The general properties of gaseous dispersoids and the application of this method to their statistical study are briefly discussed.

We wish to acknowledge the assistance in a portion of the work of Cpl. P. J. Olin, the friendly coöperation of the whole Dispersoid Section in which laboratory the work was done, but especially the constant inspiration and suggestion of its Chief, Major R. C. Tolman.

[Contribution from the Chemical Laboratory, University of Wisconsin.]

A CONTRIBUTION TO THE CHEMISTRY OF TELLURIUM SULFIDE.[1]

By Aaron M. Hageman.

Received December 2, 1918.

A careful study of any compounds which tellurium is able to form with sulfur is of special interest to the inorganic chemist from a twofold viewpoint. First, it may serve more definitely to establish the true chemical character of tellurium, and second, it may furnish positive information regarding the possible complexity of that element whose atomic weight has already been more exhaustively studied than any other element known to chemists.

Although Berzelius,[2] in 1826, reported that two sulfides of tellurium could be prepared by passing hydrogen sulfide gas into acidified aqueous solutions of tetravalent and hexavalent tellurium, respectively, Becker[3] showed that the resulting precipitates were not true chemical compounds since a large part of the sulfur could be extracted with carbon disulfide. The existence of true sulfides of tellurium was therefore questioned.

However, Becker was unable to remove completely all the sulfur from these precipitates by carbon disulfide. He states that a minimum of 3.69% of sulfur is always retained by the tellurium. This phenomenon has attracted the attention of chemists who have seen a clue to the suspected complexity of tellurium, since the unidentified hypothetical impurity in tellurium must have a higher atomic weight than tellurium, and consequently ought to form a more stable sulfide.

Such has been the assumption of Brauner,[4] of Gutbier and Flury,[5] and of others.

However, none of these workers has been able to obtain positive evidence of the existence of any compound between these two elements, while

---

[1] Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] *Pogg. Ann.*, **8**, 411 (1826).

[3] *Ann.*, **180**, 257 (1876).

[4] *Monats.*, **1889**, p. 456.

[5] *Z. anorg. Chem.*, **32**, 272 (1902).

all attempts to remove completely the sulfur from the precipitate have failed, though Gutbier and Flury have succeeded in reducing the amount of sulfur retained by the tellurium from 3.69% as reported by Becker to 1.19%.

Snelling,[1] more recently, has reported the isolation of an unstable compound of tellurium and sulfur having the formula TeS. He obtained this compound by passing hydrogen sulfide into an acid solution of tellurous acid of known strength at 0° C. After passing in the gas for twenty minutes, 30 cc. of carbon disulfide which had also been cooled to 0° C. was added and allowed to stand in contact with the precipitate for twenty minutes. The undissolved portion was collected on a filter and analyzed. His analysis showed tellurium and sulfur approximately in the ratio required by the compound TeS. Consequently he has stated that at the moment of precipitation one-half of the sulfur is chemically combined with the tellurium as TeS while an equal amount of sulfur exists in the precipitate as free sulfur. He further states that the compound TeS is unstable, decomposing at 0° C. in about four hours, or instantly if heated.

The work about to be described was undertaken in the hope of throwing some light upon the chemical condition of this small amount of sulfur which resists the action of carbon disulfide, and to investigate further any true chemical union which may exist between tetravalent tellurium and sulfur. The latter problem was attacked by first carefully repeating Snelling's[2] experiments in aqueous solution and then carrying out the precipitation of tellurium sulfide in non-aqueous solutions in order to determine whether the medium had any effect upon the composition and stability of the precipitate produced.

Materials.

Tellurous Acid.—Crude tellurium containing, as its principal impurities, small amounts of copper and selenium, was oxidized with aqua regia. The tellurium dioxide thus obtained was freed from nitric acid by gentle ignition, dissolved in concentrated hydrochloric acid, its solution diluted with an equal volume of water, and filtered. From this solution selenium and tellurium were precipitated by sulfur dioxide. After washing with water until free from chlorides, they were fused with KCN at a dull red heat with the formation of potassium selenocyanate and potassium telluride. The fusion product was dissolved in hot water and the tellurium precipitated by means of a current of air, the selenium remaining in solution. This gave very pure tellurium.

