It is pointed out that at 700° silicobromoform is almost wholly decomposed into silicon tetrabromide, silicon and hydrogen.

The corrected boiling points of the products were: $SiBr_4$, 153.4°; $SiHBr_3$, 111.8°; SiH_2Br_2, 64.0°. The freezing point of silicobromoform was fixed at $-73 \pm 1°$.

As concerns the mechanism of the reaction, it is believed that the primary products are silicon tetrabromide and hydrogen and that the former is reduced in part by the hydrogen to form the other products. Experimental evidence in favor of this hypothesis is given.

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A STUDY OF THE QUANTITATIVE PRECIPITATION OF CALCIUM OXALATE IN THE PRESENCE OF THE PHOSPHATE ION

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In the course of the analytical work involved in a previous problem,[1] the authors found it necessary to make calcium determinations on a large number of solutions containing an excess of phosphoric acid. To avoid the long and tedious process of removing the phosphate ion as the ferric salt, a short method was devised whereby the calcium oxalate precipitation was made in the presence of the phosphate ion. Consistent results were obtained by the method, and on the completion of the previous problem a study was made to determine the general applicability of the method.

The method is based on the assumption that the so-called tertiary calcium phosphate, which forms on the addition of ammonium hydroxide to the solution, having a much greater solubility product than calcium oxalate, would go into solution and the calcium oxalate form. Consequently, if the solution be allowed to stand long enough for this metathesis to be complete, it would be possible to precipitate calcium oxalate in the presence of the phosphate ion. In order to determine the most favorable conditions under which to carry out the precipitation, several series of analyses were made to determine the time required for a complete transformation of calcium phosphate into calcium oxalate and the effect of temperature and alkalinity of solution at time of precipitation.

After first having found the minimum time necessary for the complete precipitation, series of analyses were made to determine the difference in results, if any, caused by adding the precipitating agent before and after the solutions were made alkaline with ammonium hydroxide. These series were run both at 20 and at 100°. Some preliminary experiments indicated

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[1] Mebane, Dobbins and Cameron, *J. Phys. Chem.*, **33**, 961 (1929).

that an excessive amount of the ammonium hydroxide, when added first to the solution, hindered the formation of the calcium oxalate. Consequently two series were made using a slight excess of ammonia in one case and a 10-cc. excess of concentrated ammonium hydroxide solution in the other, in order to determine the effect of the concentration of ammonium hydroxide on the solution.

Procedure

A 0.1 *N* solution of calcium chloride was prepared by dissolving a weighed quantity of Iceland spar in hydrochloric acid. Approximately 0.1 *N* solutions of disodium phosphate and potassium permanganate were made. As the precipitating agent, a saturated solution of ammonium oxalate was used.

Twenty cc. of the standard solution was taken for each analysis. To this solution 25 cc. of the disodium phosphate was added to give an excess of phosphate ions, then an excess of ammonium oxalate. The precipitates were filtered, washed by decantation with distilled water containing a small amount of ammonium hydroxide and transferred on the filter paper to the precipitation beaker. The precipitates were dissolved in dilute sulfuric acid, the solution was brought almost to boiling temperature and titrated with the 0.1 *N* permanganate solution. It was found that unless the titration required an unusually long time for completion, the presence of the filter paper in the titration beaker did not affect the results. It was found that as accurate results were obtained by titrating the precipitate first formed as by following the usual procedure of dissolving and reprecipitating the calcium oxalate. The losses involved in redissolving the precipitate are as great as the error caused by the adsorption of ammonium oxalate by the precipitate. In all cases the precipitation was carried out in a volume of 80–90 cc.

Data

EFFECT OF TIME OF STANDING. 20 CC. *N*/10 CALCIUM SOLUTION USED IN ALL CASES

	Made alkaline with ammonia before addition of oxalate		Made alkaline with ammonia after addition of oxalate	
Time, hours	20° *N*/10 $KMnO_4$, cc.	100° *N*/10 $KMnO_4$, cc.	20° *N*/10 $KMnO_4$, cc.	100° *N*/10 $KMnO_4$, cc.
0.25	15.40	19.80	20.30	19.80
0.5	20.80	20.05	20.62	19.75
1	20.01	19.95	20.05	19.95
1.5	19.96	20.00	20.00	20.00
2	20.00	20.00	20.05	19.96

EFFECT OF TEMPERATURE, CONCENTRATION OF AMMONIA AND ORDER OF ADDING REAGENTS

Ammonium hydroxide added to the solution before ammonium oxalate. One hour allowed for reaction

