

weight from the total ferrosilicon added. The weight of the lower chlorides, most of which was disilicon hexachloride, was found from the residue after distilling out the silicon tetrachloride.

An inspection of the table shows that the yield of lower chlorides can be greatly increased by the addition of silicon tetrachloride to the chlorine up to a certain point. Beyond that, a further addition reduces the yield which indicates that the first increase is due to a retarding of the final chlorination and not to the reduction of silicon tetrachloride by silicon.

The authors are indebted to the Chemical Warfare Service for the supply of silicon tetrachloride used.

### Summary

1. The ferric chloride formed by the chlorination of a mixture of iron and silicon does not act as a catalyst to increase the yield of lower chlorides of silicon nor to lower the temperature at which silicon is chlorinated.
2. The yield of disilicon hexachloride can be increased by passing silicon tetrachloride with chlorine over ferrosilicon heated to 200°.
3. This increase is due to the retarding of the final chlorination of disilicon hexachloride to silicon tetrachloride and not to the reduction of the latter by silicon.

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[CONTRIBUTION FROM THE MICHIGAN COLLEGE OF MINES]

## BASIC STANNOUS SULFATE

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RECEIVED DECEMBER 8, 1925

PUBLISHED APRIL 5, 1926

It is well known that water decomposes stannous salts with the formation of basic salt precipitates and that sodium hydroxide forms similar precipitates from solutions containing stannous ion. The composition of the precipitates for stannous chloride has been determined by Carson<sup>1</sup> and it seemed desirable that the basic salts of stannous sulfate should likewise be examined.

The stannous sulfate samples obtained from two prominent American manufacturers contained such a large amount of insoluble material that they were quite unsuitable either for direct use or as raw material for the manufacture of a pure product. A good quality of the salt may be made from tin and sulfuric acid but the following method is better for small scale operation.

About 25 g. of cupric sulfate is added to 200 cc. of water and 10 cc. of sulfuric acid in a 500cc. flask, and after the solution has been heated to boiling, small fragments of tin foil are dropped in, until 20 to 25 g. has been used. With continued boiling, the

<sup>1</sup> Carson, *THIS JOURNAL*, **41**, 1969 (1919).

solution loses its blue color in less than half an hour and while still hot is filtered from the precipitated copper. The filtrate is evaporated on the water-bath until only about 10 cc. of liquid remains and a deposit of pure white crystals is obtained; but if the crystalline material shows a yellow tinge, it should be rejected. The liquid is decanted and 20 to 50 cc. of methanol is added to the residue, the crystalline stannous sulfate is filtered off, washed with alcohol and then dried in a steam oven. The product is pure white and dissolves completely in water.

In each experiment of the first series to be recorded here, 5 g. of stannous sulfate was placed in a 50cc. flask and to it was added 10 cc. of sodium hydroxide solution, the concentration of which was varied by taking from 1 to 10 cc. of a 3 *N* solution and diluting with water to 10 cc. The corked flask was suspended in boiling water and shaken for one hour which was found to be sufficient for the attainment of equilibrium and the resulting mixture, while still hot, was filtered quickly. The precipitate without being washed or even thoroughly drained was enclosed in the filter paper which was then pressed between successive papers until nearly all of the liquid was removed, and drying was completed in a steam oven. Obviously, the mother liquor cannot be totally removed in this way but, as will be shown later, the amount remaining and the composition of it may be determined.

In the analysis of the dried precipitate for tin and the sulfate radical, the substance was ground, 0.5 g. was dissolved in hydrochloric acid, the solution was made alkaline with ammonium hydroxide and then acid with acetic acid. The tin was precipitated as stannous sulfide and weighed as the dioxide; the determination of the sulfate radical was made in the filtrate from the stannous sulfide.

The results of the first experimental series are given in Table I.

