

ACTION OF TELLURIUM AND SELENIUM ON GOLD AND SILVER SALTS.

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HISTORICAL.

THAT metallic tellurium and selenium act as reducing agents upon solutions of gold and silver salts has been known since the early part of the last century, still their action has not been studied quantitatively.

N. W. Fischer¹ found that tellurium acts as a reducing agent on salts of gold, silver, platinum and palladium in solution, the reduction being incomplete in all cases, and that its action on gold solutions is the most rapid, the tellurium after a short time becoming coated with metallic gold, stopping all further action even at a high temperature. Fischer states that the action of tellurium on silver nitrate in solution is slower than on a gold solution, and that the black powder which remains is not silver but a union of tellurium and silver, each in the lowest state of oxidation. He also observes that selenium reduces a gold solution at a high temperature, the action then being the same as that of tellurium while silver and the remaining metals are not reduced.

Parkham² found that red selenium is blackened in a solution of silver nitrate, some flakes of selenious acid being formed at the same time; after the latter has been removed by sodium hydroxide the black powder which remains contains both selenium and silver in quantity but no unchanged selenium is visible under the microscope. He notes that tellurium in a silver nitrate solution gives a black precipitate which shows no metallic luster under pressure. After digesting tellurium for four days with an excess of a saturated silver nitrate solution he obtained a precipitate, which appeared homogeneous under the microscope, contained both tellurium and silver and no tellurous acid, and concludes that if metallic silver is precipitated by tellurium then under these conditions nearly all of the tellurium should be in solution. He analyzed neither of the precipitates but he found that selenium in a copper solution gives a precipitate which analyzed for Cu_2Se

¹ *Pogg. Ann.*, **12**, 502.

² *Chem. Centrbl.*, **33**, 813.

and that tellurium in a copper solution gives, according to conditions, Cu_2Te or CuTe , and because of this he concludes that selenium in silver solutions forms silver selenide, Ag_2Se , and that tellurium in silver solutions precipitates Ag_2Te , the telluride of silver.

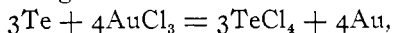
Sendersens¹ found that selenium reduces a boiling solution of silver nitrate, either dilute or concentrated, with the formation of silver selenide and selenium dioxide. When the reaction was carried out in a closed tube he obtained a blue color which he thought indicated the formation of nitrogen pentoxide. The action of tellurium on a silver nitrate solution was found to be less rapid than that of selenium at 100° but similar to it; also at ordinary temperatures both metals reduce silver nitrate, the action being slow but complete.

PROCEDURE.

The following investigation was undertaken to find out whether gold and silver are precipitated from solutions of their salts by elementary tellurium and selenium. Pure tellurium and selenium were used. They were ground to a powder in an agate mortar and weighed quantities, usually about 0.1 gram, of them kept in contact with the solution of gold or silver for a definite length of time under definite conditions. The precipitate obtained was collected on a Gooch filter, dried at 100° in an air-bath and weighed; the precipitate was usually tested for either metal that it might contain and in some cases both the precipitate and the solution were analyzed. In most cases solutions containing known quantities of silver and gold were used, so that all the data necessary for an analysis was the determination of the amount of these metals remaining in the solution.

TELLURIUM IN GOLD SOLUTIONS.

In preliminary experiments on the reducing action of tellurium on solutions of gold chloride, considerable difficulty was first experienced in obtaining results consistent with the equation



since when tellurium is brought in contact with a gold solution the gold is apt to deposit as a coating on the tellurium, protecting it

¹ *Compt. rend.*, 104, 175.

from all further action, a fact also noted by Fischer. This was in part obviated by grinding the tellurium to an impalpable powder and even when this was done the tellurium was apt to mass in little balls which it was necessary to crush with a glass rod in order to bring all of the tellurium in contact with the gold solution. That some tellurium not infrequently escaped contact with the gold solution was shown by extracting the precipitate with such solvents as sulphur monochloride and nitric acid. None could be dissolved, showing that the tellurium present was completely enclosed by the gold; but when the precipitate was dissolved in *aqua regia*, the nitric acid evaporated off and the tellurium and gold precipitated with sulphur dioxide and this precipitate either tested for tellurium by the above solvents or by fusion with potassium nitrate, invariably where the weight of the precipitate was below that required by the above equation, tellurium could be detected.

