

TABLE IV.

Concentration.	Resistance.
0.1	208.5
0.01	1024.0
0.001	6420.0

Again assuming that at all the concentrations employed the values of the migration ratios remain constant, the value of K was determined by the same formula as for aqueous solutions. As these values vary somewhat (see Table III), it seems probable that the migration ratios of Ag^+ and NO_3^- are not constant even for concentrations below 0.1 N . Taking $K = 0.074$, the value of v is 0.62.

Summary.

The electromotive forces of concentration cells containing solutions of silver nitrate in water at 25° are in accord with the Nernst formula for dilute solutions. Where higher concentrations were employed the calculated value of the electromotive force is greater than the observed because the migration ratio v is smaller at the higher concentrations. This affects two factors in the Nernst equation, *viz.*, $2v/u + v$ and $\log c_1/c_2$. The latter factor is affected because the ratio of the ion concentrations c_1/c_2 is determined from conductivity measurements and this method of determination is valid only when the migration velocity remains constant. The value of the migration ratio for dilute solutions calculated from the above results agrees closely with the values found by direct experiment.

For ethyl alcohol solutions the migration ratio apparently varies even at concentrations below 0.1 N . The value of v calculated from the most dilute solution was 0.62.

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A STUDY OF THE METALLIC TELLURITES.

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Since the early work of Berzelius¹ very little has been contributed to the chemistry of the tellurites. What work has been done has been largely incidental rather than a systematic study.

In our work the tellurites of potassium, sodium, silver, barium, magnesium, cadmium, nickel, cobalt, manganese, lead, and ammonium were studied. In addition to the normal tellurites, the di- and tetratellurites of the alkali metals were also studied. The normal and ditellurites of potassium and sodium were prepared by fusing tellurium dioxide with the calculated quantities of the alkali carbonates. The tetratellurites of

¹ *Jahresb.*, 1833; *Pogg. Ann.*, 28, 396 (1833); *Kongliga Svenska Vetenskaps Akademiens Handlingar*, 1833, 277; *Pogg. Ann.*, 32, 1-577 (1834); *Ann. chim. phys.*, [2] 58, 225 (1835).

potassium and sodium were obtained by the decomposition of the corresponding ditellurites with water. The tellurites of the other metals were prepared by precipitation from solutions of their salts (usually the chlorides) by means of sodium tellurite.

The tellurium dioxide used was prepared from elementary tellurium by solution in aqua regia and precipitation from the hydrochloric solution by sodium bisulfite. The impure tellurium thus obtained was fused with an excess of potassium cyanide, the fusion extracted with hot water, when a solution was obtained of potassium telluride, selenocyanate, and thiocyanate. The insoluble residue was invariably refused and treated again as before.

Air was then bubbled through the solution, precipitating the tellurium, while the seleno- and thiocyanates were unaffected. The tellurium, after filtering and washing; was dissolved in dilute nitric acid and recrystallized as the basic nitrate. The nitrate was finally heated strongly in a platinum crucible, and tellurium dioxide obtained. The dioxide was then fused, to insure complete removal of oxides of nitrogen. The product was perfectly white.

Methods of Analysis.

In the analysis of the tellurites studied, the following methods were used. Water was usually determined by loss of weight on heating. In some cases a temperature of 450° was necessary for the complete dehydration of the substance, but in such cases it was not necessary to continue the heating for more than 15 minutes. In the case of the alkaline tellurites, on account of the oxidation of these salts on heating in the air, it was also deemed advisable to weigh the water directly, after first absorbing in sulfuric acid.

The tellurium and basic element were then separated by one of the following general methods. (1) Volatilization of the tellurium oxide in a stream of hydrochloric acid gas. This method was used by Hutchins¹ in the analysis of a number of tellurates. (2) Precipitation of the tellurium in presence of the other metal, by means of sulfur dioxide and hydrazine hydrochloride,² and the subsequent determination of the base in the filtrate by one of the usual methods.

The first of these methods is not applicable to the tellurites of those metals whose chlorides are sensibly volatil. It was used in the analysis of the potassium, sodium, silver and lead salts. A weighed amount of the substance to be analyzed was placed in a porcelain boat and heated in a combustion tube in a current of hydrochloric acid gas. That part of the tube which contained the boat, was surrounded by a sheet-iron jacket, leaving an air space of about one inch between the jacket and the glass

¹ THIS JOURNAL, 27, 1157 (1905).

² Lenher and Homberger, *Ibid.*, 30, 387 (1908).

tube. The object of this arrangement was to make the heating more uniform. The tellurium was volatilized as $\text{TeO}_2 \cdot 2\text{HCl}$. The greater portion of the tellurium was condensed in the cooler part of the tube. The excess of hydrochloric acid, together with a little tellurium was absorbed in water.

The chloride remaining in the boat was weighed and calculated as metal. The tellurium sublimate in the glass tube was washed into a beaker, and the solution from the wash bottle was added. After concentrating this solution, the tellurium was precipitated by means of sulfur dioxide and hydrazine hydrochloride.