TABLE I  
INTERACTION OF FIVE GRAMS OF STANNOUS SULFATE IN TEN CC. OF WATER AND 0.12 TO 1.2 GRAMS OF SODIUM HYDROXIDE

Expt.	Water, cc.	3 <i>N</i> NaOH, cc.	Sn in ppt., %	SO <sub>4</sub> in ppt., %
1	9	1	56.96	41.71
2	8	2	59.93	35.83
3	7	3	63.78	31.99
4	6	4	67.68	27.66
5	5	5	67.82	27.37
6	4	6	68.02	26.63
7	3	7	68.48	23.85
8	2	8	69.39	20.46
9	1	9	69.69	20.21
10	0	10	70.60	18.83

In each experiment of the second series, 5 g. of stannous sulfate was again used but the volume of 3 *N* sodium hydroxide solution varied from 11 to 15 cc. and the total volume was made up to 20 cc. with water,

TABLE II  
INTERACTION OF FIVE GRAMS OF STANNOUS SULFATE IN TWENTY CC. OF WATER AND  
1.32 TO 2.1 GRAMS OF SODIUM HYDROXIDE

Expt.	Water, cc.	3 N NaOH, cc.	Sn in ppt., %	SO <sub>4</sub> in ppt., %
11	9	11	73.52	15.61
12	8	12	76.05	11.80
13	7	13	78.05	9.79
14	6	14	81.48	7.03
15	5	15	83.29	3.56

In Fig. 1, the percentages of sulfate as given in Tables I and II are plotted as ordinates and the number of cubic centimeters of sodium hydroxide as abscissas. It will be seen from the horizontal portions of the curve and also from the percentages in the tables that in each pair of Expts. 4, 5 and 8, 9, the precipitates have nearly the same composition. Since the solid phases retained unknown amounts of mother liquor, however, it was not

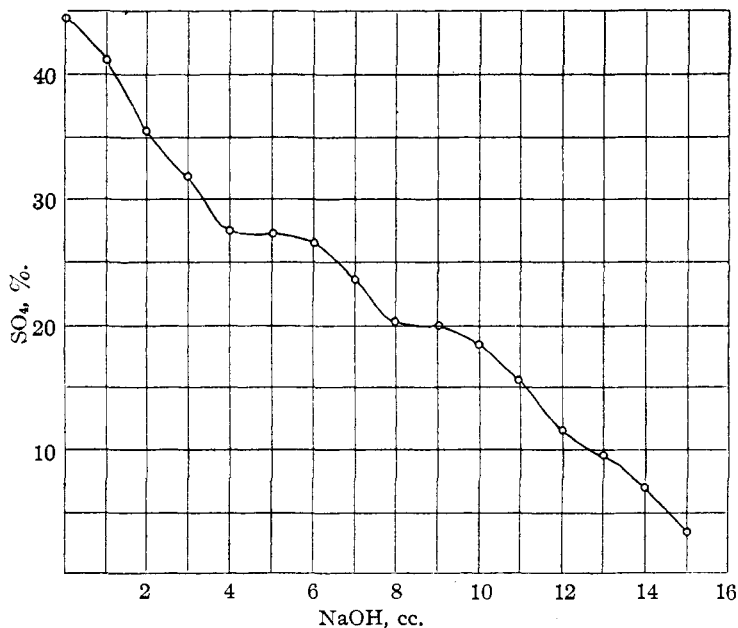


Fig. 1.

certain just how closely alike they really were. Therefore, it was necessary to carry out the experiments in question with the same proportions of substances as before but by a method that would give not only the amount of liquid phase left in the solid but also the appropriate corrections, based on the analyses of the mother liquors, to be applied to the analyses of the precipitates. Where washing with water, or other solvent, alters the basic salts to such an extent as to invalidate the results, two different

procedures for analyses have been proposed, either of which would answer the present purpose.

