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Studies in tellurium

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Studies on Tellurium.

A

THESIS

For the Degree of B. S. in Analytical Chemistry.

Submitted to the Faculty of the Missouri School of Mines

BY

V. HUGO GOTTSCHALK.

JUNE, 1898.

The following pages contain the record of six weeks' work with tellurium. The results obtained, (if results they can be called) have no claim to a place under the category "Valuable Contributions to the Chemistry of Tellurium," nor do they embody many new facts relative to compounds and reactions already known. The pursuance of the work however, has managed to keep the writer busy for six weeks, beside giving him an idea what is meant by "Research Work".

PURIFICATION OF TELLURIUM.

As the points to be investigated would be most advantageously worked out when pure tellurium was used as the starting point, the first step to be taken ^{was} the purification of the tellurium obtained by Dr. Allen from Colorado Telluride ore. Two methods presented themselves for consideration, viz; (1) Distillation of crude tellurium in a stream of Hydrogen, (2) Oxidation by Nitric acid, solution of the resulting tellurium dioxide in hydrochloric acid, and precipitation out of this solution by sulphur dioxide.

Both of these methods were tried, and compared to determine which would give the most desirable product as regards both aggregation and purity in the least time. Using method one we recovered two and thirty six hundredths grams pure tellurium out of two and five tenths crude; -- yield 94.4% from one portion when working with a blast lamp and two Bunsen flames to heat distillation tube; with blast alone obtained a maximum yield of

88.6%. With the blast alone two grams can be distilled in not less than one hour; with blast aided by two burners the same can be accomplished in forty minutes. The hydrogen gas used was purified by washing in potassium hydrate (to remove possible traces of hydrogen sulphide) and dried by passing through sulphuric acid; the only possible sources of impurity in this distillation are presented in a possibility of pieces ^{of glass adhering} appearing to the tellurium which condenses in the hard glass tube, and ^{the} distillation of some volatile impurity. After several trials the most favorable conditions for carrying out method two were found to be as follows: the powdered tellurium was placed in a casserole, covered with water, and thoroughly agitated; then about ^{10.} c. c. strong nitric acid were added; the casserole at once covered with a watch glass, then shaken to agitate its contents. In this manner a few minutes sufficed to oxidize several grams of tellurium. The contents of the casserole were evaporated to dryness, ^{is} dissolved in concentrated hydrochloric acid, ~~diluted~~ diluted with water, and saturated with sulphur ^udioxide. Warming facilitates precipitation. The precipitated tellurium was filtered, dried at 100°C ., and weighed. This precipitation is complete if allowed to stand; filtering immediately, occasions a slight loss due to incomplete precipitation. 2.47 grams of crude tellurium yielded 2.27 grams of pure tellurium; i. e. a yield of 92%; hereagain, after drying, some of the tellurium was left attached to the filter paper, to guard against contaminating impurities, i. e. foreign matter from the filter paper.

QUALITATIVE ANALYSIS FOR IMPURITIES.

In the distillation a porcelain boat was employed; this was found to be covered with peculiar, iridescent spots after all the tellurium had been distilled; from the method of preparing the crude tellurium, the only probable impurities were lead, copper, or iron: qualitative tests revealed the presence of none of these, although it is possible that they were present in such minute quantities as to evade a detection by the usual methods. So also a solution of tellurium in nitric acid was tested in the wet way by schemes to be found in Fresenius' "Qualitative Analysis" for methods of separation and detection; here too no foreign substances could be found.

COMPARISON of METHODS.

On the whole then it would seem advisable to use the second method to prepare pure tellurium for use in investigating the chemistry of tellurium and its compounds, for the following reasons: (1) - Obtained much quicker in this way, i.e. time saving.

(2) Distillation requires constant attention, while the second method, although seemingly more complex, allows the experimenter to give his attention to other affairs while preparing the samples of pure tellurium.

(3) The yield is about the same in both methods.

(4) The chances of purity are much greater in the second method.

It was the object of the writer's work to establish two main points, viz; the cause of the beautiful purplish-red color obtained on treating tellurium with concentrated sulphuric acid; and the preparation of pertellurates; or, to be more modest, attempt to throw a ray or two on these subjects. What has ~~been~~ actually been ^caccomplished is merely the acquisition of a number of facts, which will facilitate further investigation in this subject. The literature of the subject, as far as available to us, threw but little light on the work in hand, and the difficulties encountered were more than was anticipated.

