some results which were not so good, but, on the whole, the method is quite promising and will be the subject of further study by me, which I trust may result in a somewhat more accurate and more convenient method than those now in general use.

AGRICULTURAL EXPERIMENT STATION,
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ON CERTAIN PHENOMENA OBSERVED IN THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF POTASSIUM ANTIMONYL TARTRATE.

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I HAVE elsewhere called attention to the behavior of solutions of tartar emetic when treated with solutions of other salts, (see *Am. Jour. Sci. and Arts*, October, *1889* and October, *1890*) and with Mr. H. E. Sauer have determined the conditions of precipitation by carbonates, acetates, and phosphates. (*J. Anal. Appl. Chem.*, March, *1891*.)

When to solutions of the antimony salt sulphates, chlorides, nitrates, and oxalates of the alkali metals are added no precipitation occurs, even with elevation of temperature. With carbonates, acetates, phosphates, borates, thiosulphates, sulphites, tungstates, and some other compounds, clear solutions can be made at a low temperature, but precipitation follows at a higher point. The precipitate, in nearly all cases, consists of hydrated antimony oxide, and its amount is a function of time, temperature, and amount of added salt.

With mixtures of the tartrate and sodium carbonate, for instance, it was found that in the cold, at the end of twenty-four hours, amounts were precipitated as shown in the following table. In each test five grams of the tartrate were dissolved in sixty cc. of warm water and cooled to 20°. Then different weights of pure sodium carbonate were dissolved in thirty-five cc. of water; these solutions were added to the others and the mixtures were brought up to 100 cc. They were allowed to stand until precipitation was complete, usually over night or longer. An aliquot part of the clear supernatant liquid was taken and the amount of antimony in solution determined. This was calculated to tartrate in the whole:

No. of experiment.	Na_2CO_3 added.	$KSbOC_4H_4O_6.\frac{1}{2}H_2O$ left in solution.
1	0.1 gram	99.93 per cent.
2	0.3 "	85.22 " "
3	0.5 "	70.36 " "
4	0.7 "	56.76 " "
5	0.9 "	40.87 " "
6	1.2 grams	29.17 " "
7	1.5 "	13.94 " "
8	2.0 "	3.88 " "

In another series of experiments the solutions of carbonate and tartrate were mixed as before at 20° and then brought to 100°, and maintained at this heat one hour. The precipitates formed immediately, and at the end of the hour were separated by filtration. The filtrates were tested for antimony remaining. The results are shown in the third column below.

No. of experiment.	Na_2CO_3 added.	$KSbOC_4H_4O_6.\frac{1}{2}H_2O$ left in solution.
9	0.2 gram	79.23 per cent.
10	0.5 "	46.70 " "
11	0.8 "	21.74 " "
12	1.1 grams	8.69 " "
13	1.5 "	6.33 " "
14	2.0 "	4.42 " "
15	3.5 "	4.66 " "
16	5.0 "	4.74 " "

On comparing the two tables, it will be seen that at first the precipitation is much more rapid in hot solution than in cold, but that finally, with excess of carbonate, a more complete decomposition of the tartrate is effected in the cold solution. Two equations can be given, according to which the reaction may take place. The first of these is:

$$2KSbOC_4H_4O_6 + 2Na_2CO_3 + 2H_2O = \\ 2KNaC_4H_4O_6 + Sb_2O_3.H_2O + 2HNaCO_3.$$

The second is:

$$2KSbOC_4H_4O_6 + Na_2CO_3 + H_2O = \\ 2KNaC_4H_4O_6 + Sb_2O_3.H_2O + CO_2.$$

The first, probably, takes place in the cold solution as no carbon dioxide escapes. The loss of carbon dioxide from the hot solution is less than called for by the equation because an excess of neutral carbonate is present and the solutions are not actually boiled. In any case the precipitation is incomplete, and by addition of increased amounts of sodium carbonate, a condition is reached in which a part of the oxide at first thrown down appears to go into solution again.

Precipitation with sodium acetate takes place imperfectly in the cold, but by heat a stronger reaction follows. In both cases it was found that the results may be expressed by the following equation:

$$2KSbOC_4H_4O_6 + 2NaC_2H_3O_2 + 2H_2O = 2KNaC_4H_4O_6 + Sb_2O_3.H_2O + 2HC_2H_3O_2.$$

With phosphates the experiments led to the conclusion that precipitation takes place in a manner represented by this equation:

$$2KSbOC_4H_4O_6 + HNa_2PO_4 + 2H_2O = 2KNaC_4H_4O_6 + Sb_2O_3.H_2O + H_3PO_4.$$

With cold solutions precipitation is very slow, but by heat an amount of the antimony oxide corresponding to seventy-five per cent. of the tartrate originally in solution is obtained.

