

SEPARATION OF STRONTIUM FROM CALCIUM.

SrCl ₂ · 6H ₂ O present. Gram.	Calcium chloride present. Gram.	Sr present.	Sr found.	Cl ₂ present.	Cl ₂ found.	Volts.	Ampere. N D ₂₅ .	Time.	
								Hrs.	Min.
0.0635	0.0500	0.0209	0.0219	0.0169	0.0180	2.30	0.022	1	40
0.0630	0.0500	0.0207	0.0215	0.0168	0.0172	2.30	0.022	1	30
0.0703	0.0500	0.0231	0.0187	0.0190	2.30	0.020	1	45
0.0622	0.0500	0.0204	0.0165	0.0170	2.30	0.021	1	30

The analysis of a mixture of barium, strontium and calcium chlorides was then attempted, with the idea of separating first the barium from the strontium and calcium, inserting a fresh anode, and afterward separating the strontium from the calcium in the mixture that remained. On closing the circuit it was found that the "break point" was much lower than was expected from the separate behavior of each salt. Moreover, on maintaining the voltage at 0.03 volt above the decomposition potential as determined and allowing the current to pass until it was estimated that all the barium chloride had been decomposed, there was no evidence of a change in the decomposition potential corresponding to the change from the barium, strontium, calcium to a strontium calcium mixture, similar to that observed, for instance, in the separation of sodium from potassium. Because of this it was impossible to determine precisely just when all the barium chloride was decomposed and when it was necessary to interrupt the current and introduce a new anode to take up the chlorine ion of the strontium chloride.

Some separations were, however, attempted and approximate results obtained. Only the halogen content of each salt was determined. This was because all the barium amalgam had not passed into the outer cup at the point when a new anode had to be inserted for the decomposition of the strontium chloride; that is, a complete determination of the barium by titrating the barium hydroxide formed in the outer cup was impossible, since some of the barium amalgam was still retained in the inner cup. The determination of the halogen content was, however, sufficient to indicate the amount of barium combined with it.

It is only fair to state that in analyzing a mixture of barium, strontium and calcium chlorides the approximate results were obtained because of a previous knowledge of the proportions of each salt originally present, thus enabling us to interrupt the current at about the right time.

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A STUDY IN TELLURIDES.

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Introduction.

Sir Humphry Davy,¹ in the course of his investigations upon the alkali

¹ *Phil. Trans. Roy. Soc.*, 27, 16 (1810).

metals, prepared the tellurides of potassium and sodium by direct union of the elements, and by the reduction of mixtures of the alkali carbonates and tellurium oxide with carbon. He describes these substances as alloys of the metals with tellurium, stating that they dissolve in water to deep red solutions and when acidified yield a gas resembling hydrogen sulphide.

Berzelius prepared and identified hydrogen telluride. He obtained red solutions similar to those described by Davy, by absorbing hydrogen telluride in solutions of the fixed alkalies, and states that these solutions contain tellurides of the alkali metals analogous to the alkaline sulphides. He also states that hydrogen telluride precipitates insoluble tellurides of the heavy metals from solutions of metallic salts. No analyses of these tellurides are recorded.

Since the time of Berzelius comparatively little work has been done upon tellurides. The more important contributions to the knowledge of the subject are due to Oppenheim, Margottet, Fabre, Brauner and Hugot. Berthelot and Fabre,¹ in 1888, prepared hydrogen telluride, and the tellurides of the alkali metals both in solution and in the crystalline condition. No analyses of the salts were published.

Eleven years later Hugot² prepared the tellurides of sodium and potassium by the action of tellurium upon the alkali ammoniums in liquid ammonia. They were analyzed and the formulas R_2Te and R_2Te_3 assigned to them.

The tellurides of the heavy metals have been prepared in the dry way only, either by direct union of the elements in an inert atmosphere, or by the reduction of the tellurides. Margottet prepared a number of these compounds, while Fabre repeated and made additions to his work in the course of a thermal study of them.

The alkali tellurides are very unstable, being immediately decomposed by air contact with the liberation of tellurium. This property makes it necessary that all work with their solutions be carried on in an atmosphere from which oxygen is excluded.

It is probable that the instability of these tellurides accounts for the lack of exact knowledge as to their composition and their reactions in the wet way.

Experimental.

The tellurium used in this work was obtained from the Baltimore Copper Rolling and Smelting Company, having been extracted from electrolytic slimes. It contained small quantities of copper, iron, antimony and selenium as its principal impurities.

