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NOTES ON THE PRECIPITATION OF TITANIC ACID BY  
HYDRIC SULPHIDE.

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When hydric sulphide is passed into a solution containing ferric salts and titanitic acid, the former are reduced to ferrous salts and a portion of the latter is precipitated. The following experiments were made to determine, in the first place, how much of the titanitic acid may be precipitated; in the second place, the conditions under which the least amount of titanitic acid or none will be precipitated from solutions obtained by fusing with hydric-potassic sulphate and taking up the fused mass with cold water; a method very frequently employed in the determination of titanitic acid.

The fact that titanitic acid may be present in the precipitate of sulphides obtained by hydric sulphide is well known, but the reason assigned in explanation of it does not seem so plain.

In Vol. II, page 318 of H. Rose's Analytical Chemistry it is stated: "It is, however, to be remarked, that the sulphides must be filtered off soon after precipitation, because some titanitic acid may readily separate even at ordinary temperatures if the solution be very dilute." The presence of the titanitic acid in the precipitate of sulphides is plainly attributed to the dilution of the solution. This may be the case in some instances, but it is not always, at least, the only cause. I have obtained solutions which would remain clear for a considerable time, while a portion treated with  $H_2S$  yielded an abundant precipitate of titanitic acid within forty-five minutes. Again, solutions of the same degree of dilution and having been allowed to

stand for the same time permit very different amounts of titanitic acid to be thrown down. This is true, too, when the amounts of titanitic acid, potassium and other sulphates present in the solutions are the same. It does not seem to be due to dilution alone or dependent upon the relative quantities of the salts present. I have seen this precipitation take place in solutions of rutile, also in solutions made of precipitated titanitic acid (it was, however, not perfectly free from ferric oxide). The amount precipitated by passing  $H_2S$  into a solution bears no definite relation to the total amount of titanitic acid in the solution.

	Precipitated by $H_2S$ .	Total $TiO_2$ .	Per cent. of total.
	(1)	(2)	(3)
Experiment I.	3.85	27.18	14.16

Conditions. Mineral (menaccanite) was fused with 6 to 7 times its weight of  $KHSO_4$  until fumes of  $H_2SO_4$  ceased to be given off and the mass had become brown. The fused mass was treated with cold water, the residue of  $Fe_2O_3$  was brought into solution by fusion with  $KHSO_4$  and its solution added to the first solution. The mixed solutions were perfectly clear and of a reddish yellow color. A moderate stream of  $H_2S$  was passed into it for two (2) hours. The precipitate was flaky, voluminous and brown from admixed  $PtS_2$ .

	(1)	(2)	(3)
Experiment II.	.0039	.3049	1.28

Conditions. Mineral fused with  $KHSO_4$  for  $1\frac{1}{4}$  hrs. at dull red heat. Fused mass white, easily soluble to an almost colorless solution.  $H_2S$  was passed into it for  $1\frac{1}{2}$  hours. Precipitate heavy, brown and flocculent.

	(1)	(2)	(3)
Experiment III.	.0330	.2940	11.23

Conditions. Fused with 7 pts.  $KHSO_4$  at strongest heat of a good Bunsen burner for 30 minutes. The fused

mass was of a greyish brown color; dissolved difficultly with separation of basic salts. The solution was made complete by re-fusing residue with  $\text{KHSO}_4$ . The solution was strongly colored but clear.  $\text{H}_2\text{S}$  was passed into it for  $1\frac{1}{2}$  hours giving a precipitate which was flocculent and almost pure white.\*

	(1)	(2)	(3)
Experiment IV.	.0020	.3005	.66

Conditions. Fused mineral with 6 pts. of  $\text{KHSO}_4$  until decomposition was complete. Fused mass dissolved readily in cold water to an almost colorless solution.  $\text{H}_2\text{S}$  was passed into it for  $1\frac{1}{2}$  hrs.; precipitate was brown. The  $\text{H}_2\text{S}$  precipitate was fused with  $\text{KHSO}_4$  and precipitated from this solution by boiling; it was quite dark and may not have been quite pure, still it gave with blow-pipe, reactions for titanic acid.