I have since investigated the behavior of several other salts as precipitants, with the results which follow.

REACTION WITH SODIUM BIBORATE.

A very sharp reaction takes place between solutions of borax and tartar emetic, which was studied in the following manner: In the first series of experiments, five grams of the tartrate were dissolved for each test in sixty cc. of water, the solutions being brought to 20°. To these were added definite weights of borax dissolved in thirty to thirty-five cc. of water at the same temperature. The mixtures were made up to 100 cc. exactly, and allowed to stand over night in a place with nearly constant temperature. In all cases a precipitate formed which was separated by filtration. The analysis of the precipitate showed it to have the same composition as that formed by the sodium carbonate; *viz.*, Sb_2O_3.aq. On drying at a high temperature most of the water is lost, leaving practically Sb_2O_3.

In each case the precipitate was separated by filtration, and the filtrate made up to 250 cc. Twenty-five cc. of this was taken and precipitated by hydrogen sulphide, after addition of tartaric and hydrochloric acids in small amount. The precipitation was finished on a hot water-bath, and the precipitate collected on a Gooch filter, washed, dried at 120°, and weighed. The sulphide was calculated to tartrate on the supposition that all the antimony in solution was left in the original form ($Sb=120$, $O=16$). The results obtained are shown by these figures:

No. of experiment.	Borax added.	$KSbOC_4H_4O_6.\frac{1}{2}H_2O$ left in solution.
1	0.1 gram	98.81 per cent.
2	0.2 "	94.74 " "
3	0.4 "	87.78 " "
4	0.8 "	74.98 " "
5	1.6 grams	46.84 " "
6	3.2 "	3.31 " "

In another series of tests the solutions containing the borax and tartrate were made up to 250 cc. instead of to 100 cc. They were allowed to stand, filtered, and treated as before, giving these results:

No. of experiment.	Borax added.	$KSbOC_4H_4O_6.\frac{1}{2}H_2O$ left in solution.
7	0.1 gram	100.00 per cent.
8	0.2 "	97.15 " "
9	0.4 "	89.05 " "
10	0.8 "	75.29 " "
11	1.6 grams	49.09 " "
12	3.2 "	6.01 " "
13	6.4 "	2.03 " "
14	12.8 "	0.99 " "

In a third set of experiments the liquid containing the borax and tartrate was diluted to 100 cc. in a flask, as in the first set. The flask was closed with a perforated rubber stopper having a long glass tube attached, and then heated in boiling water one hour. The liquid was allowed to cool, was filtered, and the filtrate made up to 250 cc. An aliquot part, on analysis, gave results which are shown below.

No. of experiment.	Borax added.	$KSbOC_4H_4O_6.\frac{1}{2}H_2O$ left in solution.
15	0.1 gram	99.88 per cent.
16	0.2 "	95.37 " "
17	0.4 "	88.81 " "
18	0.8 "	74.78 " "
19	1.6 grams	47.03 " "
20	3.2 "	3.96 " "
21	6.4 "	1.76 " "

In these tables several things are immediately apparent. It appears that the precipitation is less perfect in hot solution than in cold, although for equal weights of borax the differences are not great. It is seen also that the amounts precipitated are greater in the strongest solutions. These effects of temperature and concentration are far less marked, however, with borax precipitation than with that by the sodium carbonate.

With borax we have, in each case, a very regular rate of precipitation. By platting the weights of borax in the above table as abscissas, and the amounts of tartrate left as ordinates, we obtain a curve which is almost a straight line.

It seems practically impossible to precipitate all the antimony by excess of borax, although the amount left in solution is much less than when sodium carbonate was used as the precipitant. Direct trials showed that the solubility of the antimonous oxide in excess of borax solution is very slight, but is a trifle greater in the excess of sodium carbonate. The solubility in the Rochelle salt solution formed in the latter case will not account for this difference as will appear below.