20°C.		100°C.	
Slight excess NH_4OH $KMnO_4$, cc.	10 cc. excess NH_4OH $KMnO_4$, cc.	Slight excess NH_4OH $KMnO_4$, cc.	10 cc. excess NH_4OH $KMnO_4$, cc.
19.94	20.10	20.00	20.01
20.06	20.06	20.00	20.15
20.11	19.96	20.00	20.08
20.05	20.10	20.11	20.06
20.10	19.95	19.96	20.10

24 hours allowed for reaction

20 °C.		100 °C.	
Slight excess NH_4OH $KMnO_4$, cc.	10 cc. excess NH_4OH $KMnO_4$, cc.	Slight excess NH_4OH $KMnO_4$, cc.	10 cc. excess NH_4OH $KMnO_4$, cc.
20.06	20.06	20.00	20.00
20.00	20.06	19.94	19.94
19.94	19.96	19.96	19.80
Ammonium hydroxide added to the solution after ammonium oxalate. One hour allowed for reaction			
20.06	19.66	19.90	19.80
20.00	19.71	19.91	19.94
20.00	19.66	19.76	19.74
20.00	19.91	19.89	19.89
19.80	20.06	19.94	19.96
24 hours allowed for reaction			
20.00	20.11	20.00	20.11
20.00	20.11	19.94	20.06
20.06	20.00	20.06	19.94

Discussion

In some respects the results of these analyses were contrary to our expectations. It was thought that more time would be required for the transformation of the precipitate than is required for the usual precipitation, at least in the case where a considerable precipitate of calcium phosphate was formed before the addition of ammonium oxalate. In many cases good results were obtained when the precipitate stood for only thirty minutes, though this time seems to be too short for consistent results.

The formation of the calcium phosphate precipitates before the addition of the ammonium oxalate not only did not hinder the reaction, but seemed to be a help. These oxalate precipitates seemed to hold the flocculent nature of the phosphate which they replaced, and therefore were very easy to filter and wash. Those to which the oxalate was added first were very fine grained and difficult to filter under the best conditions. In both cases filtration was difficult when the precipitation was carried out at boiling temperature. The agitation during the boiling seemed to deflocculate the precipitate and leave a very fine grained precipitate which had a tendency to run through the filter paper and was very difficult to wash. Although some difficulty was met at first in getting good results with the addition of the ammonia before the oxalate, it was later found that better and more consistent results could be obtained by this method. The addition of the oxalate first gives accurate results, provided the solution is allowed more time in which to precipitate, but the results are likely to be low if the precipitation is carried out at boiling temperature. This may be due to the extreme fineness of the precipitate and the consequent difficulty of removing it completely from the solution.

Recommended Procedure.—Accurate results were obtained from the following procedure: the solution was made alkaline with ammonium hydroxide and 5-cc. excess of concentrated ammonium hydroxide added. An excess of ammonium oxalate was then added at room temperature, stirred and the precipitate allowed to stand for at least one hour. The precipitate was filtered off, washed with water containing a small amount of ammonium hydroxide, transferred on the paper to the precipitation beaker, dissolved in dilute sulfuric acid and titrated with a 0.1 *N* potassium permanganate solution. Considerable variation from this scheme may be made with the results obtained within the normal range of error, but the above outline was found by a large number of analyses to be the most dependable.

Summary

1. Calcium oxalate may be precipitated quantitatively in the presence of phosphate ions.
2. The solutions should be made alkaline before the addition of ammonium oxalate, and a small excess of ammonium hydroxide added.
3. The best temperature for precipitation is 20–25°.
4. Reprecipitation of calcium oxalate is not always necessary.

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THE DECOMPOSITION OF NITROGEN PENTOXIDE IN INERT SOLVENTS

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The nitrogen pentoxide decomposition has been used to test theories of reaction rates—the radiation hypothesis, the collision theory and the chain mechanism. The theory of activation through collision is promising but more experimental facts are needed. It is necessary to distinguish between activation caused by ordinary collisions and activation caused by collisions with the decomposition products.

The mechanism of activation does not affect the decomposition rate provided that the rate of activation is high enough to maintain the equilibrium number of activated molecules. A decision may be made between the collision theory and the chain theory by providing conditions which will deactivate the products of decomposition before they collide with unactivated nitrogen pentoxide molecules. Several investigators have sought to make collisions of the decomposition products with the walls relatively numerous as compared with collisions with nitrogen pentoxide. Sprenger[1]

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[1] Sprenger, *Z. physik. Chem.*, **136**, 49 (1928).