

CONTRIBUTIONS TO THE CHEMISTRY OF THALLIUM. I

J. F. HAWLEY

Received January 11, 1907.

This paper comprises a criticism and modification of Willm's method for the volumetric determination of thallium, together with a description of the preparation and properties of thallium fulminate, thallium aluminate, and a double chromate of potassium and trivalent thallium.

Determination of Thallium.—In all of the determinations of thallium in the following investigation the method of titration with potassium permanganate in the presence of free hydrochloric acid was used. This method is very exact if the conditions under which the titrations are made are carefully controlled. The standardization should be made by means of a pure thalious salt dissolved in a definite amount of water and in the presence of a definite amount of free hydrochloric acid; the titrations must be made under exactly the same conditions. Thalious sulphate is the best salt to use for standardization; it crystallizes readily and although it tends to occlude the mother liquor the water may be removed by heating the crystals just to fusion. This salt is stable at its melting point if no excess of sulphuric acid is present. In the following work fused thalious sulphate was used for the standardization, all titrations were made in hot solution, the volume of solution titrated was always 60 cc., and the free hydrochloric acid present was equivalent to 4 cc. of concentrated acid, Sp. Gr. 1.2. Under such conditions up to 0.16 gram thallium could be titrated with a perfectly sharp end point. This general method was first mentioned by Willm¹ and has since been used by Noyes² and by Dennis and Doan³ but no mention has ever been made of the fact that the thallium factor, the grams thallium oxidized by 1 cc. potassium permanganate, varies with the amount of thallium titrated. This variation is best seen when the standardization is made with varying amounts of thallium and the results expressed in the form of a curve with the thallium factors as ordinates and the volumes of potassium permanganate expressed in cubic centimeters as abscissae. Also by means of such a curve the thallium factor to be employed in determinations can be read directly from the amount of potassium permanganate used. From the curve given it will be seen that under the conditions named the thallium factor remains nearly constant above 35 cc. potassium permanganate, corresponding to about 0.10 grams thallium, but below that amount the factor decreases rapidly. This variation is just as marked when titrations are made in the cold and with a greater volume of solution. For instance, when 0.0809 gram thallium as sul-

¹ Willm, Ann. Chim. Phys., (4), 5, 5.

² Noyes, Z. Phys. Chem., 9, 608.

³ Dennis and Doan, This Journal, 18, 970.

phate was dissolved in 200 cc. of water, 10 cc. hydrochloric acid, Sp. Gr. 1.2 added and titration made in the cold, the thallium factor was 0.003387, but when 0.0449 gram thallium was titrated under the same conditions the factor was 0.003311. From this it will be seen that if the titrations are not confined to that part of the field where the factor remains nearly constant the variation of the factor with the concentration of the thallium must be taken into account, if accurate results are to be obtained. Work on the causes of this variation is at present in progress and the results will be published in a subsequent article.

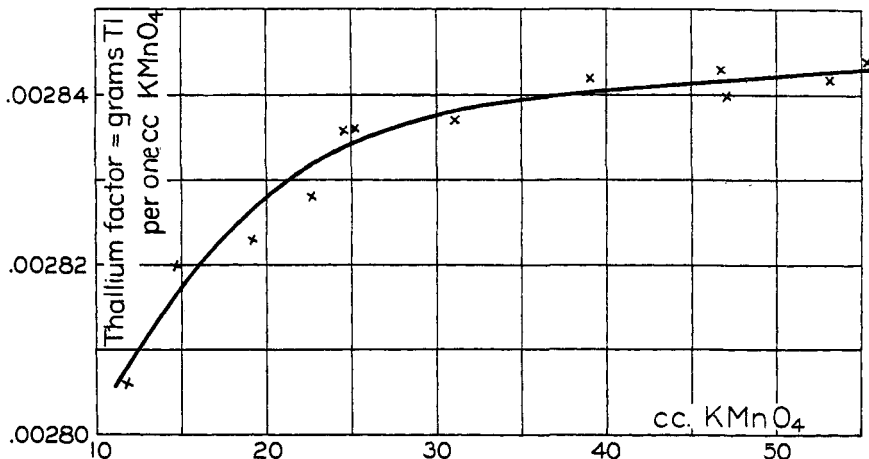


Fig. 1.