It was purified by the following method: the crude tellurium was dissolved in *aqua regia* and reprecipitated as element from hydrochloric acid solution by addition of acid sodium sulphite. The precipitated tellurium was fused at a low red heat with

¹ *An. Ch. Ph.*, [6] 14, 104 (1888).

² *C. r.*, 129, 299 (1899).

potassium cyanide to remove antimony, the fusion was dissolved in hot water, and, after filtering, the tellurium precipitated by means of a current of air. The sulphur and selenium remained in solution. The tellurium so obtained was dissolved in nitric acid and crystallized twice from dilute nitric acid solution as the basic nitrate. The basic nitrate was ignited and fused to the dioxide, the dioxide dissolved in hydrochloric acid, and the element precipitated by the addition of acid sodium sulphite. The flocculent precipitate was washed, filtered and dried, and finally fused in an atmosphere of hydrogen.

The dioxide was pure white in color, and yielded, upon analysis, by the method¹ used throughout this work, 79.91 per cent. of tellurium. By calculation, Te in $\text{TeO}_2 = 79.99$. The figure 127.6 has been used as the atomic weight of tellurium.

Alkaline tellurides have been prepared, by the direct union of the elements by the reduction of tellurites,² by the action of tellurium upon alkali amalgams,³ and by the action of hydrogen tellurides upon alkaline by hydroxides. There are no analyses of the bodies, as obtained from aqueous crystallization recorded. By the action of tellurium upon the alkali ammoniums in solutions of liquid ammonia, R_2Te and R_2Te_3 , are formed.⁴

Sodium Telluride.—Sodium and tellurium unite at about 250° with explosive violence. The reaction was carried out in an atmosphere of hydrogen in a Rose crucible placed inside of a large porcelain crucible and heated by the Bunsen flame. In the first experiment, equivalent proportions of tellurium and sodium were taken, in the second and third experiments, twice the quantity of sodium was used. After combination had taken place, the mixture was heated strongly to expel the excess of sodium and tellurium, the current of hydrogen being continued until the mass was cold. The telluride thus prepared is bronze-colored and shows a crystalline fracture. It is fairly stable in dry air.

In order to obtain a solution of this telluride out of air contact it was quickly transferred to the filtering vessel (A) of the apparatus shown in Fig. 1. This vessel had a perforated bottom carrying a paper filter. All air in the entire apparatus was displaced by hydrogen from the two generators, the gas leaving the apparatus through the mercury seal (E). The inlets and outlets for the gas were so arranged as to allow of perfect displacement of air by hydrogen. The hydrogen from the generators was passed through alkaline pyrogallic acid solution (D-D') to free it from any oxygen that it might contain.

When the apparatus was entirely freed of air, hot water from which dissolved air had been completely removed by boiling, was introduced into the funnel (B), from whence it was allowed to run into (A), where it dissolved the telluride from the filter. The solution, which was at first colored deep red, was run into the flask (G) by means of the three-way stop-cock (H) until it was light pink in color, when it was allowed to flow into the crystallizing flask (C).

The solution was evaporated to small bulk by applying the flame to (C). Hydrogen was bubbled slowly through the solution during the evaporation and passed off with the steam through the mercury seal at (E). From the concentrated solution so obtained, normal sodium telluride separates out upon standing a few hours as colorless, needle-like crystals often half an inch in length. These crystals are highly hydrated at the ordinary temperature and dissolve in their own water of crystallization at about forty degrees.

¹ Lenher and Homberger, *THIS JOURNAL*, 30, 378 (1908).

² Davy, *Phil. Trans. Roy. Soc.*, 27, 16 (1810).

³ Bineau, *Ann. chim. phys.* [2], 7, 232 (1863).

⁴ Berzelius, also Berthelot and Fabre, *Bull. soc. chim.* [2], 40, 99 (1883).

On account of the extreme instability and the highly hydrated condition of these crystals, they were analyzed and their composition established by determining their sodium-tellurium ratio.

The crystals were drained from the pink mother liquor by disconnecting the crystallizing flask from the filtering vessel and inverting it. It was left thus for several hours, after which a rapid stream of hydrogen was passed through the flask, the stopper removed and the crystals washed with cold water from a wash-bottle. When the crystals were perfectly white they were transferred into a beaker and the tellurium and sodium determined.