In order to gain further insight into the reaction I measured the amount of rotation of polarized light in a number of solutions before and after the separation of the precipitate of antimonous oxide. Some exceedingly interesting results were obtained, a few of which will be explained in detail. I dissolved five grams of the tartrate in fifty cc. of hot water and added three grams of borax in twenty-five cc. of water, made up to ninety cc., and heated one-half hour in the water-bath. The solution was allowed to cool to 20° and made up to 100.5 cc. (on account of volume of precipitate), and filtered through a dry filter. The filtrate was polarized in a 200 mm. tube, giving

$$\alpha_D = 3.596^\circ.$$

Seventy-five cc. of the filtrate, after the addition of a little hydrochloric and tartaric acids, was precipitated by hydrogen sulphide. The precipitate was collected, washed, and dried in the usual manner in the Gooch funnel. I found 0.119 gram of the sulphide, corresponding to 0.312 gram of $KSbOC_4H_4O_6.\frac{1}{2}H_2O$, in the whole filtrate. 4.688 grams had, therefore, been precipitated. From the outset it would naturally occur to one that the precipitation of antimonous oxide must be accompanied by the formation of sodium potassium tartrate, and that the polarization effect observed must, in part, be due to this, as well as to the potassium antimonyl tartrate left. I have elsewhere given the results of very accurate tests in which the rotation constants of these tartrates were determined by the use of the large Landolt-Lippich polarimeter with the 400 mm. tube (*Am. Jour. Sci. and Arts, loc. cit.*). From these it appears that the rotation of 0.312 gram of the $KSbOC_4H_4H_4O_6.\frac{1}{2}H_2O$, and 3.982 grams of $KNaC_4H_4O_6.4H_2O$ (this latter corresponding to the tartar emetic decomposed) in 100 cc. should not be over 2.6°. In the direct polarization of the filtrate I found, as given above, 3.596°. It is evident, therefore, that something else must be present to modify the result.

It is well known that the presence of boric acid increases the rotation of tartrates in a marked degree, and this can be readily accounted for here if we assume that the reaction takes place according to the following equation:

$$2KSbOC_4H_4O_6 + Na_2B_4O_7 + 6H_2O = 2KNaC_4H_4O_6 + Sb_2O_3 + 4H_3BO_3.$$

On applying tests for free boric acid its presence was readily shown. We have here apparently a reaction similar to those in which acetic and phosphoric acids are liberated from acetates and phosphates.

In the last experiment it was shown that antimony, corresponding to 0.312 gram of the potassium antimonyl tartrate was still in solution, or that 4.688 grams had been decomposed. To do this according to the above equation would require 2.697 grams of crystallized borax, and would leave in solution 3.982 grams of $KNaC_4H_4O_6.4H_2O$ and 1.751 grams of H_3BO_3. An excess of 0.303 gram of borax would be left in solution. To test the correctness of this view I prepared a solution containing in 100 cc., at 20°:

0.312 gram of $KSbOC_4H_4O_6.\frac{1}{2}H_2O$.
3.982 grams of $KNaC_4H_4O_6.4H_2O$.
1.751 grams of H_3BO_3.
0.303 gram of $Na_2B_4O_7.10H_2O$.

This solution was polarized in the 200 mm. tube and gave

$$\alpha_D = 3.590°,$$

which agrees very well with the result of the first experiment. Another solution, containing in 100 cc., at 20°,

0.150 gram of $KSbOC_4H_4O_6.\frac{1}{2}H_2O$,
4.119 grams of $KNaC_4H_4O_6.4H_2O$,
1.811 grams of H_3BO_3,

gave $\alpha_D = 3.661°$. While boric acid increases the rotation of tartrates and tartaric acid I have elsewhere shown that borax decreases the rotation of Rochelle salt slightly. The equation probably represents the facts properly.

In the above nothing has been said about certain peculiarities observed in the formation of the precipitates. When cold dilute solutions of borax and the tartrate are mixed no reaction takes place immediately, but with warm, strong solutions, a precipitate seems to form as soon as the two liquids are poured together. In a former paper (*J. Anal. Appl. Chem.*, *loc. cit.*) I pointed out the important and exceedingly curious fact that in the reaction between carbonates or acetates on the one hand, with the tartrate on the other, while no precipitate may appear immediately, perhaps not in hours, indicating a decomposition, the polarimeter shows that such has taken place. Here, also, we have evidence that a reaction has taken place even without precipitation, and this the polarimeter furnishes. The matter can be best explained by giving the details of several experiments.