	(1)	(2)	(3)
Experiment V.	.0372	.3067	12.13

Conditions. Fused with 7 pts.  $\text{KHSO}_4$  until  $\text{H}_2\text{SO}_4$  ceased to be given off and the fused mass had become of an uniform grey color. It separated easily from the walls of the crucible, was very brittle and difficultly soluble in cold water with separation of basic salts. The solution was perfectly clear and of a bright yellow color; it was treated with  $\text{H}_2\text{S}$  for one hour and a heavy, flocculent precipitate was produced.

	(1)	(2)	(3)
Experiment VI.	.0315	.3020	10.43

Conditions. Fused with 7 pts.  $\text{KHSO}_4$  for  $1\frac{1}{2}$  hrs. at the highest heat of a good Bunsen burner. The resulting mass was of a brownish grey color, adhered tenaciously to the walls of the crucible and was very difficult to get into solution. The basic salts, of which a large amount re-

\* The color of the precipitate depends mostly upon the amount of  $\text{PtS}_2$  present in it. The quantity of Pt which goes into solution varies in different fusions from the same crucible and very widely for different crucibles under apparently similar conditions.

mained undissolved, were re-fused with  $\text{KHSO}_4$ . Solution was clear and bright yellow in color; it was treated with a slow stream of  $\text{H}_2\text{S}$  for one hour.

	(1)	(2)	(3)
Experiment VII.	.1140	$\frac{2}{3}$ .3119	36.56

Conditions. Fused with 7 pts.  $\text{KHSO}_4$  until  $\text{H}_2\text{SO}_4$  had ceased to be given off and  $\text{Fe}_2\text{O}_3$  had begun to be formed on the top of the mass and on the walls of the crucible. The mass was very difficultly soluble in water and yielded a red residue which was brought into solution and added to the main portion. The solution was perfectly clear and bright yellow in color.  $\text{H}_2\text{S}$  was passed into it for  $1\frac{3}{4}$  hrs; precipitate was flesh colored.

	(1)	(2)	(3)
Experiment VIII.	.0170	$[\frac{2}{3}]$ .3119	5.45

Substance was fused with 7 pts.  $\text{KHSO}_4$  until mass was dry and spongy, then a small piece of  $\text{KHSO}_4$ , about 1 grm., was added and the mass re-fused; it was then of a grey color and very brittle but not crumbly; it dissolved readily to a clear bright yellow solution.

	(1)	(2)	(3)
Experiment IX.	.0280	$(\frac{2}{3})$ .3119	8.98

This was treated in the same way as No. VIII.

	(1)	(2)	(3)
Experiment X.	.0872	.3119	27.96

This was the result of an attempt to repeat Exp. No. VII.

Experiments XI and XII gave .0070 and .0040 respectively of  $\text{TiO}_2$ . The manipulation was the same as in experiments VIII and IX, with the substitution of  $\text{NaHSO}_4$  for the  $\text{KHSO}_4$ .

These results indicate that it is exceedingly difficult, if not impossible, to prevent the precipitation of  $\text{TiO}_2$  when

hydric sulphide is used to reduce the iron salts, and as the precipitation takes place in solutions of rutile prepared in the same manner, the reaction does not seem to be dependent upon the quantity of iron salts present.

The fact that the percentage of the  $TiO_2$  which is thrown down, varies from  $\frac{1}{2}$  to  $36\frac{1}{2}$  per cent., shows that the manipulation affects it to an extreme degree. I have found no decided difference, so far as I have compared them, between solutions prepared by the use of  $NaHSO_4$ , and those prepared with  $KHSO_4$ . It is certain, however, that the use of  $NaHSO_4$  will not prevent the precipitation. It is not absolutely necessary to reduce with  $H_2S$ , but in using solutions of  $SO_2$  or the acid sulphites, it must be remembered that the solution must not contain much  $H_2SO_4$  or the precipitation of  $TiO_2$  will not be complete. It is also necessary that the solution be diluted so that at least 1 litre of solution contain not more than 0.2 gm. of  $TiO_2$ .\*

The precipitates obtained from dilute solutions filter, as a rule, better than those obtained from less dilute ones. The precipitation of  $TiO_2$  by  $H_2S$  is not prevented when one reduces before diluting the solution.

\* This dilution is recommended in American Ed. of Will's Tables, Table XVI, note.