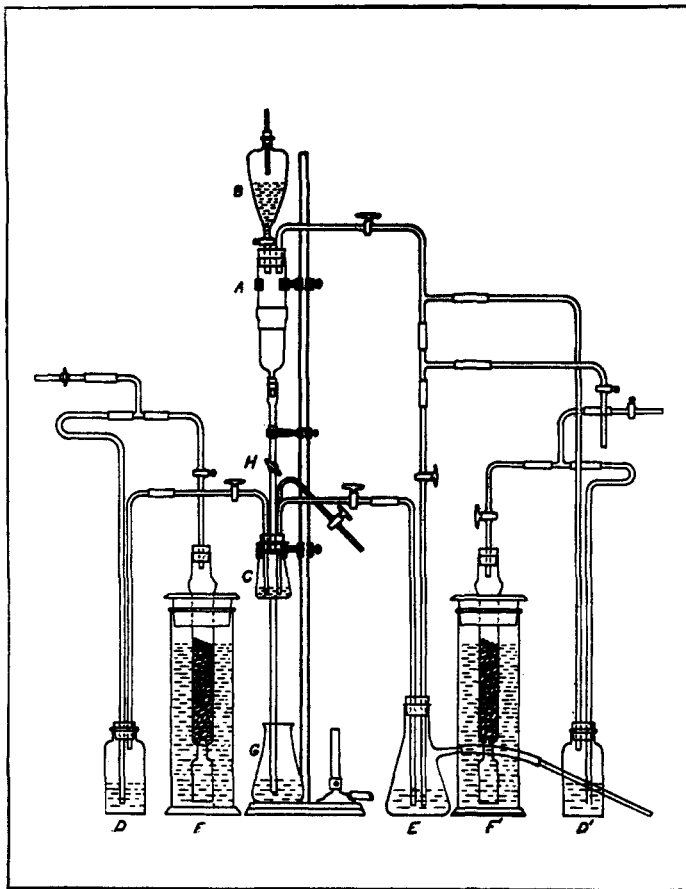


Fig. 1.

Analysis.—The determinations of tellurium were made according to the method of Lenher and Homberger¹ as modified to suit the case in hand. The solution of alkaline telluride obtained as above was boiled in a Jena beaker in contact with air until the telluride was decomposed as indicated by the disappearance of the red color. Hydrochloric acid was then added to the extent of ten per cent. of the solution, followed

¹ THIS JOURNAL, **30**, 387 (1908).

by 10 cc. of a saturated solution of sulphur dioxide, 10 cc. of a 15 per cent. solution of hydrazine hydrochloride, and finally, 25 cc. of sulphur dioxide solution. The whole was boiled for five minutes and the tellurium brought on a tared Gooch filter, washed with hot water and then with alcohol, dried at 100° – 105° and weighed. The tellurium so obtained appears as a granular precipitate which settles readily and is easily washed.

The solution from the tellurium determination was evaporated in a tared platinum dish with sulphuric acid, the residue ignited and weighed as sodium sulphate. In several cases the weight of the sulphate was checked by determining the SO_4 as barium sulphate.

The analyses gave for 127.6 parts of Te: I, 46.6; II, 46.15; III, 45.90 parts of Te. In Na_2Te , by calculation, Te : Na :: 127.6 : 46.1. The presence in the fusion of an excess of sodium does not affect the formation of normal telluride.

The red or permanganate color of alkaline telluride solutions has been ascribed¹ to the presence of polytellurides or solutions of tellurium in the normal telluride solution.

When sodium and tellurium are united in an atmosphere of hydrogen, and the tellurium is present in large excess over that which would give the normal telluride, a metallic-looking crystalline substance is formed which presents the appearance of fused tellurium. It is much more brittle than the element.

The substance, when treated with water in the absence of air, yields a dark red solution and a residue of tellurium. Upon evaporation, the solution yields crystals of the characteristic appearance of the crystals of normal telluride stained red by the dark-colored mother liquor. These crystals, on washing with water, become colorless and upon analysis show the composition of the normal telluride.

Found: Te : Na :: 127.6 : 45.4.

When a large excess of tellurium is used in the preparation of the telluride, the solution, upon evaporation and crystallization, yields not only Na_2Te crystals, but crystalline elementary tellurium as well.

The mother liquor upon analysis shows sodium and tellurium to be present in such a ratio as to indicate the existence in solution of a telluride having the composition Na_4Te_3 . It cannot be crystallized, and upon evaporation its solution yields colorless crystals of Na_2Te and crystalline tellurium.

Calculated for Na_4Te_3 , Te : Na :: 1 : 0.241.

Found, Te : Na :: 1 : 0.240.

That normal sodium telluride will not dissolve tellurium beyond the point represented by the formula Na_4Te_3 has been shown in the following manner: normal sodium telluride was prepared by the union of equivalent quantities of the elements, dissolved and filtered into the crystallizing flask which contained a large excess of moist, freshly precipitated tellurium. The solution was boiled with this tellurium for ten minutes and allowed to stand over night, when the undissolved tellurium, of which a large excess remained, settled, leaving the supernatant liquid clear. The sodium-tellurium ratio was determined in this clear solution and found to be 1 : 0.235.