This tellurium was dissolved in nitric acid and crystallized twice from dilute nitric acid as the basic nitrate. This was ignited and fused to the dioxide, which, on cooling, crystallized in long, pale yellow crystals. On

---

[1] THIS JOURNAL, 34, 802 (1912).

[2] *Loc. cit.*

grinding, a white powder resulted which yielded, upon analysis, by the method of Lenher and Homberger,[1] 80.06% Te. Calculated 79.99%.[2] Tellurium dioxide was converted into tellurous acid by dissolving in hydrochloric acid and diluting the solution with water to the strength desired.

Hydrogen Sulfide.—This gas was made by the action of hydrochloric acid on sodium sulfide. It was washed with sodium sulfide solution and dried with calcium chloride before being used.

Carbon Disulfide.—The carbon disulfide used in the investigation was freed from sulfur by allowing it to stand over copper turnings for at least two weeks. It was then filtered away from any black particles of CuS which had separated and was distilled, only those portions being saved that came over between 44° C. and 48° C. This product left no residue of sulfur on spontaneous evaporation. It was purified as used, no attempts being made to keep the purified product.

Experimental.

A solution of tellurous acid containing 5% free hydrochloric acid was prepared and its exact tellurium content determined by the Lenher-Homberger[3] method.

Three samples were taken from this solution and placed in 300 cc. Erlenmeyer flasks. Concentrated hydrochloric acid was added till the samples contained 20%, 10% and 5% of hydrochloric acid. These solutions were placed in a thermostat carefully regulated at 25° C. and after they had attained that temperature, were treated with pure, dry hydrogen sulfide gas until precipitation was complete. In all cases, the hydrogen sulfide caused the immediate formation of a dark red voluminous precipitate which increased in volume until most of the tellurium had precipitated, when it began to coagulate in small granules. Simultaneously with this decrease in volume, the color gradually became darker until the tellurium had quantitatively precipitated as a black mass which settled to the bottom of the flasks. The precipitates were brought upon tared Gooch filters, washed with water containing hydrogen sulfide gas, followed by hot water then dried in a vacuum over phosphorus pentoxide at room temperature, and weighed. The results obtained follow:

	Gram.
Weight of Te and S required for TeS_2	0.3035
Weight of Te and S found (20% HCl)	0.3031
Weight of Te and S found (10% HCl)	0.3034
Weight of Te and S found (5% HCl)	0.3038

These results establish two definite facts: First, the precipitate obtained by the action of hydrogen sulfide gas on acid solutions of tetra-

---

[1] THIS JOURNAL, **30**, 378 (1908).

[2] The figure 127.6 has been used for the atomic weight of tellurium.

[3] *Loc. cit.*

valent tellurium contains tellurium and sulfur in the ratio 1 : 2; and second, that the concentration of acid has no effect upon this ratio.

The Extraction of Sulfur from the Precipitate.—A precipitate obtained as above from a sample of tellurous acid containing about 5 g. of Te was transferred to an extraction thimble and extracted in a Soxhlet extractor with carbon disulfide for twelve hours. Then it was freed of carbon disulfide by carefully washing with alcohol, followed by ether, and a sample was analyzed for its sulfur content. This was accomplished by treating with nitric acid followed by fuming nitric acid in the cold until oxidation was complete. The solution was evaporated to dryness, the residue taken up in 8% hydrochloric acid and the sulfur determined by the usual gravimetric method.

The results showed 1.36% and 1.34% sulfur retained by the tellurium, in fair agreement with the results obtained by Gutbier and Flury.[1] By a longer extraction with carbon disulfide these investigators were able to reduce this figure to 1.19%. The experiment shows, however, that a carbon disulfide extraction of comparatively short duration will remove readily all but 1.35% of the sulfur.