Potassium Tellurite.—The normal salt was prepared by fusing in a platinum crucible a mixture of equimolecular quantities of potassium carbonate and tellurium dioxide. The mixture fused quite readily, giving off carbon dioxide. In order to prevent oxidation to tellurate, the air in the crucible was displaced by a stream of carbon dioxide from a generator. On cooling, a white crystallin mass was obtained, which was deliquescent, and extremely soluble in water. The aqueous solution slowly deposited tellurous acid on exposure to air, and more readily when air was bubbled through the solution. On heating, however, the precipitate again dissolved, showing that at higher temperatures tellurous acid will displace carbonic acid.

A small amount of a strong solution of this substance was allowed to evaporate in a desiccator over sulfuric acid. Another vessel containing solid potassium hydroxide was placed within the desiccator to absorb the carbon dioxide of the air. The solution did not crystallize but on evaporation it gradually formed a thick syrup, which finally solidified. The product was a hard, transparent and homogeneous mass, having a waxy or resinous appearance without the slightest external indication of crystallization.

Two successive portions of this material were obtained, as it solidified from solution, and were analyzed, with the following results.

Calculated for $\text{K}_2\text{TeO}_3 \cdot 3\text{H}_2\text{O}$:	K, 25.43; Te, 41.44; H_2O , 17.54.
Found I:	K, 25.25; Te, 40.62; H_2O , 17.71.
Found II:	K, 25.82; Te, 40.83; H_2O , 17.09.

These results indicate that although potassium tellurite, when prepared as described, cannot be crystallized from an aqueous solution, it is nevertheless a definite compound, $\text{K}_2\text{TeO}_3 \cdot 3\text{H}_2\text{O}$. This compound was also prepared by treating tellurium dioxide with a solution of caustic potash, either cold or hot. The combination seems to take place only in the proportion of $2\text{KOH} : \text{TeO}_2$, so that if we have more than this proportion of tellurium dioxide, some will remain undissolved. Tellurium dioxide dissolves in a hot solution of potassium carbonate, although not so readily as in caustic potash.

Potassium Ditellurite.—Potassium ditellurite was prepared by fusing together 1 gram molecule of potassium carbonate and 2 gram molecules of tellurium dioxide. It fuses more readily than the normal salt, and on cooling appears as a white crystallin mass.

Potassium ditellurite is insoluble in cold water. It dissolves in boiling water, but on cooling, the solution decomposes, yielding the normal tellurite, which remains in solution, and the tetratellurite which is precipitated. The ditellurite decomposes slightly even at the boiling temperature, for complete solution of the substance was never obtained.

Potassium Tetratellurite.—Berzelius obtained the tetratellurite of potassium by boiling a solution of potassium carbonate with tellurium dioxide, filtering the boiling solution and allowing to cool slowly. The tetratellurite separated out in the form of small grains attached to the walls of the vessel. During the present work the tetratellurite was prepared by the decomposition of the ditellurite with water. Finely pulverized ditellurite was boiled with water for a short time. The hot solution was quickly filtered. White shining flakes separated out as the solution cooled. The compound was analyzed, and its composition found to conform to the formula $K_2Te_4O_9 \cdot 4H_2O$.

Calculated: K, 9.73; Te, 63.41; H_2O , 8.95.

Found I: K, 9.76; Te, 64.51; H_2O , 8.61.

Found II: K, 10.00; Te, 64.20; H_2O , 8.35.

This salt when boiled with its mother liquor dissolves, but separates again on cooling. Prolonged treatment with boiling water decomposes it, leaving tellurium dioxide as the final product. A quantity of the salt which had been washed repeatedly on the filter with boiling water left a white powder which contained 0.66% water, 0.47% potassium, and 78.52% tellurium. It was therefore nearly 99.0% tellurium dioxide. It is probable that the carbon dioxide of the air played a part in this decomposition.

Sodium Tellurites.—Normal sodium tellurite was prepared in a manner similar to that by which the corresponding potassium salt was obtained. The properties of these two salts are quite similar. Sodium tellurite is readily soluble in water. It is not deliquescent, and can be crystallized from solution in the form of broad, flat plates of hexagonal outline. It was also obtained in slender needles, grouped in radiating clusters. The evaporation of the solution was conducted in the same manner as with the potassium salt, namely, in a desiccator over sulfuric acid and solid caustic potash.

Unlike potassium tellurite, which contains three molecules of water, sodium tellurite contains five molecules of water of crystallization, $Na_2TeO_3 \cdot 5H_2O$.

Calculated: Na, 14.79; Te, 40.94; H₂O, 28.88.

Found I: Na, 14.72; Te, 40.33; H₂O, 28.89.

Found II: Na, 14.77; Te, 40.49; H₂O, 29.14.

