XXXVII.—*The Precipitation of Lead Thiosulphate and its Behaviour on Boiling with Water.*

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THE formation of lead sulphide when lead thiosulphate is boiled with water is explained in several ways in modern works of reference. On the sole authority of Fogh (*Ann. Chim. Phys.*, 1890, [vi], **21**, 56) the reaction is frequently represented by means of the equation:

$$2PbS_2O_3 = PbS + PbS_3O_6.$$

The present authors, having failed to obtain lead trithionate by this reaction, have examined the data in Fogh's paper, and have come to the conclusion that the above equation has no justification. Apart from the fact that the lead thiosulphate used in the experiments was prepared by a method which probably gave an impure product, the actual experimental data are arithmetically untrustworthy. Starting with 5·087 grams of the thiosulphate, and boiling in a large quantity of water for three hours, Fogh obtained a precipitate which weighed 3·5160 grams, and a filtrate containing both lead and sulphur. On the basis of the above equation, 1·906 grams of sulphide and 3·181 grams of trithionate should be formed. After determining the total lead and total sulphur in both precipitate and filtrate, he expressed his results as follows: The calculated values are obtained from the assumption that the precipitate contains all the lead sulphide (1·906 grams) and 1·610 grams of the trithionate, the remaining trithionate, 1·571 grams, being in the filtrate.

	Precipitate.		Filtrate.	
	Calc.	Found.	Calc.	Found.
Lead	2·490	2·479	0·817	0·809
Sulphur	0·646	0·638	0·213	0·209

On examining these figures it will be observed that the ratio of lead to sulphur in the filtrate does not correspond with that required for PbS_3O_6, and that, in fact, the calculated quantity of sulphur should be 0·379. This error is so remarkable that it seems reasonable to assume that Fogh calculated the amount of sulphur in 1·571 grams of lead sulphide, which is 0·211 gram. In view of the close agreement between the experimental and the wrongly calculated numbers, it is impossible to base any deduction on the analytical results, and the above equation is without quantitative support.

Another equation which is frequently used to describe the change is that suggested from analogy to the similar behaviour of the silver salt, namely, $PbS_2O_3 + H_2O = H_2SO_4 + PbS$. The authors have found that only a very slight acidity is developed on boiling for many hours, so that sulphuric acid cannot be assumed to be an essential final product of the reaction. Faktor (*Zeitsch. anal. Chem.*, 1900, **39**, 351) states that the precipitate produced by adding hot concentrated sodium thiosulphate to lead nitrate solution does not blacken, but only turns grey. In the presence of ammonium chloride, however, the blackening is rapid, and he asserts that the precipitate is then composed entirely of lead sulphide. Norton (*Chem. News*, 1901, **89**, 254), who heated lead thiosulphate with water in sealed vessels to over 140°, appears to be the only worker who has recognised the presence of considerable quantities of free sulphur in the black residue. Attention to this fact, together with the observation that the change takes place most readily in the presence of excess of sodium thiosulphate, has led the present authors to the conclusion that the ordinary reaction is best represented, as far as the initial and final states are concerned, by the equation:

$$PbS_2O_3 + 3Na_2S_2O_3 = PbS + 4S + 3Na_2SO_4.$$

This change may be due to the transformation of a complex ion in solution, because the indications are much less clear in the case of lead thiosulphate alone, although even in this case the products are sulphide sulphate, and free sulphur with small amounts of sulphuric acid, the main reaction being probably analogous to the above, that is, $4PbS_2O_3 = PbS + 4S + 3PbSO_4$. It will be seen that both these reactions bear a close resemblance to the usually accepted representation of the decomposition of sodium thiosulphate when heated alone in the absence of air, $4Na_2S_2O_3 = Na_2S + 4S + 3Na_2SO_4$.

The trustworthiness of Fogh's data is still more questionable when his method of preparing lead thiosulphate is considered. In the analysis of specimens prepared by precipitation from lead acetate the authors have found that the percentage of sulphur determined gravimetrically and the amount of thiosulphate determined iodometrically are almost invariably lower than those deduced from the formula PbS_2O_3, and that the discrepancy is caused by the presence of lead acetate. From fairly concentrated solutions using equivalent quantities of lead acetate and sodium thiosulphate, the precipitate is the double salt,

$$Pb(C_2H_3O_2)_2,2PbS_2O_3,$$

which has previously been obtained in a less direct manner by Lemoult (*Compt. rend.*, 1904, **139**, 422). From more dilute solutions or in the presence of excess of sodium thiosulphate, the precipitate approximates more closely to the simple salt, PbS_2O_3, but once the double salt has been precipitated it is remarkably stable, and requires prolonged washing with water to effect any change in its composition. For this reason it is unlikely that Fogh, who mixed *N*/2-solutions of lead acetate and sodium thiosulphate,* and did not presumably take any excessive precautions in washing, obtained a precipitate containing 20·1 per cent. of sulphur, which is the theoretical figure for PbS_2O_3, and the analytical value given in his paper. It must be noted that the percentage of lead is of little value in distinguishing between the two salts, since:

PbS_2O_3 requires Pb = 64·85; S = 20·10.