Since, then, a small part of the sulfur does not dissolve in carbon disulfide, we may assume three possibilities regarding the chemical condition of this small percentage of sulfur. It may exist in the precipitate in chemical combination with the tellurium or, perhaps, with some undiscovered element more metallic in nature. Such an element would undoubtedly form a sulfide which would completely resist the action of carbon disulfide. Then, again, this sulfur may exist as a form of elementary sulfur that is insoluble in carbon disulfide, though no one appears to have considered this possibility.

To test the first two possibilities, the following experiment was carried out: A large sample of completely extracted material was treated in a large test-tube with 1 to 1 hydrochloric acid and water and gradually warmed. The test-tube was fitted with a one-holed rubber stopper and the gases which came off were directed against a filter paper saturated with a solution of lead acetate containing a large excess of sodium hydroxide. Not the faintest coloration which would indicate hydrogen sulfide could be obtained. The experiment was repeated, using stronger hydrochloric acid and also hydrobromic acid of various strengths, but with negative results. Although these experiments do not prove conclusively that no sulfide exists in the precipitate, it shows that no sulfide which either hydrochloric or hydrobromic acid is capable of decomposing exists in the precipitate.

Amorphous sulfur is known to chemists in one form which is soluble and one which is insoluble in carbon disulfide. The insoluble amorphous

---

[1] *Loc. cit.*

modification, frequently known as gamma sulfur, can be produced by decomposing sulfur monochloride with water or by the interaction of hydrogen sulfide and sulfur dioxide. It would not be surprising, therefore, if the latter variety of sulfur were formed here in the decomposition of the tellurium-sulfur precipitate.

The insoluble variety of sulfur may be converted into soluble sulfur by long boiling with alcohol or by subjecting it to a pressure of 8000 atmospheres. The latter method being impractical, the former was resorted to.

The conversion was attempted in the following manner: A large sample of tellurium sulfide was precipitated as usual and most of the sulfur extracted in a Soxhlet extractor with carbon disulfide. Then the carbon disulfide was removed carefully and the extraction continued with absolute alcohol. By this means the precipitate was subjected to the action of hot alcohol and, at the same time, sulfur was dissolved away as rapidly as it was converted to a soluble form. At the end of twenty-four hours of continued extraction, the alcohol had assumed a yellow color, indicating that some sulfur had been removed from the precipitate. On dilution with water an opalescence confirmed the presence of a small amount of sulfur. The alcohol in the flask was replaced with fresh alcohol and the extraction continued. At the end of the second day, the alcohol again became slightly opalescent upon dilution with water. This process was continued for nine days, the used alcohol being replaced with fresh alcohol each day. At the end of this period, since the alcohol showed no trace of opalescence upon dilution with water, a sample was removed and analyzed for sulfur. The analysis showed 0.95% and 0.96% of sulfur present in the precipitate. Consequently the extraction was continued for one month. Samples were again removed and the sulfur determined. 0.93% and 0.96% of sulfur still proved to be present in the precipitate.

From these results it is evident that this small amount of sulfur does not exist in the free state or, if so, in an extremely insoluble and inert form. The manner in which this sulfur exists chemically remains an unsolved problem.

The Non-Existence of TeS.—The work of Snelling[1] at 0° C. has been repeated in detail with only those changes found necessary to increase the accuracy of the results obtained. A sample representing 0.2020 g. of elementary tellurium was used. The solution was carefully cooled to 0° C. by means of an intimate mixture of pulverized ice and water. The hydrogen sulfide, after being freed from hydrochloric acid gas and dried, was passed through a long coil condenser similarly cooled. After passing the gas into the sample for twenty minutes, 60 cc. of purified carbon disulfide cooled to 0° was added. By a whirling motion, the precipitate was completely forced into the carbon disulfide which occupied the bot-

---

[1] *Loc. cit.*

tom of the flask in which the precipitation was made. After standing in the freezing mixture for 15 minutes, the carbon disulfide assumed a yellow color and the precipitate became black and granular. The contents of the flask was brought upon a tared, Gooch filter which had also been cooled to 0° C. The precipitate was washed with water and dried *in vacuo* over P_2O_5.