An interesting, though not unusual, case of equilibrium was discovered in the system, sodium tellurite, water and alcohol. If to a strong solution of sodium tellurite we add about twice its volume of 95% alcohol, the two liquids do not mix. There is, however, a redistribution of the water between the alcohol and the tellurite. The alcoholic layer increases in volume by abstracting water from the tellurite solution, while the latter becomes more concentrated. Long standing and repeated shaking will not produce any further changes in this system. If, now, we add solid sodium tellurite, it will slowly dissolve, increasing the volume of the tellurite solution, and withdrawing water from the alcoholic layer. But if we add, instead, about five volumes of absolute alcohol, the water is almost completely withdrawn from the sodium tellurite, and the latter is precipitated. Potassium tellurite and alcohol behave similarly.

The sodium di- and tetratellurites are analogous to the corresponding potassium salts, both in their methods of preparation and in their properties. Both of these compounds fuse below a red heat, and on cooling form clear glasses. The ditellurite, like the corresponding potassium salt, can also be obtained crystalline by fusion. The tetratellurite, when prepared by decomposing sodium ditellurite with water, has the composition $\text{Na}_2\text{Te}_4\text{O}_9 \cdot 4\text{H}_2\text{O}$.

Calculated: Na, 5.97; Te, 66.07; H₂O, 9.32.

Found I: Na, 6.06; Te, 65.78; H₂O, 9.64.

Found II: Na, 5.78; Te, 66.35; H₂O, 9.43.

Ammonium Tellurite.—Berzelius attempted to prepare ammonium tellurite by dissolving tellurous acid in ammonia, and then adding ammonium chloride or alcohol. In both instances he obtained a flocculent precipitate, which was insoluble in water but dissolved readily in ammonia. He also obtained the same substance by warming a solution of ammonium carbonate with tellurous acid or tellurium tetrachloride, and adding ammonium chloride. On heating this compound, ammonia was evolved, and a residue of tellurium dioxide remained. The amount of this residue in one case was 83.1%; in another it was 83.87%, while the calculated amount of tellurium dioxide in the compound $(\text{NH}_4)_2\text{Te}_4\text{O}_9 \cdot 4\text{H}_2\text{O}$ is 83.7%. He therefore concluded that his precipitates were tetratellurites, exactly analogous in composition to the corresponding salts of potassium and sodium. Berzelius also evaporated to dryness, with the aid of gentle warming, a solution of tellurous acid in ammonia. He found the residue to be principally hydrated tellurium dioxide containing a little ammonia.

In the present work tellurium dioxide was dissolved in ammonium hydroxide (sp. gr. 0.91) by heating in sealed tubes for 10 hours at a tem-

perature of 95–100°. After cooling and filtering the solution was allowed to evaporate spontaneously. As the solution evaporated, small crystals were obtained in the form of short needles arranged in radiating groups, or clusters of thin transparent plates. On drying these became opaque. They dissolved readily in ammonia, but were insoluble in water.

They were analyzed as follows: A weighed amount of the residue was placed in a porcelain boat inside of a glass combustion tube. This tube was connected to an absorption apparatus containing a standard solution of sulfuric acid. While a slow current of dry air was drawn through the tube, the boat was heated, gently at first, increasing the temperature gradually to the full heat of the Bunsen burner. A considerable amount of moisture was condensed upon the cooler part of the tube. The residue in the boat was weighed as tellurium dioxide. The excess of acid in the absorption apparatus was then titrated with standard alkali, and the amount of ammonia estimated. The water was estimated by difference.

The following composition was found: ammonia 1.69%, tellurium dioxide 89.19%, and water 9.12%. This would correspond to the formula $\text{NH}_3 \cdot 5\text{TeO}_2 \cdot 5\text{H}_2\text{O}$ or $5\text{H}_2\text{TeO}_3 \cdot \text{NH}_3$. It is not believed that this is a definite compound. It is more likely that this is but one stage in the decomposition of ammonium tellurite to hydrated tellurium dioxide. The crystals obtained from the ammoniacal solution were probably a definite ammonium tellurite. This compound, however, is so unstable that it can exist only in solution, or when surrounded by the mother liquor, and when dried it spontaneously decomposes, even at the ordinary temperature.

Magnesium Tellurite.—This substance was obtained from a solution of magnesium chloride by adding a solution of sodium tellurite. It is a white flocculent precipitate, which is slightly soluble in water. On standing for a time in the mother liquor or in water, it becomes granular and heavy. The composition of the precipitate is not affected by varying the proportion of the two salts from which it is formed.

This tellurite was found to have the composition, $5\text{MgTeO}_3 \cdot 9\text{H}_2\text{O}$.

Calculated:	Mg, 10.84;	Te, 54.91;	H ₂ O, 13.94.
Found I:	Mg, 9.98;	Te, 55.29;	H ₂ O, 13.48.
Found II:	Mg, . . .	Te, 54.91;	H ₂ O, 13.62.
Found III:	Mg, 9.91;	Te, 55.39;	H ₂ O, 13.65.
Found IV:	Mg, 9.70;	Te, 55.10;	H ₂ O, 14.29.
Found V:	Mg, 9.93;	Te, 55.59;	H ₂ O, 13.36.

