

XLVII.—*Experiments on the Action of Potassium-amalgam, Sulphuretted Hydrogen, and Potassic Hydrate respectively, on Tetra- and Penta-thionate of Potassium.*

By VIVIAN LEWES, Assistant in the Laboratories, Royal Naval College.

(1.) *Action of Potassium-amalgam on a Solution of Potassic Tetra-thionate.*

SOME pure well-defined monoclinic crystals of anhydrous potassic tetrathionate, prepared by the process described by me in the *Chem. Soc. Journal*, 1881, 68, were dissolved in distilled water, and small pieces of potassium-amalgam added until the solution gave a slight alkaline reaction with litmus-paper.

No sulphur separated, and after the mercury and slight scum from the amalgam had been filtered off, the solution gave the following qualitative reactions.

- a. Argentie nitrate gave a white precipitate, darkening on warming.
- b. Baric chloride, slight white precipitate on standing, dense white precipitate on addition of alcohol, soluble in boiling water, and recrystallising on cooling.
- c. Hydric chloride on standing or warming gave a precipitate of sulphur, with evolution of sulphurous acid, but no sulphuretted hydrogen.
- d. Ferric chloride, deep violet colour, disappearing on standing.

From these reactions it is evident that the tetrathionate has been decomposed, with formation of thiosulphate.

The portion of the solution left after the foregoing experiments had been performed, was again tested with litmus-paper, and the faint alkaline reaction having disappeared, a small fragment of amalgam was added, the solution filtered, and excess of baric chloride and alcohol added; a dense white precipitate formed, which was filtered off, washed with cold water, and then boiled with excess of water,

which dissolved the whole of the precipitate, and on cooling deposited a crop of crystals.

These crystals were drawn, rinsed, dried, and analysed, giving results agreeing with the composition of baric thiosulphate.

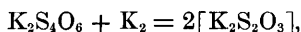
A saturated solution of potassic tetrathionate was then taken and potassium-amalgam added until it gave a faintly alkaline reaction. The clear liquid was decanted from the mercury and placed to crystallise over hydric sulphate in a vacuum, and yielded a crop of needle-shaped prismatic crystals, giving all the reactions of potassic thiosulphate.

A third solution of potassic tetrathionate was then taken, and potassium-amalgam added until the solution became strongly alkaline, the scum and mercury filtered off, and the clear solution tested, with the following results:—

- a. Argentic nitrate gave an immediate black precipitate;
- b. Plumbic acetate, a black precipitate;
- c. Hydric chloride, a precipitate of sulphur, with evolution of sulphurous acid and sulphuretted hydrogen;

these reactions showing the presence of sulphide as well as thiosulphate.

From the foregoing experiments it is evident that potassium amalgam added to a solution of potassic tetrathionate causes a decomposition of the tetrathionate with formation of thiosulphate—



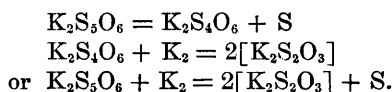
and that the addition of more potassium than is required for this decomposition causes the formation of sulphide.

## (2.) *Action of Potassium-amalgam on Potassic Pentathionate.*

Some fine crystals of potassic pentathionate were dissolved in water, and potassium-amalgam was added piece by piece to the solution, causing at once a considerable precipitate of sulphur. As soon as the liquid became slightly alkaline, the sulphur was filtered off, but on standing, the clear solution again became opalescent; it was again filtered, and the solution remained clear, and behaved in all respects like the potassic thiosulphate formed by the reduction of the tetrathionate.

A further addition of potassium-amalgam to this solution caused the formation of sulphides.

Hence it is evident that the pentathionate is first reduced to tetrathionate with separation of sulphur, and that the tetrathionate is then converted into thiosulphate.



(3.) *Action of Sulphuretted Hydrogen on Potassic Tetrathionate.*

Five grams of potassic tetrathionate were taken, dissolved in water, and well washed, and hydric sulphide passed through the solution until it became saturated; it was then allowed to stand in a well stoppered bottle for several hours, at the end of which all smell of hydric sulphide had disappeared, and a considerable deposit of sulphur had taken place.

The solution was again saturated with the gas, and again, on standing, all smell disappeared; at last, after several saturations, the smell of hydric sulphide became constant, even after standing a week, and the solution was then filtered through a paper, the weight of which was known, and the clear filtrate placed in a dish, over lumps of potassic hydrate in a desiccator, to free it from all undecomposed hydric sulphide. The solution was then evaporated to dryness in a vacuum, and deposited a crop of prismatic needles, round the base of which an amorphous salt was deposited. This amorphous salt on recrystallisation yielded prismatic needles of the same form as the previous ones.

The sulphur deposited on the tared filter was weighed, after having been well washed and dried, and the weight of salt formed by the decomposition was also ascertained.

Sulphur deposited = 2.604 grams  
Salt formed = 3.1 „

The salt formed was then analysed qualitatively, with the following results:—

- a. Argentic nitrate gave with an aqueous solution of the salt, a white precipitate, darkening on warming.
- b. Hydric chloride gave on standing a precipitate of sulphur, with evolution of sulphurous acid gas.
- c. Ferric chloride gave a deep violet coloration.
- d. Baric chloride gave a white precipitate, soluble in excess of hot water, and recrystallising on cooling.

The remainder of the salt was then analysed quantitatively, the sulphur being determined by oxidation with fuming nitric acid, and weighed as baric sulphate after due precautions had been taken to free it from baric nitrate.