Te in sample, 0.2020 g.; required for TeS_2, 0.3035; required for TeS, 0.2527 g.; weights of Te and S found, 0.2540, 0.2537 and 0.2542 g.

These results were of special interest since the weights of tellurium and sulfur found were always slightly higher than the weights required for TeS and considerably lower than those required for TeS_2. A number of such determinations were made and all tended to show that a compound containing more sulfur than TeS was at first produced.

Assuming that TeS_2 might be produced at first, a series of experiments was carried out in which the time elapsing between the first introduction of hydrogen sulfide gas into the solution and the final removal of the precipitate from the carbon disulfide was reduced from thirty-five to ten minutes. These results seemed desirable since the rapid change in color taking place immediately after precipitation might indicate the gradual dissociation of the product first formed into its elements. Hydrogen sulfide was passed in for five minutes and the resulting precipitate extracted with carbon disulfide for five minutes.

The results obtained furnished further evidence that TeS was not formed primarily. However, it was difficult to obtain uniform results and it appeared that all the factors had not been taken into account. The two chief uncertainties were, whether the tellurium was completely precipitated in this length of time and whether the carbon disulfide was in contact with the precipitate a sufficient length of time to remove all free sulfur.

A qualitative test of the filtrate showed small amounts of tellurium still remaining in solution, indicating incomplete precipitation. In order to determine the exact amount of tellurium in each case the Gooch crucibles containing the completely dissociated precipitates were extracted with carbon disulfide until they failed to lose weight. Since all but 1.35% sulfur could be removed, the weight of tellurium in the precipitate was easily calculated.

The use of this method made it necessary to determine whether tellurium itself was entirely insoluble in carbon disulfide. A series of extractions of precipitated tellurium with carbon disulfide in a manner exactly similar to the extractions given the tellurium-sulfur precipitate proved this to be the case. Consequently a series of experiments was carried out using carbon disulfide as the extraction agent. The exact weight of tellurium precipitated in each case was calculated from the weight of the completely extracted precipitate. The precipitates were allowed to stand in contact with the precipitate for exactly five minutes. The results of the experiments are given in the following table:

Wt. of Te. G.	Required for TeS. G.	Required for TeS_2 G.	Wt. of TeS ppt. G.	S in Te·S ppt. %.
0.1956	0.2931	0.2447	0.2884	32.18
0.1968	0.2957	0.2462	0.2891	31.93
0.1990	0.2990	0.2490	0.2943	32.34

Beside explaining why it was impossible to obtain uniform results in the previous experiment, these results furnish more complete evidence that the original precipitate could not have had the composition TeS.

In order to determine whether five minutes was sufficient time for all separated sulfur to be taken up by the carbon disulfide, the following experiment was carried out: Since hydrogen sulfide has no action on carbon disulfide it was found possible to have carbon disulfide present during the precipitation. This provided for a ten-minute extraction of the greater part of the precipitate. Results of such experiments follow:

Wt. of Te. G.	Required for TeS_2 G.	Required for TeS. G.	Wt. of TeS ppt. G.	S in Te·S ppt. %.
0.1858	0.2792	0.2334	0.2733	32.02
0.1879	0.2823	0.2351	0.2751	31.70
0.1932	0.2903	0.2417	0.2855	32.32

These results showed that five minutes was adequate for the removal of all free sulfur since these results were in close agreement with those obtained by the five-minute extractions. Moreover, they appear to warrant the conclusion that the first product produced by the action of hydrogen sulfide upon aqueous tellurous acid solutions is not a compound represented by the formula TeS but must be a compound containing a greater amount of sulfur.