SOLUTION of TELLURIC in CONCENTRATED SULPHURIC ACID.

It seemed very simple to ^{is}dissolve tellurium in sulphuric acid, ^{re}precipitate the same by addition of water, and comparing the weights of the original tellurium and of the product obtained: the ^ddifficulty however was the ^{is} incomplete and extremely slow solubility of tellurium in sulphuric acid. It was tried time and again to ^caccomplish this, with ever decreasing amounts of tellurium in greater and greater quantities of the most concentrated acid the laboratory could afford; there always remained a residue of tellurium ^sundissolved. As the red solution has been observed to ^{re}precipitate tellurium on exposure to the air, we used a glass stoppered ^{bottle} with no better results. Finally ^ea rough estimation of ^{of} solubility of tellurium in sulphuric acid was made as follows; A weighed amount of powdered tellurium was put in a glass stoppered bottle; after filling the bottle half full of concentrated

sulphuric acid (sp.g.1.83) the stopper was put in securely, and the bottle shaken from time to time, -- allowed to stand in sunlight (i.e. slightly heated.) After several consecutive days' treatment in this way the sulphuric acid solution was decanted, and its volume measured; the residue of tellurium was washed out onto a counter poised filter, dried, and weighed; it was thus found that 36 c.c. of sulphuric acid (sp.g.1.83) dissolved ^s 0.0481 grams of tellurium, or 1 c.c. H_2SO_4 dissolves .00134 grams tellurium. With this as a guide, weighed amounts of tellurium were treated with quantities of sulphuric acid about twice that given by the above determination; still a residue remained. It was suspected that the particles of tellurium were not fine enough, as such particles remaining undissolved seemed rather large; on grinding the tellurium in an agate mortar, it was found that the pressure ^s was sufficient to make the small particles adhere to form plates; these were separated from the fine material by sifting through ~~bolting~~ bolting cloth; the fine material was then again subjected to the treatment with strong sulphuric acid with no better results. This latter treatment, (with the finest particles of tellurium that could be got), with larger relative amount of sulphuric acid was tried once more, with the same discouraging result. At this stage, it was decided to give up this line of investigation, at least until means to overcome the difficulties encountered, could be devised; however, the time for pursuing the study of this problem further has not been forthcoming, and the unfruitful ^{labor} outlined in the foregoing few words, leaves us with no significant positive result. A few observations made during the above experiments may

be recorded here as of some probable advantage to a later worker on the same subject:--

(1) Heat aids the solution of the tellurium in concentrated sulphuric acid; but at a temperature not yet determined the tellurium reduces the sulphuric acid, itself changing to tellurous acid, ^{while} ~~and~~ the color of the solution ^{is being} lost. ^{we} ~~Here~~ was encountered the difficulty of attaining the correct temperature, as in all trials made, even on rather gentle warming, evolution of sulphur^u dioxide was noticed. With no means of accurate adjustment of temperature, exact data on this point could not be obtained, without sacrifice of time which had to be employed otherwise.

(2) The observations given in reference books that the red solution deposits tellurium on standing in the air have been confirmed incidentally in several of the experiences tried above: also, on heating the red solution, the solubility of the tellurium was found to be increased, as it deposits tellurium on cooling (when allowed to stand in corked test tubes).

(3) The red solution precipitates its tellurium on addition of water. It was found however that when the solution was poured into from six to eight times its volume of water, a very perceptible reddish tinge remains: after two days' standing, the tellurium having all settled, the red tinge had disappeared.

While the above tabulated experiments were going on, attention was also being directed to the other problem in mind, viz; the preparation of pertellurates.

PREPARATION of TELLURIC ACID.

By the electrolysis of sulphates a class of salts known as persulphates $M_2S_2O_8$ (where M is some monovalent element or group) is obtained; ^{the S} a possibility of analogous salts of tellurium $M_2Te_2O_8$ is great enough to tempt one to investigate this subject. To begin them we must have some soluble tellurate; -- consequently the first step in the prospective preparation of pertellurates, is to obtain a salt of telluric acid which would be sufficiently soluble so as not to present conditions adverse to successful electrolysis. It was supposed that such a salt would be normal potassium ^{or} ~~and~~ ammonium tellurate; these were to be made by dissolving telluric acid in an alkali.