Thallium Fulminate.—An attempt was made to prepare thallium fulminate in the same manner as the mercury fulminate. Metallic thallium was dissolved in nitric acid with the aid of heat, retaining the nitrous fumes in the flask as much as possible, and the warm solution was poured into one-half the requisite amount of alcohol. This mixture was then returned to the first flask and shaken to absorb the nitrous fumes. The other half of the alcohol was added as required to check the violence of the reaction. The reaction resembled that taking place during the formation of mercury fulminate, but thallium nitrate was the only product of the thallium.

Since thallium fulminate could not be prepared as above, the method of replacement by metallic thallium was used. Mercury fulminate suspended in water was treated with fine shavings of metallic thallium until there was no mercury left in the solution. The mercury was deposited on the thallium, and thallium fulminate was formed in solution. This solution was rapidly evaporated in a vacuum desiccator until very fine, colorless needles of the fulminate were deposited. The crystals were

washed with a little water, pressed between filter papers and dried over calcium chloride. The analyses follow :

	I	II	Calculated for $Tl_2C_2N_2O_2$
Tl	82.83	83.14	82.94
C	4.90	4.75	4.87
N.....	5.75	5.74	5.70

The presence of the fulminate radical interfered with the permanganate titration, so the thallium was separated by precipitating it by ammonium sulphide, filtering and redissolving in sulphuric acid. The carbon and nitrogen were determined by the usual combustion methods, except that the fulminate was mixed with a very large quantity of cupric oxide in order that the combustion might proceed slowly and quietly.

Thallium fulminate turns slightly yellow on drying and very slowly becomes brown and non-explosive on exposure to the air, but it does not entirely lose its explosiveness when kept in a glass stoppered tube for several months. It explodes violently on percussion, on bringing it into contact with concentrated sulphuric acid or on suddenly heating it. If, however, it is gradually heated to 140° and kept there for a few hours, it turns brown without change of weight and becomes non-explosive. It dissolves readily in water, but the solution decomposes quite rapidly, turning brown and depositing a brick-red amorphous mass, which is non-explosive and is not of constant composition.

Thallium Aluminate.—The aluminates of all metals, except thallium, which have soluble hydroxides have been prepared by Allen and Rogers¹ and an aluminate of thallium can be prepared in the same manner. Unlike the other soluble hydroxides, thallos hydroxide does not evolve hydrogen when it acts on metallic aluminum, but instead, thallium is deposited as aluminum goes into solution. The solution of aluminum in thallium hydroxide was evaporated in a vacuum desiccator over potassium hydroxide to insure absence of carbon dioxide, and either aluminum hydroxide or yellowish green crystalline thallos hydroxide was deposited first, depending on which was in excess of the ratio $2Tl : 1Al$, (aluminum will replace thallium from a hot, concentrated solution of thallos hydroxide until the ratio of Tl to Al is nearly $1 : 1$). In one instance, colorless, prismatic crystals of a hydrated thallos hydroxide were obtained on evaporating a solution of the aluminate containing an excess of $TlOH$. These crystals contained not a trace of carbonate and a determination of thallium gave 82.05 per cent. Not enough of them were obtained to make a determination of the percentage of water, but the percentage of thallium indicates the formula, $2TlOH \cdot 3H_2O$, (calculated 82.27 per cent. of thallium).

¹ Am. Ch. J. 24, 305.

Probably the same compound was obtained by Willm¹ also accidentally, although he gave it the formula $\text{TlOH} \cdot \text{H}_2\text{O}$. The conditions under which this hydrate is formed are not known, but it is apparently a metastable form. The thallium aluminate is very soluble and comes down only as the very last of the solution evaporates as a white powdery mass which can be separated from the crystals of TlOH first formed. The following analyses were obtained :

	I	II	Calculated for $\text{Tl}_4\text{Al}_2\text{O}_6 \cdot 7\text{H}_2\text{O}$
Tl	76.40	76.76	75.84
Al	5.24	4.90	5.01
H_2O diff.	10.55	11.60	11.70

The white powder of $\text{Tl}_4\text{Al}_2\text{O}_6 \cdot 7\text{H}_2\text{O}$ is insoluble in absolute alcohol ; is not completely soluble in water, being slowly hydrolyzed, but is readily soluble in dilute acids and in the fixed alkalis. In solution it is decomposed by carbon dioxide, giving Tl_2CO_3 and $\text{Al}(\text{OH})_3$.