Kenrick<sup>2</sup> adds to the original mixture a substance, called a tell-tale, that will take no part in the reaction and so will not enter the true solid phase. By analysis, the amounts of this substance both in the impure precipitate and in a weighed portion of the liquid phase are determined and in this way the weight of liquid retained by the solid is calculated. Schreinemakers<sup>3</sup> analyzes both the liquid phases and the partially separated solid phases for different original mixtures, plots the results with reference to rectangular coordinates and draws a straight line through the two points belonging to each mixture. A point where two or more of these lines intersect represents the composition of a compound. Kenrick's method, with ammonium sulfate as the tell-tale substance, was first tried but was abandoned in favor of another plan. A description of this process as applied to Expt. 4 will now be given.

Five g. of stannous sulfate was heated as before with 4 cc. of 3 *N* sodium hydroxide solution and 6 cc. of water. The mixture, while still hot, was filtered and 1.5 cc. of the filtrate was pipetted into a weighed bottle which was then weighed again. The bottle was placed in a steam oven and after evaporation of the mother liquor, the weight was again taken and the remaining solid was analyzed for tin and the sulfate radical. The main precipitate was dried as thoroughly as possible between filter papers and while still slightly moist was transferred to a weighed bottle and the weight was determined. After being completely dried at 100°, the precipitate was weighed and analyzed.

The following are the data for the repetition of Expt. 4:

Wt., g.	Ppt., moist	Dry	Loss	1.5 cc. of mother liquor	Loss on evapn.	Residue	Mother liq. resi- due in ppt.
	2.0283	1.8843	0.1440	1.8691	1.3832	0.4859	0.0506

By analysis, 0.4859 g. of mother liquor residue was found to contain 0.1987 g. of tin and 0.2396 g. of sulfate radical. Therefore, 0.0506 g. of the same residue, which was the amount retained by the solid phase, would contain 0.0207 g. of tin and 0.0249 g. of sulfate radical. The total dried precipitate contains 1.2752 g. of tin and 0.5210 g. of sulfate radical, so that the true basic salt is made up of 1.2545 g. of tin and 0.4961 g. of sulfate radical. The ratio, molecules of sulfate to atoms of tin, from the corrected analysis is 1:2.047 and, therefore, the precipitate has very nearly the composition  $\text{SnSO}_4 \cdot \text{SnO}$ .

A similar procedure for Expt. 5 gave the atomic ratio 1 to 2.067 of tin, while in a new experiment with 5 g. of stannous sulfate, 4.5 cc. of 3 *N*

<sup>2</sup> Kenrick, *J. Phys. Chem.*, **12**, 695 (1908).

<sup>3</sup> Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).

sodium hydroxide solution and 5.5 cc. of water, the ratio 1 of sulfate to 2.047 of tin was obtained. It appears, then, that the precipitate  $\text{SnSO}_4 \cdot 1.047 \text{ SnO}$  remained constant when the amount of sodium hydroxide was varied by about 12%. A modification of the experimental method will now be described to support the conclusion that a compound of approximately that composition is formed.

Five g. of stannous sulfate was thoroughly mixed in a flask with a boiling solution containing 5 cc. of 3 *N* sodium hydroxide solution and 45 cc. of water and the mixture was allowed to settle. After a few minutes, the clear mother liquor was decanted into a clean, dry flask and was cooled slowly. A white crystalline deposit formed, which was separated by filtration and dried between filter papers. Analysis showed the crystals to have the composition  $\text{SnSnO}_4 \cdot 0.964 \text{ SnO}$ . A similar preparation that was washed thrice with water and then dried had the composition  $\text{SnSO}_4 \cdot 0.982 \text{ SnO}$ . Similar crystalline precipitates with slightly varying compositions were obtained from a mixture of 10 g. of stannous sulfate, 5 cc. of 3 *N* sodium hydroxide solution, 10 cc. of water and also from 10 g. of stannous sulfate, 5 cc. of 3 *N* sodium hydroxide solution, 20 cc. of water. No corrections were made for the adhering mother liquor as the time for this was not available, but undoubtedly the true composition in each of the three cases just described is close to  $\text{SnSO}_4 \cdot \text{SnO}$ .