In the above table, numbers I, II, and III were precipitated from solutions containing excess of sodium tellurite, while IV and V were precipitated from solutions containing an excess of magnesium chloride.

Owing to the somewhat unusual ratio of the water to magnesium tellurite in this compound, a more careful study was made of this relation. A quantity of the dried precipitate, equivalent to 1 gram of an-

hydrous tellurite, was heated at various temperatures until the weight became constant. Then, from the total water content and the loss in weight at each temperature, it was possible to calculate the amount of water still retained.

Temp.	H ₂ O held by 1 g. MgTeO ₃ .	Temp.	H ₂ O held by 1 g. MgTeO ₃ .
20°	0.1545	260°	0.0758
100°	0.1360	300°	0.0250
130°	0.1170	330°	0.0130
175°	0.0965	360°	0.0080
200°	0.0860	400°	0.0050
220°	0.0838	450°	None

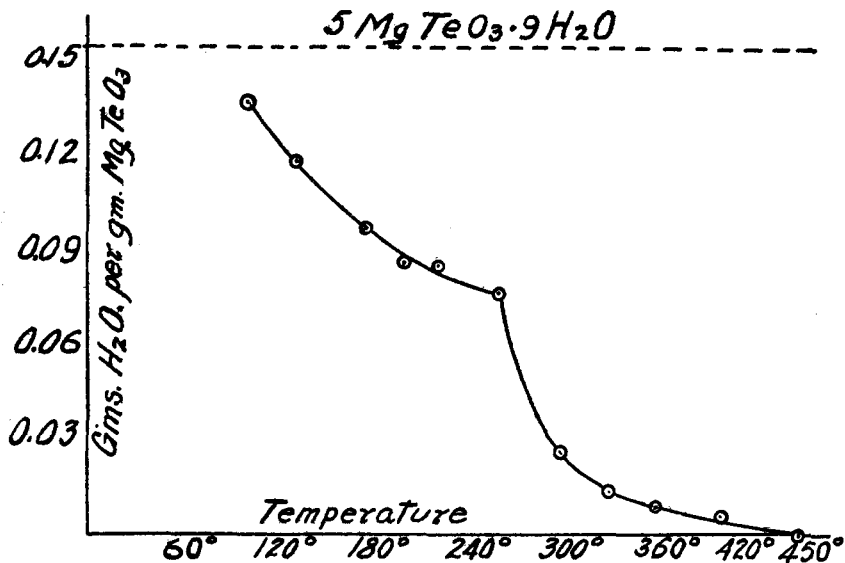


Fig. 1.

If these results are plotted in a curve it will be seen that at about 260° there is a sharp break in the curve, and that the amount of water retained at this temperature is very nearly one-half of the original amount, 0.1545 gram. Above this temperature there is a rapid falling off in the water content, until at 450° all of the water can be driven off in 15 minutes.

This experiment indicates that between 450° and ordinary temperature, there exist at least two definite hydrates of magnesium tellurite, namely, $5\text{MgTeO}_3 \cdot 9\text{H}_2\text{O}$, and $10\text{MgTeO}_3 \cdot 9\text{H}_2\text{O}$. It might also be noted that the composition at 100°, as calculated from the above results, is $2\text{MgTeO}_3 \cdot 3\text{H}_2\text{O}$ although this may have no special significance, since no data were obtained for temperatures below 100°. It is also quite evident that most of the water in this compound is quite firmly held.

Barium Tellurite.—To obtain this substance, a solution of sodium tellurite was added to a solution of barium chloride. A white flocculent precipitate was obtained, which was only slightly soluble in water. Attempts were made to obtain barium tellurite in crystallin form but were unsuccessful. Analysis of different samples showed a considerable variation in composition. Investigation showed that the precipitates always contained barium chloride, and sometimes in considerable quantities. This barium chloride could not be washed out completely by repeated and long-continued boiling with large quantities of water. Accordingly the precipitation was performed in dilute solutions, containing exactly equivalent quantities of the two salts. Even under these conditions the precipitates always contained small amounts of barium chloride which could not be washed out.

The analysis of this substance was carried out in the following way. Water was determined as usual. The chlorine was determined by precipitation with silver nitrate, from a nitric acid solution of the barium tellurite. After removing the excess of silver nitrate by adding hydrochloric acid, the barium was precipitated by means of ammonium sulfate. The filtrate from the barium sulfate was evaporated to dryness, and the residue treated repeatedly with hydrochloric acid to remove all of the nitric acid. Finally from this hydrochloric acid solution the tellurium was precipitated by sulfur dioxide and hydrazine hydrochloride. The method of volatilization in hydrochloric acid gas could not be used in this case, since all of the tellurium could not be driven off without raising the temperature so high that barium chloride would volatilize.

The proportion of barium to tellurium was greater than the normal salt should have. But in all cases the precipitates also contained chlorine in appreciable quantities. If the chlorine contained be calculated as barium chloride, and the tellurium as normal barium tellurite, the results agree with the analysis obtained. This is particularly evident in those samples which were precipitated in presence of excess of barium chloride.