It is not necessary that the gold chloride solution should contain more gold than is required by the reaction, for if a large excess of gold solution is used the results are the same, while if an insufficient supply is used it is entirely bleached, all of the gold being deposited. The action of tellurium on gold in solution is fairly rapid; warming a few minutes will bring down sufficient gold to color the precipitate a decided yellow, yet time is a considerable factor in bringing about complete precipitation, from two to three hours being necessary with continued heating, or several days at room temperatures. The only conditions to be observed, in order to obtain quantitative precipitation of the gold by the tellurium, are sufficient time and the direct contact of all the tellurium with the gold solution.

Experiment 1.—0.1010 gram of tellurium gave 0.2125 gram of gold; the theory, for total precipitation of the gold by the tellurium according to the equation given, requires 0.2091 gram. The gold solution used contained 0.4346 gram of gold and was in contact with the tellurium for three hours and was boiled continuously during that time. No test for tellurium could be obtained in the precipitate either before or after dissolving in *aqua regia*.

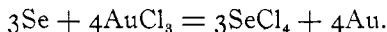
Experiment 2.—0.1099 gram of tellurium gave 0.2257 gram of precipitate; the theory requires 0.2243 gram. The gold solution

contained 0.2351 gram of gold and was in contact with the tellurium for six days at room temperature. The precipitate contained no tellurium.

Experiment 3.—0.0789 gram of tellurium gave 0.1642 gram of gold; the theory requires 0.1635 gram. The precipitate gave no test for tellurium either before or after dissolving in *aqua regia*.

SELENIUM IN GOLD SOLUTIONS.

The selenium used was prepared from sublimed selenium dioxide by precipitation with sulphur dioxide in the presence of hydrochloric acid. The selenium was dried, fused, and ground to a fine powder. The fused variety of selenium does not reduce a solution of gold chloride at room temperature. One experiment was made allowing the selenium to remain in contact with the gold solution for three months at room temperature with no visible action. At the boiling temperature the action is nearly as energetic as that of tellurium and is analogous to it, being expressed by the reaction



The same difficulties were encountered with the selenium as with the tellurium and were overcome in the same way. From six to eight hours of continued boiling are necessary to insure complete precipitation, or better from two to three days at a temperature of from 70° to 80°.

Experiment 1.—0.0712 gram of selenium gave 0.2345 gram of gold, the calculated being 0.2336 gram.

Experiment 2.—0.1058 gram of selenium gave 0.3455 gram of precipitate; the theory requires 0.3470 gram. The amount of gold contained in the solution was 0.4346 gram and it was in contact with the selenium for three days at a temperature of about 80°. The precipitate gave no test for selenium after dissolving and reprecipitating.

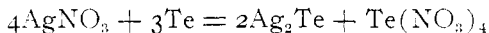
Experiment 3.—0.1502 gram of selenium in a solution of gold chloride boiled for five hours gave 0.4892 gram of gold; the amount required by the theory is 0.4926 gram; the precipitate gave no test for selenium.

TELLURIUM IN SILVER SOLUTIONS.

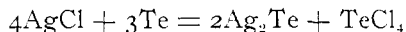
The first salts used were ammoniacal solutions of the nitrate and

the chloride of silver. In both cases the solutions were reduced by the tellurium, slowly in the cold and more rapidly if heated, yet tellurium digested with silver nitrate solution for a long time would not completely go into solution leaving metallic silver. Where an ammoniacal solution of silver nitrate was used the weight of the precipitate and the amount of silver in the precipitate, was in excess of that required for silver telluride. The amount of silver and tellurium as determined by analysis did not add up to the total weight of the precipitate and in several cases small plates of metallic silver were formed. On repeating the experiment with no tellurium present it was found that when silver nitrate stands in contact with ammonia for some time or is warmed with it a deposit is formed which is insoluble in ammonia. This deposit is probably silver nitride, but when the solution is boiled or kept warm several days the precipitate contains plates of metallic silver. In subsequent experiments the silver nitrate solution was used without ammonia and the silver tellurite formed was removed by washing the precipitate with ammonia.