One phase of the methods employed up to this point was not entirely satisfactory, namely, the use of a numerical constant in determining the actual weight of tellurium precipitated. An apparatus was consequently devised which permitted a gravimetric determination of the tellurium precipitated, thereby giving a direct instead of an indirect method for the determination.

The apparatus is shown in Fig. 1. The five-liter bottles B contained a supersaturated solution of sodium sulfide. Hydrogen sulfide was generated in this bottle by slowly dropping in 1 : 1 hydrochloric acid contained in the bottle A by means of a siphon and stopcock. It was purified from hydrochloric acid gas by passing through the sodium sulfide wash bottles D and E. After passing through the drying tower F, which contained calcium chloride, the gas was reduced to 0° C. by passing through the coil condenser G, which was completely surrounded by a cooling mixture. After cooling to 0° C. it entered the reaction chamber K, which consisted of a 500 cc. separatory funnel contained in an asbestos-covered iron box with the stem and stopcock protruding through the bottom of the box. The box was completely filled with a cooling mixture for one hour before and during use, thus insuring that all parts of the reaction chamber with which the precipitate might come in contact would be at 0° C. Precipitations were carried out in the presence of 100 cc. of carbon disulfide into which the precipitate was forced as formed by a constant whirling motion of the box during the introduction of hydrogen sulfide gas. After allowing the precipitate to stand in contact with the carbon disulfide the desired length of time, the carbon disulfide and the precipitate which had collected in it were drawn off through the stopcock on a large Gooch filter. The Gooch crucible also was jacketed and surrounded by a freezing mixture.

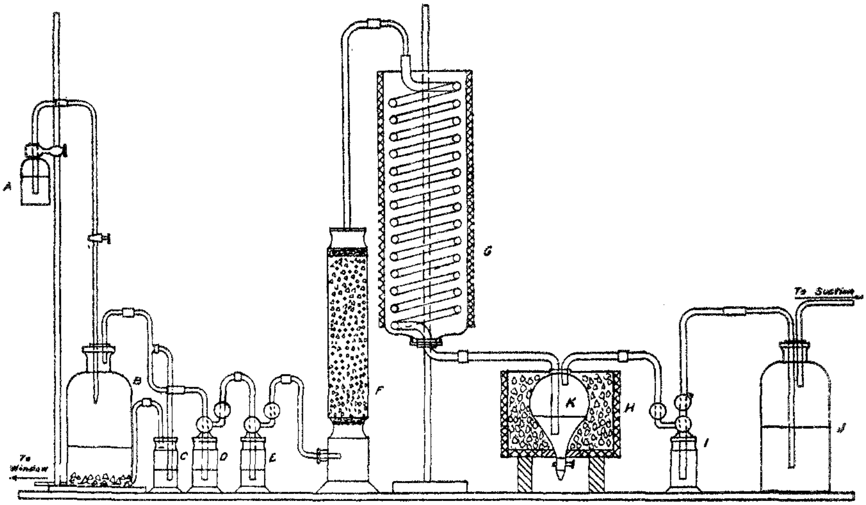

Fig. 1.

The advantages of this apparatus deserve mention. The gas was thoroughly cooled to 0° C. before entering the reaction chamber by passing through the long coil condenser surrounded by ice and water. The rate of flow was not great, owing to a fine jet between B and D, but was uniform. The reaction chamber was at 0° C. by being completely surrounded by the cooling mixture. After extraction, the carbon disulfide and that part of the precipitate that had actually been extracted could be drawn away. There was always a small amount of precipitate which remained in a fine suspension in the water above the carbon disulfide which was not extracted, but this never reached the filter. Moreover, the difficulty of filtering two immiscible liquids was overcome. The filter being jacketed with the freezing mixture insured its temperature to be at 0° C., so that at no stage during the operation was the precipitate subjected to any temperature other than 0° C.