FIRST METHOD:-- For the preparation of the telluric acid the following method was first tried;-- tellurium is oxidized to tellurium dioxide by means of nitric acid; the tellurium dioxide is fused with a mixture of two parts of potassium hydroxide, and two parts potassium chlorate,-- taken up with water. The potassium tellurate formed is precipitated as barium tellurate and filtered; the precipitate dried, mixed with its weight of water and one fourth its weight of concentrated sulphuric acid, and heated until action ceases. The barium tellurate and sulphuric acid interact to form telluric acid and barium sulphate, which are separated by filtration, and the telluric acid crystallized out of the filtrate. In the first trial of this method about 1.5 grams of tellurium were treated as above, fusion being affected in a porcelain crucible. The potassium hydroxide and chlorate attacked the porcelain crucible considerably; further, the

effervescence due to the giving off of gases caused frothing and running over of the contents of the crucible. The barium tellurate obtained when treated with amounts of water and sulphuric acid directed, gave a thick paste; after action had ceased this was diluted and filtered; some product, supposed to be telluric acid, was obtained by crystallization; this was regarded as only a preliminary test. The yield was very small. To obtain a better yield a second trial was made under slightly bettered conditions, namely:-- an iron crucible, more capacious than the porcelain crucible was employed; 2.5 to 3 grams of tellurium were taken; care was taken to avoid more than the prescribed amount of potassium hydroxide. The potassium chlorate and hydroxide attacked the iron appreciably leaving a brownish black oxide; When the mass was extracted with water, the filtrate was colorless, hence free from iron. The telluric acid was precipitated here with barium chloride as before and filtered; the precipitate was boiled with much water, and filtered through a hot water funnel for recrystallization; however, the precipitate could not be got to go into solution completely; in fact, the large amounts of the clear filtrate gave but an inconsiderable amount of residue on evaporation. The difficulty with which the barium tellurate went into solution, indicated that, either the reference ^{books} give a misleading impression of the solubility of barium tellurate, or that the product obtained under these conditions is not the normal tellurate; no quantitative estimations could be found. Without purification by recrystallization, the product, so insoluble in hot water, yielded telluric acid on treating with sulphuric acid and

water, filtering and recrystallizing out of the filtrate.

Clearly, however, this method is not very advantageous because of the small yield, difficulties encountered, and probable impurity of a product, -- so nothing further was attempted with this method.

SECOND METHOD:-- Before trying this method again, it was deemed expedient to attempt to prepare telluric acid by another method which, being simpler, promised less complications; this method is as follows:-- Tellurium dioxide is dissolved in nitric acid, lead dioxide added, and the whole boiled, then filtered; lead precipitated with sulphuric acid and filtered; the filtrate evaporated to dryness at 100°C , leaving a residue of telluric acid crystals, $\text{H}_2\text{TeO}_6 \cdot 4\text{H}_2\text{O}$. The first attempt at preparing telluric acid by this method seemed propitious, as the first portions crystallizing out consisted of beautiful crystals, with no sign of admixture; they dissolved in water comparatively easily, out of which solution a precipitate was obtained with barium chloride (sulphuric acid having been carefully washed out by means of alcohol and ether); dissolved readily in potassium hydroxide solution; further, a water solution gave liberation of iodine with ^{potassium}~~potassium~~ iodide and hydrochloric acid, and gave a black precipitate of tellurium with sulphuric acid. The other portions on crystallizing gave no such product, but one which contained much lead (as sulphate) and tellurium in a lower state of oxidation was found in the residue after washing with alcohol and ~~ether~~ ether. It was afterwards found that evaporating down ^{the} mixture of alcohol and ether used to wash the product as indicated above, gave well formed crystals which, on making the usual tests, proved to be telluric acid. In this experiment 2.55 grams of crude tellurium