When silver chloride in ammonia was used, it was allowed to stand in contact with the tellurium at room temperature or only slightly warmed, an excess of ammonia always being present to keep the silver chloride in solution. When the nitrate was used a greater range of temperature was possible and the solution was either boiled continuously or kept at a temperature of about 80° for a long time. At the end of the experiment the precipitate was collected on a Gooch filter, washed several times with ammonia to remove any silver tellurite and then with water. In this way results were obtained which agree very well with those required by the equation



where the nitrate of silver is used, and



where the chloride in ammonia was used. Either the chloride or the nitrate of tellurium would be decomposed by water and would then react with more silver nitrate or chloride to form the tellurite of silver.

Experiment 1.—0.1099 gram of tellurium gave 0.1848 gram of precipitate; the calculated amount of silver telluride was 0.1978

gram. The solution contained 0.4320 gram of silver as the chloride and was in contact with the tellurium for eight days.

Experiment 2.—0.1005 gram of tellurium in a solution of silver chloride containing 0.2160 gram of silver gave 0.1843 gram of precipitate, that required for silver telluride being 0.1809 gram; the time of the experiment was ten days.

Experiment 3.—0.0994 gram of tellurium in a solution of silver chloride containing 1.0800 grams of silver gave 0.1767 gram of precipitate, the calculated for silver telluride being 0.1789 gram. The time of the experiment was three months, and during that time it was kept in a warm place and ammonia added occasionally.

Experiment 4.—0.1018 gram of tellurium in a solution of silver nitrate which contained 2.0601 grams of silver gave 0.1871 gram of precipitate, that required for silver telluride being 0.1841 gram. The silver remaining in the solution was determined as the chloride and found to be 1.9404 grams which would make the loss from the solution or the amount of silver in the precipitate as 0.1192 gram and the amount of tellurium in the precipitate 0.0693 gram. The calculated amount of silver in 0.1871 gram of the telluride is 0.1178 gram and the tellurium 0.0693 gram.

The low results in the above series of experiments can be attributed in a large measure to small amounts of tellurium which were so thoroughly enclosed in the mass that they could not be brought to enter into the reaction.

An attempt was made to prepare silver telluride in order to study its properties and compare it with the precipitate obtained from the reduction of the silver solution by tellurium. An excess of aluminum was fused with tellurium and hydrogen telluride evolved from this by treatment with dilute hydrochloric acid. The hydrogen telluride was passed into an ammoniacal solution of silver nitrate in an atmosphere of carbon dioxide to prevent any decomposition of the hydrogen telluride by the oxygen of the air. This gave a black precipitate which was washed repeatedly with water, then dried in an air-bath at 105°. Analysis showed the substance to contain 22.3 per cent. tellurium and 77.3 per cent. of silver while the theory for silver telluride requires 37.1 per cent. of tellurium and 62.9 per cent. of silver. The silver in another sample, prepared in a similar way, was determined by heating the substance in a boat in a current of chlorine gas; the tellurium distilling off as the tetrachloride and the silver chloride remaining

was weighed. The per cent. of silver obtained in this way was 75.4.

The substance thus prepared fused without loss of tellurium as was indicated by the absence of fumes, to a porous mass which cut with a metallic luster. It was acted on by sulphur monochloride, forming tellurium tetrachloride; it reduced a gold solution, depositing metallic gold, but no action could be observed with a silver solution.

The action of hydrogen telluride on silver nitrate may be explained by the decomposition of hydrogen telluride in presence of silver nitrate into nascent hydrogen and tellurium and these then would reduce the silver solution, the first causing metallic silver to be deposited while the latter would give rise to silver telluride, and this would explain the high percentage of silver.