$Pb(C_2H_3O_2)_2,2PbS_2O_3$ requires Pb = 64·46; S = 13·32 per cent.

Fogh states that from *N*/2-solutions he obtained a filtrate containing only sodium acetate and a precipitate, which contained, after washing, 20·1 per cent. of sulphur. The authors obtained a

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* For this purpose a *N*-solution of sodium thiosulphate contains half a gram-molecule per litre. It is, of course, only *N*/2 referred to iodine.

filtrate containing a considerable quantity of thiosulphate and a precipitate with less than 17 per cent. of sulphur. The exact nature of the equilibrium between lead acetate, sodium thiosulphate, and water is being made the subject of further inquiry, but it is safe to conclude that the thermochemical and other data and conclusions of Fogh, based on the assumption that his precipitate was pure thiosulphate, are not correct. In the present investigation all specimens of lead thiosulphate for the study of its decomposition were obtained from the nitrate by adding an equivalent quantity of sodium thiosulphate, a process which is found to yield the pure salt.

EXPERIMENTAL.

The Precipitation of Lead Thiosulphate.—12·5 Grams of sodium thiosulphate and 19·0 grams of lead acetate (equivalent quantities) were each dissolved in about 150 c.c. of water, and the solutions mixed. The resulting precipitate was washed by decantation several times, collected, and dried in a vacuum desiccator. It was first analysed by oxidising with bromine, removing the lead sulphate, and then treating the filtrate with barium chloride to obtain the rest of the sulphur as barium sulphate. Owing to the amount of hydrobromic acid produced in the oxidation, the lead is not all precipitated as sulphate, so that the results for lead may be expected to be rather low. As the mean of several analyses we obtained Pb = 63·54; S = 13·33 per cent. The precipitate is obviously not pure lead thiosulphate (S = 20·10 per cent.), but corresponds closely with $Pb(C_2H_3O_2)_2,2PbS_2O_3$, which only requires 13·32 per cent. of sulphur. As a check on this analysis the iodometric method of Lemoult (*loc. cit.*) was used. The precipitate was dissolved in concentrated potassium hydroxide, the solution diluted, neutralised with sulphuric acid, using phenolphthalein as indicator, and finally titrated with $N/10$-iodine. In this way it was found that 1 gram of precipitate required 20·5, 20·4, and 20·5 c.c. of $N/10$-iodine (S = 13·1 per cent.). The pure thiosulphate requires 31·3 c.c., and the double salt 20·8 c.c. A specimen of thiosulphate precipitated in a similar manner from lead nitrate gave Pb = 64·50 and S = 20·32 per cent., and 1 gram required 30·8, 31·0, and 30·7 c.c. of $N/10$-iodine. In this case the product is practically pure lead thiosulphate. On repeating the precipitation from lead acetate, using very dilute solutions ($N/50$), the precipitation was much slower, and the product, which separated in a crystalline form, gave analytical data which showed that it was nearly pure thiosulphate. One gram required 30·6 c.c. of $N/10$-iodine (S = 19·6 per cent.). A few experiments were carried out to determine the effect of the concentrations of the reacting solutions, with equivalent quantities and with excess of sodium thiosulphate. As a result, it may be stated that the double salt is precipitated almost pure when solutions more concentrated than about $N/3$ are mixed in equivalent quantities, but that with excess of sodium thiosulphate the tendency to form the double salt is greatly diminished. The double salt, once precipitated, however, is not rapidly decomposed by washing with water, as the following experiment shows. The solutions are of the same concentration as those used by Fogh, although there is no indication that he washed his precipitate so thoroughly. 12·5 Grams of sodium thiosulphate and 19 grams of lead acetate were each dissolved in 200 c.c. of water ($N/2$-solutions), mixed, and well stirred. The precipitate settled quickly, and the clear liquid, which still contained a great deal of thiosulphate, was poured off and replaced by 300 c.c. of water. This was left in contact with the precipitate for an hour, being stirred repeatedly. This process was repeated five times, and after filtering, the precipitate was dried as before. On analysis 1 gram was found to require 26·2 c.c. of $N/10$-iodine ($S=16{\cdot}8$ per cent.), that is, it still contains about one-sixth its weight of lead acetate.