I made five solutions by dissolving five grams of the tartrate as before in fifty-five to sixty cc. of warm water, cooled to 20°, and added certain weights of borax in small volumes of water, making the solutions finally to 100 cc. at 20°. These solutions were polarized immediately in the 200 mm. tube, with the following results:

No. of experiment.	$KSbOC_4H_4O_6.\frac{1}{2}H_2O$ taken.	$Na_2B_4O_7.10H_2O$ added.	α_D
1	5 grams	0.5 gram	12.08°
2	5 "	1.0 "	9.40°
3	5 "	2.0 grams	5.53°
4	5 "	3.0 "	4.10°
5	5 "	4.0 "	3.75°

The normal rotation of the tartrate at 20° in the 200 mm. tube, with a concentration of five grams in 100 cc., I have shown to be

$$\alpha_D = 14.103°.$$

The effect of the borax is therefore marked, but the extent of the decrease in rotation depends on the number of minutes intervening between the mixing of the solutions and the completion of the observation in the polarimeter. A gradual decrease in the readings was in all cases observed, until the solutions became finally too turbid for observation from the beginning precipitation. The first solution, for instance, in the above table was read as follows:

10 hours, 30 minutes, $\alpha_D = 12.08°$
10 " 45 " " $= 11.87°$
10 " 55 " " $= 11.80°$

After standing some hours, the solutions deposited a precipitate and cleared up. On again polarizing I found:

No.	α_D
1	11.52°
2	9.01°
3	5.29°
4	3.92°
5	3.65°

These observations were made in a 200 mm. tube, but similar solutions were polarized in a 400 mm. tube with perfect sharpness, the readings agreeing within 0.02°, as is possible with the large and excellent instrument used. I mention this to prove the perfect transparency of the liquids, and to show that the decreased rotations observed at the start were not due to any loss through precipitation, but were in consequence of changes preceding precipitation, these changes taking place very gradually.

We have here a phenomenon reminding one of the birotation of solutions of certain sugars, but depending on a different cause undoubtedly. In the reaction between the same tartrate and sodium carbonate the same change was observed, but through a longer period. A solution containing in 100 cc. one-tenth gram of the carbonate and five grams of the tartrate gave, at the end of five minutes in a 400 mm. tube, a rotation of 25.582°, after thirty minutes, 25.580°, that is, practically the same, but after twelve hours, 24.480°. A perfectly clear mixture can be made containing five grams of the tartrate and nine-tenths gram of sodium carbonate in 100 cc. When polarized immediately, I found with this in the 400 mm. tube $\alpha_D = 11.57°$, after ten minutes, 11.50°, after twenty-five minutes, 11.132°, and after sixty-five minutes, 10.55°.

In the normal reaction between carbonates or borates and the potassium antimonyl tartrate a precipitate should be formed, but we find that at a low temperature this is much delayed. If precipitation alone were taken as the indication of a reaction it would necessarily appear that at the outset no reaction takes place, but the behavior with polarized light shows the error in this view. It is evident that a reaction begins immediately and progresses far toward completion in some of the cases considered before even the first polarization can be made, that is within two or three minutes. This first part of the reaction is the beginning stage of precipitation and may consist in the formation of some intermediate product, which finally decomposes. I have elsewhere shown (*Am. Jour. Sci. and Arts, loc. cit.*) that the rotation of potassium sodium tartrate is decreased by the addition of sodium, thallium, and lithium salts, but is increased by the addition of potassium and ammonium salts and that this reaction is fully accounted for if we assume the formation of sodium tartrate, sodium thallium tartrate or sodium lithium tartrate in the one case or of potassium or potassium ammonium tartrate in the other. In the present instance we evidently must admit the formation of sodium potassium tartrate from the instant the solutions are mixed, but that the reaction is a progressive one. The potassium antimonyl compound with a high rotation gives place to the potassium sodium compound with a much lower rotation. There is nothing to show, however, in what form the antimony is held.

Possibly the reaction may be explained by assuming the formation of an intermediate product according to this equation:

$$2KSbOC_4H_4O_6 + Na_2B_4O_7 = 2KNaC_4H_4O_6 + (SbO)_2B_2O_7.$$

If the last compound is formed it must break up in this manner:

$$(SbO)_2B_4O_7 + 6H_2O + XH_2O = 4H_3BO_3 + Sb_2O_3.XH_2O,$$

leaving a hydrated oxide of antimony with more water than the final precipitate contains. By loss of water, possibly, this hydrated compound must, in time, settle out as a precipitate. It has been explained that by boiling, the precipitate forms and subsides soon. At 20°, even after what I have called the preliminary stage of precipitation, may have occupied hours, the actual formation of the precipitate may consume an equally long time. The precipitate is a growth through an invisible and a visible stage, and what is true here is true of the next case to be given.