Using this apparatus, a final series of experiments was carried out which served as a check on the results previously given. The details of procedure may be described as follows: A sample of tellurous acid, acidified with hydrochloric acid representing approximately 0.2500 g. of tellurium, was placed in this apparatus along with 100 cc. of carbon disulfide. Hydrogen sulfide was passed in for three minutes. During this time the reaction chamber was shaken to transfer the precipitate down into the carbon disulfide as formed. At the end of nine minutes, the carbon disulfide and precipitate contained in it were passed rapidly through a suction filter consisting of a Gooch crucible fitted with a small disc of filter paper. One minute was thus allowed for the filtration. The suction on the precipitate was continued for ten minutes to remove the last traces of carbon disulfide. The precipitate thus collected was removed from the paper, placed in a P_2O_5 desiccator, and evacuated overnight. A sample of the precipitate was then weighed carefully, oxidized with fuming nitric acid in the cold, and the nitric acid removed by careful evaporation at 80° C. The residue was taken up in ten per cent. hydrochloric acid and the exact tellurium content determined. A short table of results follows:

Wt. of Te found. G.	Required for TeS_2. G.	Required for TeS. G.	Wt. of TeS ppt. G.	S in Te-S ppt. %.
0.1824	0.2740	0.2282	0.2682	31.98
0.1650	0.2478	0.2063	0.2424	31.90
0.1168	0.1755	0.1461	0.1708	31.62

These results appear to be in fair agreement with those yielded by the previous method. Hence since the weights of tellurium and sulfur found far exceed the weights required for TeS, the only conclusion at which one can arrive is that TeS is not formed primarily by the action of hydrogen sulfide on tetravalent tellurium. This is in direct contrast to the results obtained by Snelling.[1]

A Study of the Conditions Necessary for the Existence of TeS_2.—It will be noted that all data thus far presented have shown that TeS does not exist. Moreover, the weights of tellurium and sulfur obtained have approximated the weights necessary for the compound TeS_2. Furthermore, the color of the precipitate first produced is invariably a red-brown. At 25° C. the duration of this color is short, a gray-black color rapidly developing accompanied by the coagulation of the precipitate into granules. At 0° C. the precipitate retains its red-brown color for a considerably longer period. In view of these facts and remembering that ten minutes after precipitation, carbon disulfide removes a definite amount of sulfur, it seems justifiable to assume that TeS_2 is at first produced,

---

[1] THIS JOURNAL, 34, 802 (1912).

but the affinity between sulfur and tellurium being very weak, dissociation takes place, and the chemical compound separates partially into its elements.

Since the affinity between elements of this character is usually increased at reduced temperatures, a preliminary experiment was carried out at about —40°. A bath of acetone was cooled to —40° C. by the addition of solid carbon dioxide. In it was placed a large test-tube containing 50 cc. of carbon disulfide and 20 cc. of tellurium chloride dissolved in concentrated hydrochloric acid. After the contents of the tube had assumed the temperature of the bath, hydrogen sulfide cooled to 0° was passed in. The red-brown precipitate produced was forced into the carbon disulfide as completely as possible. After standing at this temperature for one hour, the precipitate still remained a red-brown and the carbon disulfide still remained perfectly colorless, showing no indications of dissolved sulfur. A second tube containing 50 cc. of carbon disulfide was also cooled to —40° C. To it was added some previously prepared tellurium-sulfur precipitate which had been allowed to decompose at room temperature. This carbon disulfide immediately assumed a yellow color, indicating the presence of dissolved sulfur.

Although this experiment was only qualitative it indicated that tellurium and sulfur form a stable compound at this temperature, since it was shown that small amounts of sulfur impart a distinct yellow color to carbon disulfide. If this be true, it was of interest to determine the highest temperature at which this compound was still stable.