It is of interest to note that the polytelluride Na_2Te_3 of Hugot,² formed from sodamide and tellurium in liquid ammonia, does not form in aqueous solution, and that normal sodium telluride has but a slight solvent action upon tellurium as compared with the solubility of sulphur in sodium sulphide.

Potassium Telluride.—Elementary tellurium and metallic potassium combine violently at 250° , the union being much more energetic than that of tellurium and sodium.

¹ Demarçay, *Bull. soc. chim.* [2], 40, 99 (1883).

² *C. r.*, 129, 299 (1899).

The telluride formed is of a dark, iridescent purple color, with a metallic luster when freshly broken. It is crystalline in structure and dissolves in water to a purple solution, which, upon evaporation, does not yield crystals but forms a thick, syrupy liquid. From this thick liquid alcohol precipitates small, indistinct crystals. The crystals, after washing several times by decantation with alcohol, were analyzed.

As in the case of normal sodium telluride, normal potassium telluride is formed whether the amount of potassium used in the preparation is equivalent to that required for the normal telluride or whether it is in large excess.

Analyses gave for 127.6 parts of tellurium: I, 76.91, and II, 80.00 parts of K. By calculation for K_2Te , $Te : K :: 127.6 : 78.3$.

Aqueous potassium telluride is even more unstable on exposure to air than the corresponding sodium telluride solution. It was never obtained colorless.

Tellurides of the Heavy Metals.—A number of metallic tellurides have been obtained by double decomposition between metallic salts and sodium salts and sodium telluride in aqueous solution. When normal sodium telluride is employed, normal tellurides either hydrated or anhydrous are formed. The dark red solution of the polytelluride Na_4Te_3 , on the other hand, precipitates metallic tellurides of corresponding composition.

In the preparation of the metallic tellurides the same apparatus was employed as in the preparation of the alkaline tellurides, modified somewhat to suit the changed conditions.

A wide-mouthed Erlenmeyer flask of 400 cc. capacity was substituted for the 100 cc. crystallizing flask shown in Fig. 1. This flask contained the freshly boiled solution of the metallic salt. Sodium telluride solution was prepared in the usual way and introduced into the precipitating flask.

The tellurides of the heavy metals are thrown down as heavy amorphous precipitates which are granular and settle readily.

The solutions of the metals employed must be of such character as would dissolve any metallic hydroxide formed by traces of sodium hydroxide in the telluride solution, but which, on the other hand, would be without action upon the telluride after it is precipitated. For the most part, solutions of metallic acetates, acid with acetic acid, were found to be best.

On account of the ready oxidation of some of the tellurides when in the moist condition, it was necessary to wash, filter and dry the precipitates out of air contact. This was accomplished as follows: the precipitated telluride was allowed to settle and the supernatant liquid, which always contained an excess of metallic salt, was transferred into a fil-

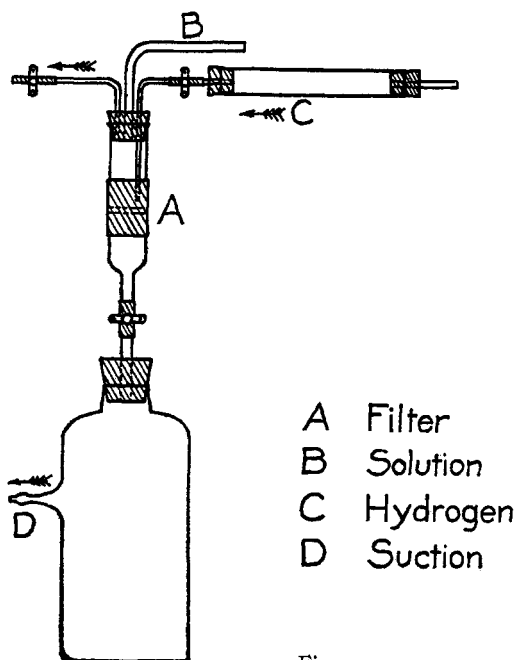


Fig. 2.

tering flask and the precipitate washed by decantation with hot, freshly boiled water until free from dissolved salt. The precipitate was then filtered by means of a Gooch filter in hydrogen, dried as far as possible by suction, and further dried by passing over it a current of hot hydrogen, after which it was transferred to a vacuum desiccator containing phosphorus pentoxide. When dry, the tellurides are stable in the air. Even with the great precautions taken in the preparation of the tellurides, it was in some cases almost impossible to prevent small quantities of tellurium from contaminating the precipitates.