REACTION WITH SODIUM TUNGSTATE.

Cold solutions of the tartrate give no immediate precipitate when mixed with cold solutions of ordinary sodium tungstate, but on standing the mixtures gradually become turbid and finally deposit a sediment. The composition of this depends largely on the temperature and concentration. The precipitate formed in the cold, collected and dried at 105°–110° C. consists, essentially of antimony oxide. A precipitate formed by mixing hot solutions has practically the same composition, but if obtained after long heating it contains a relatively larger amount of tungstic acid.

In a series of tests made by mixing hot solutions of the two salts, and allowing the mixtures to stand several hours to cool, the following results were obtained :

$KSbOC_4H_4O_6.\frac{1}{2}H_2O$ in 100 cc.	$Na_2WO_4.2H_2O$ in 50 cc.	Wt. of ppt.	Sb_2S_3 from same.	Per cent. of Sb. in ppt.
1 gram	2 grams	0.3087	0.3467	80.22
2 grams	2 "	0.6442	0.7291	80.84
4 "	2 "	0.5728	0.6486	80.88
5 "	2 "	0.7222	0.8170	80.79

The mixtures were made in platinum dishes holding about 200 cc., and as the precipitates formed as a coherent coating on the dishes they were easily washed, dried at 110°, and weighed. They were then dissolved in diluted hydrochloric acid, which left a small amount of tungstic acid in each case in flocculent form. The solutions were then filtered, and, after the addition of some tartaric acid, were precipitated by hydrogen sulphide in the usual manner. The sulphide precipitates were collected on a Gooch, dried at 110°, and weighed. It will be seen that the results are a little low to correspond to pure antimony oxide as the composition of the white precipitate. This compound contains 83.3 per cent. of antimony. The compound $Sb_2O_3.H_2O$ contains 78.4 per cent. The lower results are doubtless due to the small amounts of tungstic acid left in each case on treatment with hydrochloric acid, and referred to above.

In a second series of experiments constant amounts of the tartrate in hot solution were mixed with varying amounts of the tungstate likewise in hot solution. The white precipitates which formed were collected and weighed as before, with the following results, which show the effect of excess of tungstate on the amount of precipitate. In each case two grams of the tartrate was taken in 100 cc., and the tungstate in fifty cc.:

Tungstate taken.	Ppt. obtained.
0.5 gram	0.1070
1.0 "	0.4598
2.0 grams	0.5762
3.0 "	0.5861
4.0 "	0.6143
5.0 "	0.6185

From this, it is plain that the amount of precipitate is not much increased by great excess of the tungstate beyond a certain point. In the cold, precipitation is much less perfect, while, by boiling, fully three-fourths of the theoretical yield of oxide from the tartrate can be obtained.

By working with cold solutions a mixture may be made which remains clear long enough to permit polarimeter observations to be taken. I dissolved five grams of the tartrate in sixty cc. of water, cooled to 20°, and added five-tenths gram of the tungstate in twenty cc. of water. The mixture was made up quickly to 100 cc. at 20° and polarized in the 200 mm. tube immediately and after intervals of five minutes. I found without refilling the tube:

1st observation $\alpha_D = 11.66°$
2nd " " $= 12.03°$
3rd " " $= 12.13°$
4th " " $= 12.53°$

The solution became now too turbid, from separation of a precipitate, for further tests. On standing some hours the remainder of the solution in the flask cleared after subsidence of its precipitate. A portion of this examined gave

$$\alpha_D = 12.74^\circ.$$

Another portion of the same solution, heated and then cooled to 20°, gave the same. A new solution prepared in the same manner gave, after standing some time,

$$\alpha_D = 13.11^\circ.$$

I made next a solution containing in 100 cc. five grams of the tartrate and one gram of the tungstate. This examined, immediately, at 20°, gave

$$\alpha_D = 9.42^\circ,$$

but it soon became turbid and deposited a precipitate. After clearing, I found

$$\alpha_D = 11.48^\circ,$$

which increased to 11.87° by heating the liquid.