Much greater uncertainty exists in applying the corrections for retained liquid phase in Expts. 8 and 9 than in 4 and 5, for which two causes are responsible. In the first place, the precipitates in Expts. 8 and 9 were not so well crystallized as were those in 4 and 5 and, therefore, retained more liquid; and, in the second place, the liquid in Expts. 8 and 9 differs much more from the solid than that in Expts. 4 and 5. Thus in Expt. 4 the uncorrected and corrected ratios tin to sulfate were 1.980 and 2.047, respectively, while in Expt. 8 the uncorrected and corrected ratios were 2.700 and 3.017. It will be seen that the correction in Expt. 8 is more than four times that of Expt. 4, and consequently the error in calculating the true composition of the solid is greater.

Expts. 8 and 9 were repeated and corrections such as those introduced for Expts. 4 and 5, were made. The modified analyses showed that the precipitates were respectively  $\text{SnSO}_4 \cdot 2.017 \text{ SnO}$  and  $\text{SnSO}_4 \cdot 2.098 \text{ SnO}$  with undetermined amounts of water. While these results do not warrant the conclusion reached by Ditte<sup>4</sup> that a pure compound  $\text{SnSO}_4 \cdot 2 \text{ SnO} \cdot 1.5 \text{ H}_2\text{O}$  exists, nevertheless, they indicate the probability.

It may appear that the corrections introduced in the results of Expts. 4, 5, 8 and 9 are based on a faulty method since the amount of water driven off when the moist precipitates are dried exceeds the mere water of solution in the adhering mother liquor. In the experiments mentioned,

<sup>4</sup> Ditte, *Ann. chim. phys.*, [5] 27, 145 (1882).

the mother liquors were weakly acid and therefore during evaporation the acid interacted with the basic salt with liberation of water. The error from this cause, however, does not amount to more than 1% of the correction and may be ignored.

In Expt. 15, where the amount of sodium hydroxide was almost sufficient to transform the stannous sulfate into stannous oxide, the unwashed but dried precipitate contained 83.29% of tin and 3.56% of sulfate radical. With the correction as applied before, the analysis showed only 1.9% of sulfate. As 1.80 g. of sodium hydroxide was used and 1.86 g. is required, according to the ordinary equation for the complete transformation into stannous oxide, it is evident that this reaction takes place very nearly as the equation indicates.

The volumes of liquid in proportion to the weight of stannous sulfate were kept small in this work since preliminary experiments showed that when the volumes were large, the less basic precipitates could not be obtained. This is always true for salts of considerable solubility.

### Summary

1. The precipitates formed at 100° by adding sodium hydroxide solution in various amounts to stannous sulfate have been analyzed.
2. Within two regions of alkali variation, the precipitates remain nearly constant in composition. The formula  $\text{SnSO}_4 \cdot \text{SnO}$  probably represents a compound and  $\text{SnSO}_4 \cdot 2\text{SnO}$ -unknown- $\text{H}_2\text{O}$  may possibly do so.
3. A method is described for correcting the analyses of incompletely separated solid phases for the retained liquid phase.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## THE FREE ENERGY OF HYDROGEN FLUORIDE

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RECEIVED DECEMBER 9, 1925

PUBLISHED APRIL 5, 1926

### Introduction

The determination of the free energy of fluorine compounds is a problem of extraordinary interest on account of the unique position of fluorine as the most electronegative of the elements. Attempts to determine the free energy of the fluorine electrode made in this Laboratory by Simons and Hildebrand<sup>1</sup> were unsuccessful. Electrodes of various noble metals and of graphite surrounded by fluorine did not give reproducible potentials either in liquid hydrogen fluoride or in fused potassium acid fluoride. These experiments seemed to indicate little prospect of success for the method and that the only hope would lie in measuring the dissociation

<sup>1</sup> Simons and Hildebrand, *THIS JOURNAL*, **46**, 2223 (1924).