The apparatus for filtering and drying in hydrogen is shown in detail in Fig. 2.

Telluride of Zinc.—Margottet¹ describes this substance as an amorphous gray powder obtained by direct union of the elements in an atmosphere of hydrogen. It is decomposable by dilute hydrochloric acid with the evolution of hydrogen telluride.

When sodium telluride comes in contact with a solution of zinc acetate, acid with acetic acid, a heavy yellow-brown precipitate is formed. This telluride, when moist, is readily oxidized by the oxygen of the air with the separation of tellurium, as indicated by rapid darkening of the precipitate when in contact with air.

The dry telluride is of brown color. It is decomposed by dilute hydrochloric acid yielding hydrogen telluride and is readily oxidized by nitric acid. Dilute sulphuric acid has no action upon it.

Its composition is represented by the formula $ZnTe.H_2O$.

Calculated: Zn, 31.00; Te, 60.47; H_2O , 8.53.

Found: Zn, 30.32; Te, 59.48; H_2O , 9.63.

Anhydrous zinc telluride obtained by heating $ZnTe.H_2O$ out of air contact, is of a dark dull-red color. Its deportment toward reagents is entirely similar to that of the hydrated compound.

Telluride of Cadmium.—Cadmium telluride, $CdTe$, has been obtained by direct union of the elements in an inert atmosphere¹ and by the reduction of the telluride at a red heat in hydrogen.²

When precipitated by sodium telluride in a manner entirely similar to that for the preparation of zinc telluride, $CdTe$ appears as a heavy, maroon-colored precipitate, which is almost black when dry. The telluride is quite stable with respect to dilute acids, nitric acid alone attacking it in the cold. When moist it is readily oxidized by the air.

For $CdTe$: Calculated: Cd, 46.98; Te, 53.02; H_2O , 0.00.

Found: Cd, 43.97; Te, 53.05; H_2O , 3.02.

Telluride of Cobalt.— $CoTe$ was prepared first by Margottet³ and later by Fabre,³ by direct union of the elements in an inert atmosphere. It is described as a gray crystalline substance of metallic luster, quite indifferent to acids other than nitric.

When sodium telluride solution acts upon solutions of cobalt acetate acidulated with acetic acid, a heavy black precipitate is formed which, upon analysis, shows the composition $Co_2Te_3.4H_2O$, corresponding to the telluride of sodium, Na_4Te_3 . Acids other than nitric have no action upon it in the cold.

When heated in an atmosphere of hydrogen, $Co_2Te_3.4H_2O$ loses water at about 200° , and at a red heat, tellurium. If the heating is continued until the weight of substance is constant, the residue consists of the normal telluride $CoTe$, which is entirely similar to the compound described by Margottet and by Fabre.

¹ *These de Paris* (1879).

² Oppenheim, *J. pr. Ch.*, **71**, 226 (1857).

³ *Loc. cit.*

For $\text{Co}_2\text{Te}_3 \cdot 4\text{H}_2\text{O}$: Calculated: Co, 20.42; Te, 67.00; H_2O , 12.57.

Found: Co, 20.40; Te, 67.19; H_2O , 12.72.

CoTe in $\text{Co}_2\text{Te}_3 \cdot 4\text{H}_2\text{O}$: Calculated, 65.14; found, 65.00.

Telluride of Nickel.—The telluride Ni_2Te_3 , melonite, is found in nature. NiTe was prepared by Margottet and by Fabre and is described by them as possessing properties entirely similar to those of the corresponding cobalt compound.

Sodium telluride precipitates from acetic acid solutions of nickel acetate, $\text{Ni}_2\text{Te}_3 \cdot 4\text{H}_2\text{O}$, which is not acted upon by cold hydrochloric or sulphuric acid, but is readily oxidized by nitric acid.

When heated in an atmosphere of hydrogen, $\text{Ni}_2\text{Te}_3 \cdot 4\text{H}_2\text{O}$ loses water and tellurium until the composition NiTe is attained, when it remains constant.

For $\text{Ni}_2\text{Te}_3 \cdot 4\text{H}_2\text{O}$: Calculated: Ni, 20.37; Te, 67.07; H_2O , 12.58.

Found: Ni, 19.93; Te, 67.77; H_2O , 12.28.

Telluride of Lead.—Lead telluride, by direct union of the elements, has been prepared by Margottet¹ and studied by Jay and Gilson.² It occurs in nature as the mineral altaite.