These reactions are especially interesting when compared with those between the tartrates and other salts. We have here, as before, a marked decrease in the specific rotation on mixing the solutions of the active and inactive substances. But in the case of the tungstate on standing, there is an increase instead of a decrease in the rotation observed in the other cases. This behavior finds its explanation probably in the action of the liberated tungstic acid. The reaction between the two salts undoubtedly follows this equation :

$$2KSbOC_4H_4O_6 + Na_2WO_4 = 2KNaC_4H_4O_6 + Sb_2O_3 + (WO_3)x.$$

The precipitation of the tungstic acid is very slow and incomplete. While in solution, it may combine with the soluble tartrate to form a body with increased rotation, the possibility of which is shown by the researches of Gernez and others. The delay in the appearance of the precipitate may be due to the formation and slow breaking up of intermediate products containing the antimony and tungstic oxides in temporarily soluble condition. With liberation of the tungstic acid we have a gradual increase in the already decreased rotation. This change in the rotation, before precipitation, is well shown in the following observations. I dissolved five grams of the tartrate and two and five-tenths grams of the tungstate, mixed at a low temperature and made up to 100 cc. as before, and at exactly 20° C. A reading with the 200 mm. tube was made as soon as possible and, without changing the solution, this was repeated at frequent intervals. The results were as follows :

3 hours, 28 min. $\alpha_D = 5.66^\circ$
" $= 5.96^\circ$
" $= 6.45^\circ$
" $= 6.83^\circ$
" $= 7.15^\circ$
" $= 7.32^\circ$
3 hours, 44 min. " $= 7.43^\circ$
3 hours, 58 min. " $= 7.90^\circ$

At this point the liquid began to grow slightly turbid, so that the observations could not be continued. The remainder of the liquid was then heated in a closed flask to complete the precipitation, cooled to 20°, and tested. I found now

$$\alpha_D = 9.13^\circ.$$

The liquid still remaining was filtered, fifty cc. of the filtrate taken and precipitated with hydrogen sulphide, yielding finally 0.4045 gram of antimony sulphide. From this it appears that of the tartrate originally taken, 1.599 grams remained in solution in the 100 cc. (no allowance being made for the volume of the precipitate).

From this we have

$KSbOC_4H_4O_6.\frac{1}{2}H_2O$ decomposed = 3.401 grams.
" " remaining 1.599 "
$KNaC_4H_4O_6.4H_2O$ formed 2.888 "

Now, the rotation corresponding to the tartar emetic remaining is 4.50° and that to the Rochelle salt formed is 1.25° from which we should expect a total rotation of 5.75°. This, in fact, corresponds very nearly to what was observed at the beginning of the test, and seems to bear out the suggestion made above: *viz.*, that the principal reaction here occurs before actual precipitation appears. A splitting of the tartar emetic is indicated by the immediate decrease in the rotation and then the complex effect of addition of the liberated tungstic acid to the alkali tartrate in solution appears from the gradually increased rotation

Precipitation finally follows as the end of the reaction; the separated part assumes the insoluble form.

It will be recognized that the phenomenon in this case is much more complex than in the other. There is nothing to show that while the rotation is being increased by the action of the tungstic acid there is not also a tendency toward decrease because of progressive decomposition of the potassium antimonyl tartrate. In all probability the observed rotation is a resultant effect.

REACTION WITH SODIUM THIOSULPHATE.

Cold dilute solutions of the thiosulphate and potassium antimonyl tartrate can be mixed without immediate precipitation. Application of heat, however, produces a light yellow precipitate which grows deeper and finally becomes bright red. This precipitate is the substance commonly known as antimony cinnabar, used as a pigment, and on the large scale is made by decomposing the thiosulphate by antimony chloride. In the reaction between the thiosulphate and tartar emetic the precipitate appears very heavy, but the decomposition is far from complete as shown by the figures given below.

There seems to be some doubt as to the composition of this precipitate. Roscoe and Schorlemmer (**2**, part 2, 324) give it as, probably, SbS_2O, referring, however, to other formulas. Dammer's Handbuch gives $Sb_2O_3.Sb_2S_3$ as the probable formula. Others are also given. Recently Baubigny (*Compt. rend.*, No. 17, *1894*), has given reasons why the formula Sb_2S_3 should be considered the correct one and the proof he presents appears to be satisfactory. There remains a possibility, however, that the composition may, under certain circumstances, vary with the method of preparation. In fact, some of my own results seem to show this and I am now engaged in studying the question further. But as made in the reaction in hand the composition seems to be $2Sb_2S_3.H_2O$. This was determined by the following considerations: The precipitate dissolves in hydrochloric acid without liberation of sulphur, yielding a perfectly clear solution. A solution made in this way was heated, mixed with a little tartaric acid solution, and precipitated by hydrogen sulphide in the usual manner. On filtering off the orange-yellow precipitate so obtained in a Gooch crucible, drying at 120°, and weighing, the weight was always found less than that of the antimony cinnabar taken.