A Double Chromate of Potassium and Trivalent Thallium.—Carstanjen², Heberling,³ and Strecker⁴ have mentioned precipitates obtained by potassium chromate or dichromate and different solutions of trivalent thallium, but no idea has been offered concerning their composition. In an endeavor to prepare $\text{Tl}_2(\text{CrO}_4)_3$, thallic hydroxide was dissolved in chromic acid and the solution evaporated ; it was found that the excess of chromic anhydride crystallized out first and no good deposit of a thallic chromate could be obtained by further evaporation. On adding potassium hydroxide to the solution to precipitate the thallium, it was noticed that a yellow precipitate was formed before the excess of chromic acid was neutralized and before the brown thallic hydroxide commenced to precipitate. If the solution is made not quite neutral with potassium hydroxide and then allowed to stand, the yellow precipitate comes down in quite large quantities. Care must be taken that the solution is so dilute that the potassium dichromate does not crystallize out. The precipitate obtained as above was found to hydrolyze so readily that it could not be washed with water, so it was filtered through asbestos and dried as completely as possible on a porous plate and then over calcium chloride. Analyses showed that this product was not free from the mother liquor, since it contained an excess of chromium. But by adding the potassium hydroxide very slowly, (about one drop every two or three hours), a more crystalline precipitate was obtained, which did not retain the mother liquor as much as the first product, and which could be washed with a dilute solution of chromic acid without hydrolyzing. This

¹ Loc. cit.

² J. Pr. Chem., 102, 65.

³ Ann. Pharm., 134, 11.

⁴ Ann. Pharm., 135, 207.

product was dried to constant weight over calcium chloride and then analyzed as follows :—

It was dissolved in sulphuric acid and both the thallium and the chromium were reduced by sulphur dioxide; the chromium was precipitated by ammonia and filtered and weighed in the usual manner. The filtrate, containing the thallium, was acidified with sulphuric acid, and boiled six minutes to expel the excess of sulphur dioxide, or longer if necessary to evaporate to the required volume, then titrated with potassium permanganate after adding the usual amount of concentrated hydrochloric acid. Water of crystallization was determined by the loss of weight on heating to 200°. The potassium was weighed as the sulphate after reducing the thallium and chromium with sulphur dioxide and removing them by precipitation with ammonium sulphide.

	I	II	Calculated for $KTl(CrO_4)_2 \cdot 2H_2O$
Tl	39.90	40.70	39.98
Cr	20.30	20.13	20.35
K	7.72	7.54	7.65
H ₂ O	7.03	7.00	7.04

This double chromate of potassium and trivalent thallium is a yellow crystalline precipitate, difficultly soluble in a solution of potassium dichromate, but quite readily soluble in dilute mineral acids. It is quickly hydrolyzed by water unless a large excess of the CrO_4 ion is present. It gives off its water of crystallization below 200° and if heated to about 300° it melts with loss of weight. The melted mass is apparently a mixture of $K_2Cr_2O_7$ and $Tl_2Cr_2O_7$, since all the thallium is in the thallos condition and the loss of weight corresponds to the loss of two atoms of oxygen for every molecule of Tl_2O_3 .

Loss of weight on melting		Calculated for loss of one atom of oxygen from $KTl(CrO_4)_2 \cdot 2H_2O$
I	II	
3.13 %	3.06 %	3.12 %

In conclusion I wish to thank Professor L. M. Dennis for many valuable suggestions.

CORNELL UNIVERSITY,
January, 1907.

ON FERROUS AND FERRIC SULPHIDES.

BY H. N. STOKES.

Received January 11, 1907.

The appearance of a paper by Kongschegg and Malfatti¹ on the soluble sulphide of iron causes me to call attention to some uncompleted experiments made some time ago by myself in the laboratory of the U. S. Geological Survey. Being unable to continue the work, I state them

¹ Z. Anal. Chem., 45, 747 (1906).