In another experiment 3·841 grams of lead thiosulphate prepared from the nitrate were shaken with about 50 c.c. of N-lead acetate solution. After filtering and drying, the precipitate was found to weigh 5·634 grams, and 1 gram required 20·8 c.c. of $N/10$-iodine ($S=13{\cdot}3$ per cent.). Complete formation of the double salt would have been accompanied by an increase in weight to 5·797 grams. The difference is partly due to the appreciable solubility of the double salt.

A corresponding double salt was prepared from lead butyrate by treating a concentrated solution with sodium thiosulphate. The analytical data given by this preparation were:

0·5438 gave 0·4688 $PbSO_4$. $Pb=58{\cdot}9$.

0·5715 required 11·35 c.c. of $N/10$-iodine.

$Pb(C_4H_7O_2)_2,2PbS_2O_3$ requires $Pb=60{\cdot}94$ per cent. and 11·2 c.c.

With lead trichloroacetate there appears to be little or no tendency to the formation of a double salt, as the following figures show:

4·140 Grams of anhydrous lead trichloroacetate (3 mols.) were dissolved in a small quantity of water, and 8·36 c.c. of $1{\cdot}04N$-sodium thiosulphate (2 mols.) of sodium thiosulphate were added. After allowing to remain, filtering, and washing with a little water the filtrate contained much lead and only a little thiosulphate. The whole of the filtrate required 1·0 c.c. of $N/10$-iodine, and gave

0·6838 gram of lead sulphate. This corresponds with 1·408 grams of lead trichloroacetate, whereas the amount added in excess of that required for the simple salt was 1·380 grams. 0·2338 Grams of precipitate required 7·30 c.c. of $N/10$-iodine, that is, 1 gram requires 31·2 c.c. (S=20·0 per cent.), corresponding with pure lead thiosulphate.

A precipitate obtained by treating a hot saturated solution of lead formate with one-third of an equivalent of sodium thiosulphate, and rapidly cooling, was pure white, and 0·2301 gram required 7·02 c.c. of $N/10$-iodine, that is, 1 gram requires 30·5 c.c. (S=19·6 per cent.), again obviously pure lead thiosulphate. Apparently only the weak acids which are chemically similar to acetic acid exhibit similar behaviour in this respect.

The Boiling of Lead Thiosulphate with Water.—In an attempt to repeat Fogh's experiment, 5·002 grams of the thiosulphate were boiled with 600 c.c. of water for four hours. A lead acetate paper held in the steam was very slowly blackened, showing that traces of hydrogen sulphide were evolved. After filtering, the filtrate was made up to a litre, and was found to be only slightly acid (100 c.c. required less than 1 c.c. of $N/10$-alkali), and to contain only very little undecomposed thiosulphate (100 c.c. required only 0·35 c.c. of $N/10$-iodine). Determinations of lead and sulphur were made in the filtrate, and the dried precipitate was extracted with pure carbon disulphide for the determination of free sulphur. The extracted residue was not found to contain more than small amounts of thiosulphate or of any thionic acid, but was almost entirely composed of sulphide and sulphate. The results of this and other similar experiments are summarised in the following table:

Weight of thiosulphate taken...............	5·002	4·578	2·377
Lead contained (calculated)..................	3·247	2·971	1·542
Sulphur ,, ,, ...	1·003	0·920	0·476
Weight of residue	4·441	4·163	2·113
Free sulphur in residue	0·316	0·277	0·125
Combined sulphur in residue	—	0·463	—
Lead in residue	2·999	2·855	1·421
Sulphur in filtrate	0·172	0·137	0·108
Lead ,, ,, ...	0·198	0·155	0·103
Total sulphur found	0·953*	0·877	0·453*
,, lead ,, ...	3·197	2·970	1·524

* Assuming the atomic ratio S : Pb in the extracted residue =1 : 1. In the other experiment this ratio is slightly exceeded.