Sulphur determinations were made by dissolving a gram or less of the substance in strong S-free solution of potassium hydroxide and then oxidizing the sulpho-salt formed by washed chlorine gas, (method of Rivot). The results of these tests were as follows:

	Calculated for $2Sb_2S_3.H_2O$.	Found.
Sb	69.56	69.80
S	27.83	27.72

No determination of the water was made, but its presence was shown in the substance dried at 120° by heating to a higher temperature in a narrow glass tube.

In a series of experiments on the precipitation a number of portions of the tartrate, of five grams each, were weighed out and dissolved in 150 cc. of water. Varying amounts of the thiosulphate in fifty cc. of water were added and then water enough to make exactly 250 cc. The flasks holding the mixtures were closed with perforated stoppers containing long glass tubes and then heated in the water-bath one hour. In this way evaporation was practically avoided. At the end of the hour the precipitates were collected on a Gooch funnel, dried at 120°, and weighed with the following results:

No. of experiment.	Weight of $Na_2S_2O_3.5H_2O$ added.	Weight of precipitate.
1	0.1 gram.	0.0039 gram.
2	0.2 "	0.0068 "
3	0.4 "	0.0111 "
4	0.8 "	0.0178 "
5	1.6 grams.	0.0363 "
6	3.2 "	0.0803 "
7	6.4 "	0.2112 "
8	12.8 "	0.4809 "

In a second set of tests I dissolved, in each case, ten grams of the tartar emetic in 100 cc. of hot water and added the thiosulphate in fifty cc. of hot water. The mixtures were kept at 100° two hours and then filtered. Results as follows:

No. of experiment.	Weight of $Na_2S_2O_3.5H_2O$ added.	Weight of precipitate.
9	5 grams.	0.1915
10	10 "	0.4041
11	15 "	0.5162
12	20 "	0.6818

It is evident from these figures that in both sets of experiments the reaction is far from complete and not easily determined. It is, perhaps, quite complex. I noticed in no case the escape of hydrogen sulphide or sulphurous oxide and the gradual change in color during precipitation from very light yellow to bright red suggests that it takes place in two stages. Vortmann (*Ber. d. chem. Ges.*, **22,** 2307) has studied the general problem of decomposition of thiosulphuric acid and states that it breaks up into H_2S, O, and SO_2. In presence of certain metals, tetra- and pentathionates seem to be formed. It is certain that no sulphate is formed in the reaction in hand, but the proof of formation of the several thionic acids is difficult because of the incompleteness of the reaction and the presence of the great excess of thiosulphate. In cases of complete reaction, however, Vortmann and Vaubel, also, (*Ber. d. chem. Ges.*, **22,** 2703) have shown that these acids are formed.

I suggest, therefore, this explanation of the present reaction. At the outset there may be, as with borax, a decomposition according to this equation,

$$2KSbOC_4H_4O_6 + Na_2S_2O_3 + H_2O = Sb_2O_3 + 2KNaC_4H_4O_6 + H_2S_2O_3,$$

then

$$Sb_2O_3 + 2H_2S_2O_3 = Sb_2S_3 + 2H_2O + SO_2 + O_5,$$

the oxygen and sulphur dioxide being held, however, to form polythionates.

The gradual change of color can be accounted for by the gradual change of oxide into sulphide of antimony and it seems possible that under certain conditions of concentration and temperature a part of the oxide should remain unchanged, accounting for the results of some of the analysts who have examined the precipitate. In several instances I modified the experiment by mixing warm solutions of the tartar emetic with warm thiosulphate solutions, and then throwing the mixture into a large volume of cold water the instant a precipitate began to form, to check the reaction. The precipitate which now settled was very light colored instead of red, and appeared to be a mixture of oxide and sulphide. The microscopic appearance of this precipitate is distinctly different from that of the antimony cinnabar.

As explained at the outset some time elapses after mixing cold solutions before a precipitate appears. In the beginning of the interval the solution may be so clear that accurate polarimetric observations are possible. But, contrary to expectations, based on the behavior in other cases recorded, I find the specific rotation of the tartar emetic, in this stage of the reaction, quite unchanged. After precipitation a marked decrease was observed as usual. This is shown in the following table in which the filtrates from the last precipitates referred to were made up to 250 cc. before polarization:

No. of experiment.	Thiosulphate added.	α_D observed.	α_D calculated.
9	5 grams.	10.90°	10.89°
10	10 "	10.43°	10.46°
11	15 "	10.07°	10.24°
12	20 "	9.69°	9.93°

In the last column the rotations were calculated on the assumption that antimony is precipitated and Rochelle salt formed according to the last equations. In the eleventh and twelfth experiments the thiosulphate is present in amount much in excess of that necessary to complete precipitation by these reactions, and it is evident that a decomposition of the active molecule has taken place not indicated by the amount of precipitate.