Several samples were analyzed, in all of which the proportions of barium chloride, tellurite and water varied considerably. The following analyses are typical examples. The first sample was precipitated in presence of excess of barium chloride; the second one from equivalent quantities of this salt and sodium tellurite.

1. Calculated for $8 \text{ BaTeO}_3 \cdot 5 \text{ BaCl}_2 \cdot 4 \text{ H}_2\text{O}$: Ba, 49.50; Te, 28.29; Cl, 9.82; H_2O , 1.99.
Found: Ba, 48.68; Te, 29.23; Cl, 9.43; H_2O , 1.90.
2. Calculated for $20 \text{ BaTeO}_3 \cdot \frac{1}{2} \text{ BaCl}_2 \cdot 20 \text{ H}_2\text{O}$: Ba, 41.89; Te, 37.95; Cl, 0.53; H_2O , 5.35.
Found: Ba, 41.83; Te, 38.33; Cl, 0.53; H_2O , 5.07.

Cadmium Tellurite.—This salt was obtained as a white amorphous, insoluble precipitate, by the interaction of cadmium chloride and sodium tellurite.

In its analysis the method of volatilization could not be used for the separation of the tellurium, on account of the volatility of cadmium chloride. The tellurium was therefore first precipitated from a hydrochloric acid solution of the material by means of sulfur dioxide and hydrazine hydrochloride. In the filtrate from the tellurium, the cadmium was determined in one of two ways. (1) The solution was evaporated to dryness, the residue taken up in water, and the cadmium precipitated as carbonate by means of potassium carbonate, and weighed as oxide. (2) The solution was first neutralized with potassium hydroxide, and potassium cyanide was added until the precipitate first formed just dissolved. This solution was then electrolyzed, using a current density of 0.5 to 0.8 amperes per 100 sq. cm., with about 4 to 4.5 volts. After 5 hours the voltage was increased to 5 volts for an hour.

The composition found did not agree with the normal tellurite. The tellurium was always slightly high and the cadmium correspondingly low. The following gives the average composition found, together with the calculated results for $3\text{CdTeO}_3 \cdot 2\text{H}_2\text{O}$.

Calculated: Cd, 37.47; Te, 42.53; H_2O , 4.00.
Found: Cd, 36.09; Te, 44.20; H_2O , 3.67.

The regular discrepancies appearing in the analysis are explained by the fact that when tellurium is precipitated in the presence of cadmium, it carries down some of the cadmium with it. This is made quite evident from the following experiments.

I. Some tellurium which had been precipitated in the presence of cadmium, was dissolved in aqua regia, and the solution evaporated to dryness. The residue was then taken up in dilute hydrochloric acid and precipitated by means of hydrogen sulfide. This precipitate was digested for several hours in a warm place with yellow ammonium sulfide. The residue left by the ammonium sulfide was treated with hot concentrated hydrochloric acid and filtered. After nearly neutralizing the filtrate with potassium hydroxide, it was treated with hydrogen sulfide. A small amount of cadmium sulfide was obtained.

II. A weighed amount of pure tellurium dioxide was mixed with cadmium chloride (about 0.8 gram). After dissolving in hydrochloric acid, the tellurium was precipitated with sulfur dioxide and hydrazine hydrochloride. The following results were obtained.

Te found: 0.7037; calculated: 0.6929,
0.9476. 0.8754.

It will be noted that the apparent weight of the tellurium precipitated was in each case considerably greater than the calculated amount.

III. A determination of tellurium by means of sulfur dioxide and hydrazine hydrochloride was made in a weighed amount of pure tellurium

dioxide. The tellurium thus obtained was again dissolved and the determination repeated. The results were as follows:

Te found: 0.4045;	Te used: 0.4052,
0.4034.	0.4045.

IV. Exactly equivalent quantities of cadmium chloride and sodium tellurite, both in solution, were brought together, and the resulting precipitate filtered off. The clear filtrate was evaporated to a small bulk and treated with hydrogen sulfide. No precipitate was formed, showing that both cadmium and tellurium had been completely removed in the first precipitate. This precipitate, therefore, could have been nothing other than the normal tellurite.

Silver Tellurite.—When a solution of sodium tellurite is added to a solution of silver nitrate, a pale lemon-yellow, flocculent precipitate is formed. This precipitate remains pale yellow as long as the silver nitrate is in excess, but when sodium tellurite is added in excess the color of the precipitate quickly changes to white. On drying, both precipitates assume a buff color, and are almost indistinguishable from each other. On standing, however, the one which was precipitated in presence of an excess of silver nitrate begins to turn dark in color, and in the course of a week or two has changed completely to a dark bluish gray color. The other does not change, and has actually been kept for twenty months without undergoing any modification.

Nevertheless, both of these precipitates have the same composition, and when dried, both are anhydrous. In the following Table I and II were precipitated in presence of an excess of silver nitrate, while in III and IV the proportion was reversed.