The potassium was estimated as potassic sulphate—

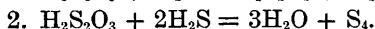
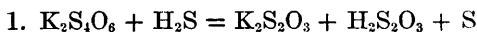
Potassium = 35.8 per cent.  
Sulphur = 33.2 „

which nearly agrees with the calculated composition of Kessler's potassic hyposulphite ( $3[\text{K}_2\text{S}_2\text{O}_3]\text{H}_2\text{O}$ ).

From these results it appears that sulphuretted hydrogen, when passed into a solution of potassic tetrathionate, reduces it to potassic thiosulphate with precipitation of sulphur.



and this reaction probably takes place in two stages—



If we now take this equation and calculate from it the amount of sulphur deposited and potassic thiosulphate produced by the decomposition of 5 grams of potassic tetrathionate, we obtain numbers agreeing very closely with those found in the foregoing experiments:—

	Calculated.	Found.
Salt taken . . . . .	5.0 grams	5.0
Sulphur deposited ..	3.14 „	3.1
Hyposulphite formed	2.64 „	2.634

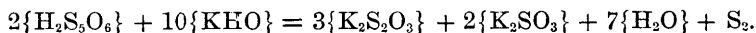
In order to make sure that the sulphur deposited did not contain any salt, it was ignited—

Crucible + ash	= 15.87
Crucible	= 15.868
Ash	= 0.002

and as the ash of the filter used would weigh 0.0015 gram, the sulphur was practically pure.

#### (4.) *Action of Potassic Hydrate upon a Solution of Potassic Pentathionate.*

If potassic hydrate be added in excess to a solution of Wackenroder pentathionic acid, the higher thionates are entirely decomposed with formation of thiosulphate, sulphite, and precipitation of sulphur—



This can easily be proved qualitatively, as has been done by Messrs. Takamatsu and Smith (*Chem. Soc. J., Trans.*, 1880, 592), but no quantitative proof of the correctness of the equation is possible, owing to the uncertain composition of the Wackenroder acid.

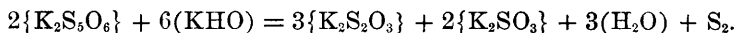
Some pure crystals of potassic pentathionate were taken, weighed, and dissolved in a few drops of water, and 5 c.c. of a potassic hydrate

solution of known strength added. This produced an immediate precipitate of sulphur, which was made to coagulate by shaking, and was then filtered off, the filtrate and wash-water being titrated with standard acid, to determine the amount of potassic hydrate used up in the decomposition of the salt.

Weight of potassic pentathionate taken was 0.914 gram, which required for its decomposition 0.4318 gram of potassic hydrate, and if these numbers are divided by the molecular weight of the compounds to which they refer—

$$\frac{0.914}{0.334} = 0.0027; \quad \frac{0.4318}{56} = 0.0077.$$

quotients are obtained which stand to one another nearly in the ratio of 1 to 3, pointing to the equation—



(5.) *Action of Potassic Hydrate upon a Solution of Potassic Tetrathionate.*

Pure crystals of potassic tetrathionate were taken, dissolved in water, and known quantities were mixed with potassic hydrate in solution in the ratios—

(1.)	2 molecules	$K_2S_4O_6$	to	4 molecules	KHO
(2.)	3	„	„	8	„ „
(3.)	4	„	„	12	„ „

These mixtures were sealed up in tubes, and allowed to stand for some days, and were then opened, and after being made up to a known volume with distilled water, were carefully examined, the object being to ascertain if sulphates were formed when potassic hydrate acts upon the tetrathionate in any of the above proportions.

In no case was any trace of sulphate found, the reactions seeming to be always productive of thiosulphate and sulphite.

The presence of these products of decomposition was proved in the case of tube (3), by precipitating them with baric chloride, and boiling the precipitate for some time with excess of water, filtering hot, and washing the precipitate with boiling water.

The precipitate was then dried and weighed, the filtrate and wash-water being concentrated and placed to crystallise.

The potassic tetrathionate taken in this experiment weighed 2.94 grams, and yielded 2.3 grams of baric sulphite, equivalent to 1.7 grams of potassic sulphite.

This baric sulphite was entirely soluble in hydric chloride, but after

standing the acid solution became slightly opalescent, showing that a small quantity of thiosulphate had remained in the sulphite.

If these numbers be divided by the molecular weights of potassic tetrathionate and sulphite respectively, we obtain quotients standing to each other nearly in the ratio of 1 to 1, the slight discrepancy being due to the trace of thiosulphate remaining undissolved.

The filtrate and wash-water from the baric sulphite on standing deposited a fine crop of small rectangular prismatic crystals, which were drawn, and dried over hydric sulphate, weighed, and analysed quantitatively, giving—

Barium = 50·8 per cent.

Sulphur = 23·3 „

agreeing with the composition of baric thiosulphate, with 1 mol. of water of crystallisation.

2·435 grams of potassic tetrathionate were then dissolved in a little water, and were sealed up in a glass tube with a known quantity of potassic hydrate, and allowed to stand in a warm place for two days. No separation of sulphur took place. The tube was then opened, and the amount of potassic hydrate remaining uncombined determined by rapid titration with a solution of standard acid.

It was found that 1·3288 grams of potassic hydrate had been required for the decomposition of the 2·435 grams of potassic tetrathionate, and dividing these numbers by 302 and 56 respectively, we obtain the quotients 0·008 and 0·0024, which stand to each other as 1 to 3.

From these experiments it is evident that when potassic hydrate acts upon potassic tetrathionate, potassic sulphite and thiosulphate are formed; also that for every molecule of the tetrathionate, 3 molecules of potassic hydrate are required, and 1 molecule of potassic sulphite is formed, results which conclusively point to the equation—



I have been for some time at work upon other reactions of the higher thionates, and hope shortly to place the results before this Society.