There seems to be a fundamental difference between the reaction with the thiosulphate on the one hand, and those with the borate, carbonate, phosphate, acetate, and tungstate on the other. In the first case we appear to have no breaking up of the complex tartrate until actual precipitation occurs, while in the others the stages are quite distinct. I have shown that in these last reactions acids are liberated which may be readily recognized. It is also true that these acids are practically without action on antimonous oxide, from which it would follow that this substance might remain a long time, possibly in the hydrated form, in contact with the liberated acids without change. This would not be the case with liberated thiosulphuric acid. If set free in the presence of antimonous oxide, even the dry precipitate, it soon converts it into sulphide. Any cause, therefore, which acts to destroy the equilibrium in the solution of tartrate and thiosulphate must lead to the almost immediate formation of a precipitate.

In many of our most familiar cases of precipitation the formation of the precipitate is so rapid that we are accustomed to look upon it as instantaneous. But by varying the conditions of precipitation it may be shown that even the reaction between barium chloride and sulphuric acid is one which consumes an appreciable interval. In such cases, however, we have no means of knowing what takes place before the precipitate becomes actually visible. It is, doubtless, true that the liquid regarded as supersaturated for $BaSO_4$ does not begin to throw this out in solid form until a relatively large number of these molecules combine to produce a particle of a certain size, but at what rate the Ba and SO_4 ions combine can not be shown.

But in the cases before us we have evidence, first, of the gradual breaking up of the complex potassium antimonyl tartrate and then, also, that a relatively large amount of the antimony may be separated before any of it falls as a precipitate. The stage of precipitation seems to follow as a perfectly distinct and also progressive one. It is hastened, as in other cases of supersaturation, by heat or agitation. One of the reactions shows, also, that a relatively long time is consumed in combination as well as in dissociation. In the case of the mixture containing the tartrate and tungstate we have evidence of the splitting of the first molecule, and then, from the slowly increasing rotation, evidence of the addition of an element from the second to the active part of the first. Both of these phenomena are observed before precipitation appears.

It must be remembered that the several acids shown to be liberated in these experiments are all so-called weak acids, or acids but slightly dissociated in solutions. It is also true, as a test of their electric conductivities shows, that the solutions of tartar emetic are relatively little dissociated (see in this connection Hugo Haedrich, *Ztschr. phys. Chem.*, **12**, 496). There is doubtless, therefore, a close connection between the phenomena outlined above, and others depending on the degree of dissociation of the ions in solution. A study of the behavior of weaker solutions would doubtless lead to interesting results not brought out in the above experiments which were undertaken mainly to show the character and amount of precipitates formed. A discussion of the behavior of dilute solutions will follow.

CHICAGO, December, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE. XXI.]

AN EXAMINATION OF THE ATMOSPHERE OF A LARGE MANUFACTURING CITY.[1]

BY CHARLES F. MABERY.

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THE composition of the atmosphere was determined in the latter part of the last century by the classic researches of Priestley, Cavendish, Lavoisier, and others. These investigations were stimulated by Priestley's discovery of oxygen and the discovery of nitrogen by Rutherford. The proportion of nitrogen was first ascertained by Cavendish, and the precise quantitative composition was ascertained by Lavoisier, who repeated the celebrated experiment of Priestley, in which metallic mercury was heated for a long time in a confined volume of air to determine the quantity of gas absorbed and the residual nitrogen. The composition of the atmosphere with reference to the proportion of oxygen and nitrogen has since been frequently determined without showing any appreciable variation. In specimens of air collected from regions widely separated, Morley (*Am. Chem. J.*, **2**, 276) determined with the utmost precision the proportion of oxygen and nitrogen without finding any appreciable variation.

The essential constituents of the atmosphere include oxygen, nitrogen, and carbon dioxide in constant proportions, nitrous and nitric acids, sulphurous and sulphuric acids, dust, soot, moisture, ammonia, and certain other constituents in variable

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[1] The experimental work of this paper was performed under my direction by Mr. Charles G. Snyder, and it formed the subject of his thesis for the Degree of Bachelor of Science.