Calculated for Ag_2TeO_3 :	Ag, 55.14; Te, 32.59.
Found I:	Ag, 55.09; Te, 32.96.
Found II:	Ag, 54.90; Te, 32.51.
Found III:	Ag, 54.89; Te, 32.52.
Found IV:	Ag, 55.25; Te, 32.52.

Silver tellurite can exist in still other forms. When heated to a temperature of 250° , it becomes deep blue or purple in color. This change takes place without any change in weight: On heating still higher, to 450° or 500° , it again changes to a pale yellow. In this last condition it can be cooled down to ordinary temperatures unchanged, provided it is not disturbed during the cooling. But if during this cooling, and while it is still quite hot, it is disturbed by compression with a glass rod, the mass immediately changes to the purple variety.

Again, when freshly precipitated silver tellurite is treated with ammonium hydroxide it dissolves immediately, and when the solution is allowed to evaporate spontaneously brownish yellow crystals deposit. These crystals contain neither ammonia nor water, and can be heated to 500°

or higher without any change in weight. On cooling, after being thus heated, these crystals again yield the ordinary pale yellow silver tellurite.

It thus appears that silver tellurite can exist in a number of different varieties. The freshly precipitated salt is soluble in acetic and tartaric acids, also in nitric and sulfuric acids. Hydrochloric acid decomposes it with the formation of silver chloride and tellurium tetrachloride. It is insoluble in water.

An attempt was made to obtain silver tellurite in crystallin form in the same way in which Hutchins crystallized some of the precipitated tellurates.¹ The method was to allow the precipitate to stand in contact with water containing minute quantities of free acids. This method, however, proved unsuccessful with the tellurites. It might be stated that the precipitated tellurites as a rule show very little or no tendency to pass into the crystallin state.

Nickel Tellurite.— $\text{NiTeO}_3 \cdot 2\text{H}_2\text{O}$ was obtained as a pale greenish yellow precipitate on adding a solution of sodium tellurite to a solution of nickel chloride. The precipitate was light and amorphous.

Calculated: Ni, 21.72; Te, 47.21; H_2O , 13.32.

Found: Ni, 21.40; Te, 47.96; H_2O , 13.62.

When heated, the light yellow-green tellurite loses water and turns to a light brown color.

Cobalt Tellurite.— $\text{CoTeO}_3 \cdot \text{H}_2\text{O}$ was obtained by precipitation from a solution of cobalt chloride as a dark, purple-blue insoluble substance. When heated to 300–400° it melts without change of color, losing water at the same time.

Calculated: Co, 23.36; Te, 50.52; H_2O , 7.12.

Found: Co, 23.39; Te, 50.30; H_2O , 7.79.

Manganese tellurite is a very unstable compound. When a solution of manganous chloride is added to a solution of sodium tellurite, there forms a voluminous white precipitate, which is faintly pink or flesh-colored. On standing, the color gradually changes to a deep chocolate-brown. The change takes place more rapidly when it is brought into direct contact with air. This change is due to oxidation of the manganese to the trivalent state. When the chocolate colored substance is treated with hydrochloric acid, a dark, greenish brown solution of manganic chloride is formed. This color is discharged by diluting the solution with water, or by boiling; in the latter case chlorine is evolved.

If the precipitation is carried out with solutions which have been previously thoroughly boiled to expel the air, the precipitate is perfectly white, and remains so as long as contact with air is avoided.

The extent of oxidation was determined by boiling the material with hydrochloric acid, distilling the chlorine into a solution of potassium

¹ THIS JOURNAL, 27, 1157 (1905).

iodide, and titrating the iodine with sodium thiosulfate. The tellurium was precipitated from the hydrochloric acid solution by sulfur dioxide and hydrazine hydrochloride. Finally the manganese in the filtrate from the tellurium was precipitated as manganese ammonium phosphate, ignited to pyrophosphate, and weighed. The water was estimated by difference.

The atomic ratio of manganese to tellurium was found to be 1 : 1, so that the precipitate first formed was undoubtedly normal manganous tellurite. The ratio of active oxygen to manganese, however, was less than would be required for complete oxidation of the manganese to the trivalent condition, and this ratio also varied in different samples. One sample of the freshly prepared precipitate was washed by decantation, and suspended in water, while air was bubbled through the mixture for a week. Analysis showed that only about 28% of the manganese was oxidized.

The freshly precipitated manganese tellurite seems to be more sensitive toward oxygen than after it has stood for some time. White manganese tellurite was prepared by bringing together under a layer of melted paraffin freshly boiled and air-free solutions of manganese chloride and sodium tellurite. The precipitate was allowed to stand unoxidized for a week, after which it was treated for two weeks with a current of air, as in the previous case. The color changed to brown. A determination of the active oxygen indicated that about 20% of the manganese had been oxidized.

Another sample of the precipitated manganese tellurite was dried, pulverized, and left in contact with air for three weeks. At the end of this time about 38% of the manganese was oxidized, and the powder had the following composition: $3\text{Mn}_2\text{O}_3 \cdot 10\text{MnO} \cdot 16\text{TeO}_2 \cdot 10\text{H}_2\text{O}$.