From these figures it will be seen that the lead is almost completely converted into sulphide and sulphate, and that a considerable amount of free sulphur is liberated. The equation which suggests itself for such a change is $4PbS_2O_3 = 3PbSO_4 + PbS + 4S$, which requires, however, the liberation of half the sulphur in the free state. The deficiency in free and in total sulphur, and the large amount of sulphur in the filtrate, are not surprising considering the conditions of the experiment. Sulphur at 100° is appreciably volatile, and acts on water according to the equation $3H_2O + 4S = H_2S_2O_3 + 2H_2S$, or in the presence of oxygen: $3H_2O + 3S + O = H_2SO_4 + 2H_2S$ (Francis Jones, *Mem. Manchester Phil. Soc.*, 1912, **56**, No. XIV).

The excess of combined sulphur in the filtrate is accounted for by the presence of free acid and of polythionates. The filtrates in the above experiments required 16, 8, and 10 c.c. respectively of *N*/10-alkali for neutralisation. The addition of excess of sodium hydroxide produced in each case a slight turbidity of sulphur, and on keeping for some hours a precipitate of lead sulphide was deposited. Ammoniacal silver nitrate did not give an immediate precipitate, but in a few minutes the black precipitate characteristic of pentathionate was produced.

In order to obtain further information as to the nature of the change, lead thiosulphate or lead nitrate was heated with excess of sodium thiosulphate, when the blackening took place much more rapidly. A weighed quantity of the lead salt was dissolved in a concentrated solution of sodium thiosulphate of known concentration, and the solution sealed up in a glass tube. On warming for a few minutes in a steam-bath a copious, black precipitate was formed. It was first deposited as a mirror on the walls of the tube, and subsequently peeled off. A yellow cloud of sulphur could also be clearly seen. When the action had ceased, the tube was opened, and the precipitate collected. A slight odour of hydrogen sulphide was always observed on opening the tube, but the amount of sulphide in solution was practically negligible. The amount of thiosulphate in the filtrate was determined iodometrically, and the total sulphur present as thiosulphate and sulphate by oxidation with bromine and precipitation as barium sulphate. The free sulphur was extracted from the precipitate by means of carbon disulphide, the residue after this process being in all cases practically pure lead sulphide. In this way the following results were obtained:

1·3110 Grams of lead thiosulphate were heated with 20·0 c.c. of 0·990*N*-sodium thiosulphate. The filtrate after opening the tube was made up to 250 c.c. The precipitate was collected in a tared Gooch crucible, and dried in a desiccator. It weighed 1·506 grams. Twenty-five c.c. of the filtrate required 7·70 c.c. of *N*/10-iodine, so that 121 c.c. of *N*/10-sodium thiosulphate had been consumed. This represents 2·92 molecules for each molecule of lead thiosulphate. The weight of sulphur extracted was 0·520 gram, which is equivalent to 3·96 atoms. The residue after extraction, 0·986 gram, corresponds with 1·00 molecule of lead sulphide. These figures agree remarkably well with the equation:

$$PbS_2O_3 + 3Na_2S_2O_3 = PbS + 4S + 3Na_2SO_4,$$

which also requires three molecules of sodium sulphate in the filtrate. On adding bromine to 25 c.c. of the filtrate and precipitating with barium chloride, the barium sulphate produced weighed 0·6452 gram. The 7·70 c.c. of sodium thiosulphate ($N/10$) account for 0·359 gram, so that there is in the filtrate a quantity of sodium sulphate corresponding with 2·86 grams of barium sulphate. This is 1·747 grams, equivalent to 2·99 molecules per molecule of lead thiosulphate originally taken. This and similar results are collected in the following table, the italics indicating the number of equivalent molecules or atoms of the substance per molecule of lead salt. It will be noted that the numbers obtained by the use of lead nitrate lead to a similar equation.

Weight of lead salt.	C.c. $N/10$-thiosulphate consumed.	Sulphur formed.	Lead sulphide.	Sodium sulphate.
1·3110 PbS_2O_3......	121·0 (*2·94*)	0·520 (*3·96*)	0·986 (*1·00*)	1·747 (*2·99*)
1·4533 PbS_2O_3......	130·5 (*2·86*)	0·549 (*3·77*)	1·077 (*0·99*)	1·918 (*2·96*)
1·0385 PbS_2O_3......	94·0 (*2·89*)	0·394 (*3·78*)	0·748 (*0·96*)	1·353 (*2·93*)
0·9987 $Pb(NO_3)_2$ ..	116·0 (*3·84*)	0·364 (*3·77*)	0·709 (*0·99*)	1·292 (*3·01*)
1·0006 $Pb(NO_3)_2$ ..	118·5 (*3·93*)	0·370 (*3·82*)	0·723 (*1·00*)	1·301 (*3·03*)

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