represents the molecule of water remaining in the salt; this loss then is one-half of the water present. The salt dried at 200°C ., must therefore be represented as $2\text{SrS}_2\text{O}_3\cdot\text{H}_2\text{O}$, and this will not part with its water without decomposition.

A curious phenomenon was observed whilst making this experiment. As the temperature rose the salt lost its white colour, and became quite yellow, the depth of the colour augmenting with the temperature; but upon cooling, it regained its white appearance.

Hyposulphite of Magnesium was obtained in tufts of transparent colourless prismatic plates, on evaporating its solution produced by the decomposition of strontic hyposulphite and magnesian sulphate in equivalent proportions, from which the sulphate of strontium had been separated by filtration. The magnesium (estimated as sulphate) gave—

I.	II.	III.
9·94	9·86	10·0 per cent.

The formula $\text{MgS}_2\text{O}_3\cdot 6\text{H}_2\text{O}$, requires 9·83 per cent. magnesium.

The sulphur was determined in the usual manner (as in the sodium salt). This gave—

I.	II.	III.
26·2	26·0	25·9 per cent. S.

The formula $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ requires 26·2. The salt lost at 100°C .—

I.	II.	III.
22·96	22·96	22·8 per cent.,

corresponding to a little more than half the water contained in the crystallised salt. This result was fully confirmed by the estimation of the magnesium in the salt dried at 100°C .

An experiment was made in the same manner as detailed for the strontium salt, to ascertain whether further water could be expelled at temperatures above 100° , but the salt was decomposed.

Hyposulphite of Nickel was prepared by mixing solutions of strontic hyposulphite and sulphate of nickel, filtering off the sulphate of strontium thus produced, and concentrating the solution in vacuo over sulphuric acid. When of very small bulk, large crystals of a beautiful dark green colour were produced.

They seemed very stable in air, not altering in appearance when kept five or six months. The nickel (as sulphate) was found to amount to—

I.	II.
21·4	and 20·7

The formula $\text{NiS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, requires 21·1 per cent.

The sulphur was determined by oxidation with nitric acid, and weighing as sulphate of barium.

I.	II.
22·6 per cent.	and 23·0 per cent. S.

were thus obtained. The formula $\text{NiS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ requires 22·9. To determine the water, a quantity of the salt was placed in vacuo over sulphuric acid. It however slowly decomposed. The decomposition occurred rapidly when the salt was heated to 100°C .

Hyposulphite of Cobalt was obtained in the same manner as the nickel salt, using sulphate of cobalt in the place of the sulphate of nickel. The solution was pink when dilute, but when much concentrated, formed a dark blue syrup, from which the hyposulphite of cobalt separated in a dark red crystalline mass, which was deliquescent in air. The cobalt was estimated

as sulphate; this amounted to 21·2 per cent. The formula $\text{CoS}_2\text{O}_3, 6\text{H}_2\text{O}$ requires 21·5 per cent. The results of the sulphur estimation were not satisfactory.

This salt was even more unstable than the nickel hyposulphite, and decomposed when simply kept in a stoppered bottle, it was therefore found impossible to determine the water.

By the experiments above described, I am led to the conclusion that hydrogen is *not* a necessary constituent of the hyposulphites. Commencing with the sodium salt we find that it crystallises with six molecules of water, and that the whole of these are given off at 100°C ., or in vacuo over sulphuric acid. Pape (Pogg. Ann. cxxii, 408) asserts that a temperature of 215°C . is necessary to expel the last molecule of water from this salt. The barium salt crystallising with only one molecule of water, can be obtained anhydrous in the same manner. The lead salt crystallises free from water, its formula (as it crystallises) being PbS_2O_3 . The strontium salt is somewhat more complex in the arrangement of its molecule. From its analysis it would seem to crystallise with five equivalents of water. Of these four may be expelled at 100°C ., and at a higher temperature (200°C .) half a molecule more is given off, but the remaining half must be constitutional, as immediately above this temperature the salt decomposes. It is therefore probable that the molecule of this salt should be formulated thus, $2(\text{SrS}_2\text{O}_3), 10\text{H}_2\text{O}$, nine molecules only of water being expelled without decomposition of the salt. Kessler (Pogg. Ann., lxxxiv. 274) asserts that strontium hyposulphite crystallises with six equivalents of water (instead of the five found by these experiments), and that it retains one at 180°C . The magnesium salt loses at 100°C . only three out of the six molecules of water which it contains; the other three do not appear to be expelled till decomposition of the salt has commenced. The cobalt and nickel salts decompose so readily, that they are not well suited for experiments in this direction.