Calculated for $3\text{Mn}_2\text{O}_3 \cdot 10\text{MnO} \cdot 16\text{TeO}_2 \cdot 10\text{H}_2\text{O}$:

Mn, 22.46; Te, 52.11; Active O, 1.22; H_2O , 4.59.

Found: Mn, 22.26; Te, 52.39; Active O, 1.24; H_2O , 4.49.

It is probable that complete oxidation of the manganese would be accomplished in time.

Lead Tellurite.—This compound was prepared by precipitation from a solution of lead nitrate. It forms as a white flocculent precipitate.

Calculated for $3\text{PbTeO}_3 \cdot 2\text{H}_2\text{O}$: Pb, 52.45; Te, 32.35; H_2O , 3.04.

Found: Pb, 52.09; Te, 32.26; H_2O , 3.20.

Oxidation of the Tellurites.—Shortly after the work on the tellurites was undertaken it was discovered that many of the tellurites oxidize when heated in the air under certain conditions. This fact seemed to have escaped the notice of Berzelius and other investigators, as no mention of it has been found in the literature. On account of this oxidation it is not possible to prepare the tellurites, free from tellurates, by the fusion

of tellurium dioxide with carbonates, as suggested by Berzelius, without first excluding air from the mixture. Hence, in the preparation of the alkaline tellurites, the fusion was carried out in an atmosphere of carbon dioxide, as already mentioned. Tellurites which are thus prepared are completely free from tellurates, but when the precaution to exclude air during the fusion is neglected, the product always is contaminated to a greater or less extent with tellurate.

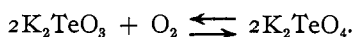
In order to ascertain how far it is possible to oxidize the tellurites by heating in the air, the following experiment was carried out. Some potassium tellurite was finely pulverized, and then spread out in a thin layer on the bottom of a crucible. The crucible was partly immersed in a bath of melted lead whose temperature was kept at 460–470°. At intervals, portions of the material were removed for analysis. The proportion of tellurate was determined by boiling the mixture with hydrochloric acid, distilling the chlorine into a solution of potassium iodide, and titrating the iodine with sodium thiosulfate. The results are given in the following table, which gives the time of heating together with the corresponding amount of potassium tellurate.

Time (in hours).	K ₂ TeO ₄ (%).
10	26.88
20	52.88
30	80.99
38	94.49
43	97.86
57	99.47

The final product was next analyzed with the following results:

	Found.	K ₂ TeO ₄ .
K	29.11	29.01
Te	47.02	47.28

In this connection it is interesting to note that when potassium tellurate is heated to redness, it loses oxygen and is reduced to tellurite. Thus between 450° and red heat we have a reversal of the reaction.



Normal sodium tellurite behaves in a manner exactly similar to the potassium tellurite.

Time of heating (in hours).	Na ₂ TeO ₄ (%).
10	35.09
20	64.77
30	90.76
40	99.09
50	99.49

While the normal alkaline tellurites can be oxidized quite readily, the ditellurites behave somewhat differently. Potassium ditellurite can be oxidized, but the reaction proceeds much more slowly than in the

case of the normal salt. Furthermore, only one-half of the tellurium seems to be oxidizable to the higher state of oxidation. The experiment was carried out in the same way as with the normal tellurites except that the temperature was kept at 440–450°, on account of the lower melting point of the ditellurite. The results obtained were as follows:

Time of heating (in hours).	Active O (%).
19	1.18
46	2.00
89	2.81
156	3.28
221	3.54

The content of active oxygen required by the formula $K_2OTeO_3 \cdot TeO_2$ is 3.72%, and that for complete conversion to ditellurate would be 7.18%. It will be seen that the content of active oxygen seems to approach the former figure as a limit.

The ditellurite of potassium is white, but when it is oxidized as above, it is slightly brown in color. This brown product belongs to a class of compounds which are formed as intermediate products in the oxidation of tellurium dioxide to trioxide, by means of alkaline oxidizing agents. These compounds Berzelius thought to be tetratellurates, but they have been shown by the work of Lenher and Potter¹ to have a more complex, as well as variable composition. Their composition might be represented by the general formula $m(K_2O) \cdot n(TeO_3) \cdot p(TeO_2)$, in which m , n , and p may be all different or all alike. These substances have been obtained by fusing tellurium dioxide with potassium nitrate or chlorate, and also synthetically by heating the dioxide with potassium tellurate. In the oxidation of the ditellurite of potassium to $K_2OTeO_3 \cdot TeO_2$, as described above, we are approaching the same class of compound from another direction. In this case, however, the composition is simpler and more definite.

Sodium ditellurite was also heated in the same way as the corresponding potassium salt, but after five days of heating it showed only a slight trace of oxidation. Neither the tetratellurites nor pure tellurium dioxide show any oxidation under similar treatment. It is therefore evident that with a higher content of tellurium dioxide the power of the tellurites to take up oxygen from the air decreases.