For this purpose determinations were carried out at —10°, —15°, and —20°, respectively. In each case the precipitate was gelatinous, thus differing from the precipitates obtained at 0°. In each experiment too, the extraction with carbon disulfide lasted one hour instead of 10 minutes, as previously. During this time, the precipitate remained a red-brown color, showed little tendency to coagulate, and was dissociated but slightly at —10° and —15°. At —20° complete stability apparently existed. The following tables show this to be the case:

Wt. of Te. G.	Required for TeS_2. G.	Required for TeS. G.	Wt. of Te-S ppt. G.
—10°.			
0.1488	0.2236	0.1861	0.2114
0.1165	0.1750	0.1457	0.1691
0.1450	0.2178	0.1814	0.2074
—15°.			
0.1594	0.2395	0.1995	0.2368
0.0882	0.1325	0.1104	0.1299
—20°.			
0.1406	0.2106	0.1759	0.2103
0.1102	0.1652	0.1376	0.1656
0.1132	0.1701	0.1416	0.1709

It would appear, therefore, that —20° is approximately the highest temperature at which the two elements, tellurium and sulfur, form a stable union.

The Action of Hydrogen Sulfide on Non-Aqueous Solutions of Certain Tellurium Compounds.—The preceding work was shown that a temperature of —20°, or below, is essential for the existence of a stable compound of tellurium and sulfur in aqueous solution. At higher temperatures the compound undergoes gradual dissociation into its elements. Although such a decomposition can scarcely be regarded as hydrolysis, the influence of the medium upon the formation and stability of this compound is of interest.

Three salts of tellurium were found to have a comparatively wide range of solubility in non-aqueous solvents, namely, tellurium tetrachloride, tellurium acid tartrate and tellurium acid citrate. Of these three, the tetrachloride showed the greatest range of solubility.

The method of testing the solubility of these compounds in non-aqueous solvents consisted in adding to about 25 cc. of the solvent approximately one gram of the finely divided tellurium compound. The mixture was thoroughly shaken and allowed to stand for at least one hour, after which any remaining solid was separated by filtration. The solvent was carefully evaporated from the filtrate, the residue taken up in dilute hydrochloric acid and a test made for tellurium with hydrazine hydrochloride. In some cases, hydrogen sulfide was passed in directly, the appearance of a red color proving to be a good qualitative test for tellurium. Assuming that the solubility might in some cases be attributed to small amounts of moisture present in the solvent, when a liquid was found to dissolve tellurium tetrachloride, the liquid was subjected to careful dehydration by shaking with KOH, P_2O_5 or to desiccation by standing over these dehydrating agents until free from moisture. The nature of the liquid determines the method employed. A test of the solubility was then repeated in the absolutely anhydrous reagent, thus insuring that water played no part.

Tellurium tetrachloride proved to be soluble in benzene, toluene, methyl alcohol, absolute ethyl alcohol, normal butyl alcohol, amyl alcohol, benzylic alcohol, xylol, chloroform, and ethyl acetate. In petroleum ether, kerosene, benzaldehyde, acetone, isopropyl bromide, and carbon tetrachloride it was but sparingly soluble while in carbon disulphide it was completely insoluble. Tellurium acid tartrate was found to be soluble in methyl alcohol, normal propiolic alcohol, ether, acetone, pyridine and acetonyl acetone. It was sparingly soluble in aceto-nitride, aldehyde-cyanhydrin, acetone-cyanhydrin, acetoacetic ester, iso-butyric alcohol, ethyl alcohol, iso-propyl alcohol, fusel oil, acetic anhydride, and benzylic alcohol. The solubility of tellurium acid citrate may be expressed as follows: Soluble in butyl alcohol, ether, absolute ethyl alcohol, ethyl acetate, and amyl acetate and slightly soluble in aniline, benzaldehyde and acetone

The combined solubilities of these three tellurium compounds offered a large number of mediums in which tellurium sulfide precipitations could be carried out. These solutions consequently furnished data which would either prove or disprove whether the medium in which the precipitation of tellurium sulfide is brought about is an influencing factor.