7 grams lead dioxide then added; and finally a great excess of sulphuric acid to ^{re}precipitate all of the lead. It was thought that the great excess of sulphuric acid used was the hinderance to complete success in this experiment; it was therefore tried again using the following amounts of substance and reagents:-- 5.04 grams powdered tellurium were oxidized to tellurium dioxide with nitric acid, dissolved in ~~an~~ small a quantity as possible of dilute nitric acid; then 12.37 grams lead dioxide were added, and the whole boiled until a clear solution was obtained; this was evaporated down to three fourths its bulk to get rid of some excess of nitric acid; as this evaporation continued a white substance was precipitated; this substance was easily soluble in water, gave a precipitate with sulphuric acid, a malleable bead on char coal and a precipitate of tellurium with sulphur dioxide, and a white precipitate with barium chloride, showing the presence of lead nitrate and telluric acid. ^{These tests} does not indicate the absence of other tellurium compounds. After having decanted from this precipitate, and cooled the liquid, a calculated amount of sulphuric acid, just sufficient to ^{re}precipitate all the lead was added;-- filtered and evaporated to dryness on a water bath. The product here was not what was expected, neither as nicely crystalline as was the one obtained in the trial of this method, nor was the yield near the theoretical;-- it was shown to contain much ~~lead~~ lead sulphate; on boiling with water and filtering, and evaporating the filtrate on a water bath, telluric acid was obtained; this was recognized by its crystalline form, and the tests given by its aqueous solution. The portion not dissolving in hot water was found to contain, besides lead sulphate, unchanged tellurium dioxide or some salt of it, as it gave tests for tellurium, but not for

The ^{tel}luric acid obtained was ^{dis}olved in a small amount ~~in a small~~ amount of distilled water, filtered, and recrystallized^l: here a very small residue, insoluble in water was obtained; this residue was so slight that it could not be distinguished on the filter~~ed~~ paper, hence no test could be made. The ~~tel~~luric acid as thus obtained consists of short, thick, colorless prisms; these prisms are easily soluble in water, and in potassium hydroxide, and slightly soluble when heated with strong ammonia water. From all these solutions, tellurium is precipitated by barium chloride as barium tellurate. With a few slight modifications, this second method could doubtless be made to give good yields of telluric acid; it has the advantage over the fusion method of being simpler; at all junctures of the X procedures there are no other salts present to complicate things, and especially, it avoids the presence of an excess of potassium hydrate, and the production of barium hydrate, and the unknown quantity barium tellurate. The second method could have been more accurately adjusted,

(1) As to the amount and strength of nitric acid most advantageous to ~~de~~ssolve the tellurium dioxide.

(2) The efficiency of the lead dioxide as an oxidizer of the tellurium dioxide;

(3) The conditions and relative amount of sulphuric acid for the lead precipitation.

The time available for the carrying out of this work had now expired, leaving the problem of the preparation of pertellurates^l at this preparation of telluric acid; although this latter point

could be further elucidated, the experiments made on it, certainly are such as to promise success if they could be repeated with the care, precautions, and modifications suggested by what has been done thus far.

During the process of preparing telluric acid, certain observations were made which, being of interest, will be stated here:

(1) The tellurate to be employed in making pertellurates is probably to be found in the potassium salt, as indicated in the slight solubility of telluric acid in ammonia as contrasted with the ease with which potassium hydroxide dissolves telluric acid.

(2) In the fusion method for the preparation of telluric acid, on attempting to crystallize barium tellurate, the surface of the liquid had big blotches of some substance or other floating on it, and the evaporating dish had an extremely tenaciously adhering layer on its inner surface; this is the usual behavior of difficulty soluble substances. This coating, after being scratched off and tested, proved to be barium tellurate. Beakers in which the solution of Barium tellurate stood for quite a while, also had this closely adhering coating. This indicates that the solubility of barium tellurate is less than previous statements would lead one to expect.

(2) Tellurium dioxide is much more soluble in dilute nitric acid than in the concentrated acid; in fact, in the latter, it is hardly appreciably soluble. What dilution is most effective was not determined.

(3) In both cases where the solution of tellurium dioxide in nitric acid was treated with lead dioxide, the amount of lead

dioxide was many times more than that required theoretically; however, the solution was boiled until it became clear. Further, in the previous pages it has been shown that with the precipitated lead sulphate there is always some tellurium compound other than telluric acid or a tellurate. This indicates an insufficiency of lead dioxide; doubtless it would be more rational, and conducive to a better yield to add lead dioxide until some of it remained unchanged after continued boiling.

Had time permitted a repetition, this would have certainly been tried.

(4) As mentioned before, 95 % alcohol and dilute ether used to wash the product of telluric acid, dissolved considerable quantities of telluric acid. Reference books speak of telluric acid as, "almost, if not quite, insoluble in alcohol." Doubtless, it would be better to use absolute alcohol and anhydrous ether.

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As mentioned repeatedly, lack of time was, in great measure, a hinderance to obtaining satisfactory results; such pieces of information as have been culled from this labor, give only an indication as to the directions in which further study may be pursued.