When sodium polytelluride solution comes in contact with a solution of lead acetate acid with acetic acid, a heavy black precipitate is formed whose composition is represented by the formula $\text{Pb}_2\text{Te}_3 \cdot 4\text{H}_2\text{O}$. It is not attacked by hydrochloric or sulphuric acids. Nitric acid rapidly oxidizes it.

Calculated: Pt, 48.65; Te, 44.06; H_2O , 8.29.

Found: Pt, 48.21; Te, 43.74; H_2O , 7.70.

When Pb_2Te_3 is heated in an atmosphere of hydrogen it loses water, then fuses, and as the heat is increased, tellurium volatilizes, leaving crystalline PbTe .

PbTe in $\text{Pb}_2\text{Te}_3 \cdot 4\text{H}_2\text{O}$: Calculated, 78.03; found, 78.57.

Telluride of Silver.—Silver telluride has been prepared by direct union of the elements,³ by the reduction of the tellurites⁴ and by the action of tellurium upon silver salts.⁵ It occurs in nature as the mineral hessite.

Sodium telluride solution precipitates Ag_2Te from silver acetate solution in the presence of acetic acid, as a dark brown or black flocculent precipitate. It is perfectly stable in the air, even in the moist condition, and is not acted upon by cold acids other than nitric.

Calculated: Ag, 62.87; Te, 37.13.

Found: Ag, 61.78; Te, 36.01.

Tellurides of Copper.—Copper and tellurium occur in nature, combined as the mineral rickardite, Cu_2Te_3 .

Cuprous telluride, Cu_2Te , was prepared by Magottet by direct union and further studied by Fabre. When elementary tellurium remains for some time in contact with solutions of copper salts, the tellurides CuTe and Cu_2Te_3 are formed according to the conditions of the experiment.⁶

When sodium telluride reacts with copper acetate solution in the presence of acetic acid, the normal telluride, CuTe , is formed as a heavy black precipitate. This substance is stable in the air either moist or dry, and is not decomposed by dilute

¹ *Loc. cit.*

² *Am. Chem. Jour.*, **27**, 81 (1902).

³ *Rose, Pogg. Ann.*, **18**, 64, 1830.

⁴ *Brauner, J. Chem. Soc.*, **55**, 398 (1889).

⁵ *Hall and Lenher, THIS JOURNAL*, **24**, 918 (1902).

⁶ *Parkman, Am. J. Sci.* [2], **33**, 328 (1862).

acids other than nitric. Hot concentrated hydrochloric acid decomposes it slowly in the presence of the air, with the formation of cupric chloride and tellurium.

The analysis of the tellurides of copper at first presented great difficulties due to the tendency that both show of precipitating together.

The author has found that acid solutions of potassium dichromate oxidize elementary tellurium to telluric acid, from which solution hydrogen sulphide precipitates but a trace of tellurium. The copper telluride was boiled with an acid potassium dichromate solution until completely dissolved, the solution cooled and saturated with hydrogen sulphide. The precipitated copper sulphide was digested with dilute nitric acid and the copper precipitated electrolytically, a very low current density¹ being employed to keep the trace of tellurium present from being deposited with the copper.

When copper acetate solutions are brought in contact with sodium polytelluride, anhydrous Cu_2Te_3 is formed.

For CuTe :	Calculated, Cu, 33.26.
	Found, Cu (1), 33.33; (2) 33.43.
For Cu_2Te_3 :	Calculated, Cu, 24.90.
	Found, Cu, 24.74.

Mercuric Telluride.—This substance occurs in nature as the mineral triemanite. Klaproth,² in his first study of tellurium, noted the ease with which it combined with mercury, and Margottet³ mentions the preparation of mercuric telluride.

Sodium telluride solution precipitates from mercuric chloride solution, a gray substance, which changes first to a yellow and then to a red color, and finally to a homogeneous light brown. The final product is mercurous chloride, and tellurium is found to be dissolved in the solution. Mercuric telluride is probably formed at first, but subsequently reacts with the excess of mercuric chloride reducing it to mercurous chloride with the formation of tellurium chloride.

Telluride of Bismuth.—Bismuth telluride occurs in nature as the mineral tetradymite. When the two elements are heated together they form various alloys which have been studied by Gutbier.⁴

Hydrated telluride is formed when sodium telluride reacts with a solution of bismuth acetate. This telluride is unaffected by hydrochloric acid or sulphuric acid in the cold, but is decomposed by both when heated in the presence of the air. Nitric acid readily oxidizes it. When heated in hydrogen, the water is first expelled, then the telluride fuses and loses both tellurium and bismuth.