The normal tellurites of most of the other metals, with the exception of silver, can also be oxidized, but the rate of oxidation is very much lower than in the case of the normal tellurites of the alkali metals.

It has been stated, in describing the methods of analysis, that water was usually determined by loss of weight on heating. In view of the fact that the tellurites take up oxygen on heating, it would seem that this

¹ THIS JOURNAL, 31, 24 (1909).

method of determining water would give low results. But, excepting the normal alkaline tellurites, the oxidation is so slow that the error arising from this source would be imperceptible. Thus when anhydrous magnesium tellurite is heated to 450° for 15 hours, the gain in weight due to oxidation is only 0.25%, and in 77 hours it is only 1.5%. Again, nickel tellurite after being heated at 450° for 70 hours, contained only 0.46% of active oxygen. In contrast with these long periods of heating, the length of time necessary to drive off all the water, is only 15 minutes.

Summary.

1. The tellurites of the alkaline metals can be prepared by fusing together tellurium dioxide and a metallic oxide, hydroxide or carbonate. Since, however, tellurous acid forms salts of different types, namely the mono-, di-, and tetratellurites, the starting material must be used in definite proportions in order to obtain a tellurite of definite composition. The tellurites of the heavier metals are best prepared by double decomposition.

2. The alkaline tellurites are soluble, the alkaline earth tellurites are slightly soluble, and those of the heavy metals are insoluble.

3. As a class, the tellurites are unstable compounds. Tellurous acid is easily displaced at ordinary temperatures in presence of moisture, by carbon dioxide.

4. The tellurites can be oxidized by heating in the air at a temperature of $440-470^{\circ}$. This oxidation is fairly rapid in the case of the normal alkaline tellurites.

5. The tellurites of most of the metals other than potassium and sodium, as well as the ditellurites of the alkali metals, oxidize when heated much more slowly than the normal alkaline tellurites.

6. In potassium ditellurite, only one-half of the tellurous acid is oxidizable by this means, forming the compound $K_2O \cdot TeO_3 \cdot TeO_2$. The tetratellurites are not oxidizable by heating in the air at 450° , neither is pure tellurium dioxide.

7. Manganous tellurite will oxidize on contact with the air at the ordinary temperature, but in this case the manganese is oxidized, passing to the trivalent state.

8. Ammonium tellurite probably exists in solution, and also in the solid state when surrounded by a saturated solution of tellurous acid in ammonia, but otherwise decomposes spontaneously at the ordinary temperature, forming hydrated tellurium dioxide.

9. Silver tellurite can be obtained in a number of different varieties. When precipitated in presence of an excess of sodium tellurite, it is white, but when silver nitrate is in excess, the precipitate is of a pale yellow color. This second form in the course of a few days turns to a bluish gray powder, while the first is stable. At 250° both turn to a deep purp-

lish blue color. Still another variety can be obtained, by crystallizing from an ammoniacal solution, as a deep brownish yellow substance. All of these forms are anhydrous.

10. The precipitated tellurites are all flocculent and amorphous, and with the exception of the magnesium salt, show practically no tendency to become crystallin.

11. These precipitates are very apt to occlude other salts as impurities, which are very difficult to remove. This tendency is most marked in the barium salt, which will occlude large quantities of barium chloride. In the case of lead tellurite, which was precipitated from a solution of lead nitrate, the precipitate contained nitrates, but these were not so difficult to remove as the chlorides.

12. With the exception of the silver salt, these precipitates are all definit hydrates, which do not readily give up their water.

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THE VOLUMETRIC DETERMINATION OF GOLD.

BY VICTOR LENHER.

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It has been shown¹ that sulfurous acid is capable of reducing auric chloride to aurous in the presence of certain other salts. Through the agency of this reagent it is possible to estimate gold volumetrically easily and accurately.

In the following work a sulfurous acid solution was prepared by evolving sulfur dioxide from sodium acid sulfite by means of hydrochloric acid and, after washing the gas, conducting it into repeatedly distilled water. The strength of the sulfurous acid necessarily varied from time to time, due to its gradual oxidation. Its strength varied from 0.005 gram Au to 0.002 gram Au per cubic centimeter. Sulfurous acid solution requires frequent standardization, owing to its ability to slowly oxidize by absorbing oxygen from the air in the container and pass over into sulfuric acid. After a large amount of experimentation under widely differing conditions the idea of using a permanganate solution as a convenient standardizing solution was abandoned. Working under the most favorable conditions, it has not been found possible to obtain results having an error lower than 1% between permanganate and sulfurous acid.

The most reliable method of standardizing sulfurous acid is through the agency of iodine. It is entirely immaterial for the methods to be described whether the sulfurous acid solution is standardized on a known weight of iodine in potassium iodide or whether solid potassium iodide is dissolved in water acidulated with sulfuric or hydrochloric acid and a

¹ THIS JOURNAL, 35, 546 (1913).