Hydrogen sulfide was passed into each solution of the tellurium compound in the organic liquid. At room temperatures the procedure consisted in precipitating the sulfide, washing it free from hydrogen sulfide with portions of the solvent, dissolving the precipitate in aqua regia, and making qualitative tests for tellurium and sulfur. In many cases, as with acetone, direct addition took place between the hydrogen sulfide and the solvent with the production of extremely obnoxious odors. No further work was carried on in such cases. In a large number of cases, especially where the tellurium compound in solution was the acid tartrate or acid citrate, colloidal solutions were obtained. This was overcome by passing in pure dry hydrogen chloride gas which usually coagulated the precipitate. When the hydrogen chloride gas reacted with the solvent this procedure could not be used.

A red-brown precipitate at the moment of precipitation was always produced which appeared identical with the one obtained in aqueous solutions. If allowed to stand at room temperature, the precipitate rapidly changed to black, indicating dissociation. The precipitate always gave distinct qualitative tests for tellurium and sulfur.

Since the deportment of the tellurium sulfide precipitated in these solutions was so similar to its conduct in aqueous solution, hydrogen sulfide gas at 0° C. was passed into each of these solutions after they had been cooled to 0° C. As it was practically impossible to make quantitative determinations of the amount of sulfur that could be extracted at this temperature in a given time, and since carbon disulfide is miscible with practically all of these solvents, use was made of the rate of change of color from red to black. It was difficult at first to determine just when this change in color had taken place, as it is a gradual one, but practice soon showed that the rate of change of color of the precipitate in these solutions very closely agreed with the rate of change in color in aqueous solutions.

A final part of the work consisted in reducing these solutions to —20° C. and passing in hydrogen sulfide which had also been reduced to a low temperature. The red-brown precipitate then remained unchanged in appearance for one hour, which was considered a sufficient length of time to indicate that no dissociation was taking place and that the precipitate was stable at that temperature. In some cases the solutions froze before this temperature could be obtained and in others so little of the tellurium compound remained in solution at that temperature that comparatively few solvents could be used. The solution of the tetrachloride in ether was very satisfactory.

All of the experiments made in non-aqueous solutions have shown that tetravalent tellurium is precipitated by hydrogen sulfide in these solutions exactly as in aqueous solutions. There is a tendency for the precipitate to separate in the colloidal form, but this may be prevented by the presence of dry hydrogen chloride. If the concentration of the tellurium solution is sufficient, this condition is not encountered. The precipitate undergoes dissociation into tellurium and sulfur at the same rate at 0° C. as in aqueous solution, while if the temperature is reduced to —20° C. a stable compound TeS_2 exists between tellurium and sulfur.

Final Conclusions.

The results of this investigation have established the following facts regarding the production and stability of a sulfide of tellurium:

1. The introduction of hydrogen sulfide into an aqueous tetravalent tellurium solution at room temperatures or below causes the immediate production of a red-brown precipitate represented by the formula TeS_2. The production of this compound is independent of the acid concentration.

2. At temperatures below —20° C. tellurium sulfide is a stable compound. At temperatures above —20° C., due to the weak affinity existing between these elements, dissociation takes place. At temperatures approximating —20° C. this dissociation is slow, while at higher temperatures dissociation takes place more rapidly. The degree of dissociation at any one time or temperature may be determined by the amount of sulfur that can be extracted with carbon disulfide.

3. Dissociation never continues to completion. The dissociated mass extracted with carbon disulfide always retains at least 0.95% of sulfur. This sulfur does not exist as a sulfide of tellurium that is decomposed by hydrochloric or hydrobromic acid of any strength nor does it exist as a variety of sulfur that is insoluble in carbon disulfide.

4. The compound TeS does not exist.

5. The production of the compound TeS_2 is independent of the medium in which it is carried out. The stability of this compound is solely a question of temperature.