Telluride of Manganese.—When sodium telluride acts upon manganous acetate in the presence of acetic acid, a light brown precipitate is first formed, which rapidly changes to a dark green. If the acetic acid be in excess or the solution hot, the telluride is decomposed with the formation of hydrogen telluride, which itself decomposes and deposits tellurium upon the walls of the vessel above the solution. The dark green precipitate is immediately blackened by exposure to air and dilute acids decompose it very readily with liberation of H_2Te .

Telluride of Arsenic.—The tellurides AsTe ,⁵ As_2Te_3 ⁶ and As_8Te_7 ⁶ have been prepared by direct union of the elements.

¹ E. F. Smith's "Electro-Analysis" (4th Ed.), p. 199.

² *An. Ch.*, **25**, 276 (1798).

³ *Loc. cit.*

⁴ *Z. anorg. Chem.*, **31**, 331 (1902).

⁵ Oppenheim, *J. pr. Ch.*, **71**, 278 (1857).

⁶ Szarvassi and Massinger, *Ber.*, **30**, 1343 (1897).

Sodium telluride precipitates from aqueous solution of arsenious oxide a telluride of arsenic contaminated with tellurium. This substance is brown in color.

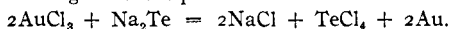
Arsenic telluride was allowed to stand for several hours in contact with a strong solution of sodium polytelluride. The solution, after filtration, was dark brown in color and careful examination revealed the presence of both arsenic and tellurium in the solution. This would seem to indicate the existence of telluro compounds analogous to the sulpho salts.

Telluride of Gold.—Telluride of gold was prepared first by Berzelius and then by Brauner¹ by direct union in proper proportions.

The naturally occurring tellurides of gold are sylvanite, calaverite, krennerite and petzite. According to Lenher,² these substances can scarcely be regarded as true chemical compounds, for he has found that these substances react with gold solutions, precipitating gold in a manner entirely similar to that of elementary tellurium.³ The alloys or tellurides formed by direct union act similarly.

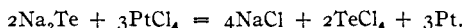
It has been found by the author that sodium telluride precipitates gold and tellurium from solutions of sodium sulphaurate, but the substances formed do not appear to be of constant composition.

When sodium telluride reacts with an excess of neutral auric chloride solution, a precipitate of metallic gold is formed which contains no tellurium. This may be due to one of two reactions, *viz.*, a telluride of gold may be formed which at once reacts with the excess of auric chloride, reducing it in a manner similar to the action of the natural tellurides; or the sodium telluride may act simply as a reducing agent toward the auric chloride according to the equation



Telluride of Platinum.—PtTe⁴ has been prepared by direct union. Platinum solutions are reduced by tellurium.⁵

Sodium telluride solution, acting upon a solution containing platinum tetrachloride⁶ in excess, produces a heavy black precipitate, which is composed entirely of platinum. The tellurium is found in the solution. The reaction may be expressed by the equation



Telluride of Iron.—Ferrous telluride was prepared by Margottet⁷ and also by Fabre,⁷ by the direct union of the elements in an inert atmosphere.

When sodium telluride acts upon a solution of ferric chloride, acid with acetic acid, a black precipitate is formed which is composed entirely of tellurium. The iron is reduced to the ferrous condition and the solution contains a large amount of tellurium as the tetrachloride. This is in accord with the fact established by Lenher⁸ that tellurium is soluble in ferric chloride, forming ferrous chloride and tellurium tetrachloride.

Telluride of Palladium.—Fischer⁹ has shown that tellurium acts as a reducing agent toward palladium solutions in a manner analogous to its action upon silver, gold and platinum solutions.

¹ *J. Chem. Soc.*, 55, 389 (1889).

² THIS JOURNAL, 24, 355 (1902).

³ Hall and Lenher, THIS JOURNAL, 24, 918 (1902).

⁴ Rössler, *Z. anorg. Chem.*, 15, 405 (1897).

⁵ Fischer, *Pogg. Ann.*, 12, 502 (1828).

⁶ Prepared by heating Ag₂PtCl₆ suspended in water.

⁷ *Loc. cit.*

⁸ THIS JOURNAL, 30, 744 (1908).

⁹ *Pogg. Ann.*, 12, 502 (1828).

Sodium telluride precipitates from sodium palladous chloride solution a very finely divided black precipitate of palladous telluride. This substance is not acted upon by hydrochloric or sulphuric acids in the cold, but is oxidized by nitric acid and very readily dissolved by *aqua regia*.

Molybdenum and Tungsten.—When sodium telluride reacts with ammonium molybdate or sodium tungstate, dark, strongly colored solutions are formed which are quite stable in the air. With these solutions hydrochloric acid yields black flocculent precipitates which contain tellurium and either molybdenum or tungsten, as the case may be. Here we have further evidence of the existence of telluro salts.

Summary.

1. Sodium telluride, Na_2Te , is a colorless crystalline salt and is highly hydrated.
2. Tellurium dissolves in sodium telluride solution with the formation of sodium polytelluride. Beyond the proportions represented by Na_4Te_3 , tellurium is not soluble in sodium telluride. Na_4Te_3 does not crystallize as such, but breaks down upon evaporation into Na_2Te and tellurium.
3. Potassium telluride, K_2Te , does not crystallize from aqueous solution, but is precipitated from strong solution by alcohol.
4. Telluride of zinc is yellow when freshly precipitated and brown when dry. Its composition is $\text{ZnTe}\cdot\text{H}_2\text{O}$. The anhydrous telluride is dark red in color.
5. Cadmium telluride, CdTe , is precipitated as a maroon colored substance, almost black when dry.
6. Nickel forms a telluride of the composition $\text{Ni}_2\text{Te}_3\cdot 4\text{H}_2\text{O}$, black. When heated in hydrogen it yields NiTe .
7. Cobalt forms a telluride of analogous composition and similar properties to that of nickel.
8. Lead forms the telluride $\text{Pb}_2\text{Te}_3\cdot 4\text{H}_2\text{O}$, which is decomposed by heat into PbTe , water and tellurium.
9. Ag_2Te is precipitated by sodium telluride from silver acetate solutions.
10. Copper forms the two tellurides CuTe and Cu_2Te_3 by precipitation with Na_2Te and Na_4Te_3 , respectively.
11. A telluride of arsenic is formed by precipitation, and is soluble in excess of Na_4Te_3 solution. This indicates the existence of a telluro salt of arsenic analogous to the sulpho salts.
12. Mercuric telluride is precipitated from mercuric chloride solution, but reacts rapidly with excess of mercuric chloride, forming mercurous chloride and tellurium chloride.
13. Sodium telluride precipitates gold from auric chloride solution and platinum from platinic chloride solution, the tellurium dissolving as the tetrachloride.

14. By the action of sodium telluride upon ammonium molybdate and upon sodium tungstate we have indications of the existence of telluro salts.

The author desires in closing to make grateful acknowledgment to Professor Victor Lenher, under whose guidance and inspiration this work has been carried out.

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THE BROMATES OF THE RARE EARTHS. PART II. THE BROMATES OF THE CERIUM GROUP AND YTTRIUM.

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In THIS JOURNAL, 30, 182, a new method for the separation of the yttrium earths was described, which involved the fractional crystallization of the bromates. As this method gave—and is still giving—excellent results, it was decided to investigate the pure bromates of all of the rare earths. This paper describes the preparation and properties of the bromates of lanthanum, cerium, praseodymium, neodymium, samarium and yttrium, each prepared from material of the highest purity. Though some of these compounds have been prepared by the early investigators, it is doubtful if their material was very pure.

The bromates are usually prepared either by dissolving the oxide of the element in bromic acid, or by the metathesis of the sulphate of the metal with barium bromate. In the former case there is nearly always an excess of bromic acid, which causes trouble during the subsequent evaporation. The latter method is preferable, since barium bromate is soluble in about 130 parts of cold water and its solubility decreases enormously in the presence of the very soluble bromates. Thus we can employ an excess of barium bromate and very readily obtain pure bromates by crystallization. Because the rare earth sulphate solutions deposit crystals upon heating, it is best to cover the barium bromate with water, heat upon the water bath and add gradually, with plenty of stirring, the sulphate of the desired element. Under these conditions one encounters no difficulties and the barium sulphate filters well.

Lanthanum Bromate, $\text{La}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$.—This salt was prepared by the double decomposition of lanthanum sulphate solution with barium bromate. The product of the reaction was filtered, the filtrate boiled down and allowed to stand, when any remaining barium bromate separated. The refiltered liquid was further concentrated and the lanthanum bromate crystallized out. The crystals were then drained upon a Hirsch funnel at the filter pump and lastly dried in the air upon filter paper. When found necessary, this material was recrystallized.

Lanthanum bromate forms colorless hexagonal prisms. However, it usually separates out in small crystals about the size of granulated sugar. When the dried salt is ground up, it apparently tends to give up a small part of its water of crystalliza-