Silver tellurite was prepared by adding potassium tellurite (obtained by fusion of equivalent weights of tellurium dioxide and potassium carbonate) to a silver nitrate solution: it was dried at 105° and as obtained was a light yellow powder, fairly permanent in the light. Analysis gave 54.95 per cent. of silver, while the formula Ag_2TeO_3 requires 55.17 per cent. This silver tellurite was reduced by heating it in a porcelain tube to the highest temperature obtainable in the blast-lamp and passing a current of dry ammonia over it for one hour. At the temperature used, tellurium alone would have entirely distilled from the boat. 1.1990 grams of the silver tellurite were used and 1.0440 grams of residue obtained; the weight required for silver telluride from the amount of tellurite used is 1.0517 grams. The compound obtained by the reduction of the tellurite was analyzed by heating in a current of chlorine. 0.2276 gram gave 0.1908 gram of silver chloride or 62.65 per cent. of silver, the calculated for silver telluride being 62.97 per cent. Another sample of silver tellurite was reduced in carbon monoxide under similar conditions and the telluride formed was similar in all respects to that obtained by reduction in ammonia.

The silver telluride obtained by the reduction of silver tellurite had a strong metallic luster, did not tarnish readily, was harder than tellurium, was brittle but not brittle enough to be ground to a powder; it was broken up as finely as possible and treated with

sulphur monochloride, gold chloride solution and silver nitrate solution. Sulphur monochloride acted on it slowly to form tetrachloride; the gold solution was bleached and the silver telluride became coated with gold. 0.2995 gram was boiled with a solution of silver nitrate for eight days; at the end of that time the solution gave no test for tellurium while the particles had lost none of their luster, showing them to be entirely unacted on.

Brauner¹ synthesized silver telluride by fusion of silver in a current of tellurium. He obtained a crystalline mass of metallic luster having approximately the composition Ag_2Te .

In an article on the "Naturally Occurring Telluride of Gold" by one of us² specimens of sylvanite, calaverite, coloradoite, kalgoorlite, and nagyagite were treated with a gold solution, and in all cases metallic gold was obtained. Recently some excellent specimens of krennerite, hessite and more specimens of sylvanite and calaverite were obtained, and as specimens of some of these minerals were not at hand at the time of the previous investigation their action on solutions of gold chloride and silver nitrate was now tried. The minerals examined were:

One specimen calaverite, Keystone, Boulder Co., Colo. (this was one of the original specimens of Genth).

One specimen calaverite and one of sylvanite from Cripple Creek, Col.

Three specimens hessite from Boles, Siebenburgen, Hungary.

One specimen hessite from Tombstone, Arizona.

One specimen krennerite, West Side Mine, Cripple Creek, Col.

One specimen krennerite, Boles, Siebenburgen, Hungary.

All of these minerals reduced gold chloride solution, becoming coated yellow and where a small quantity of solution was used bleached it, agreeing with the previous results. The hessite was without visible action on the silver nitrate solution even when boiled in it; one specimen of krennerite and one of sylvanite gave a small amount of black powder similar to that obtained from tellurium in silver nitrate solution. Hessite is telluride of silver, which as we have seen is without action on silver solutions, while the others contain both silver and gold with the tellurium, or gold with tellurium, from which it would seem that while the combina-

¹ *J. Chem. Soc.*, **55**, 388

² *This Journal*, **24**, 355.

tion of silver with tellurium is without action on silver nitrate solution that of gold with tellurium reduces silver nitrate.

In the same article reference was made to the action of tellurium on silver nitrate solution, and conclusions stated which in the light of the facts then at hand seemed correct. It was stated that the action of tellurium on silver solutions is similar to that on gold solutions, though not as complete, metallic silver being formed. The results in this later work show that tellurium in silver solutions forms the telluride of silver and not metallic silver. The error in the former statements arose from the use of ammonia in the solution while it was in contact with the tellurium; it was subsequently found that silver nitrate solution standing for a long time with ammonia, or being heated with it, gives a deposit which contains metallic silver.

SELENIUM IN SILVER SOLUTIONS.

Selenium reduces a solution of silver nitrate or of the chloride in ammonia, either in the cold or on heating. The action is less rapid than that of tellurium but similar to it, a close approximation to the selenide of silver being formed. Parkham's statement that a precipitate of selenium dioxide is formed is obviously incorrect as he used aqueous solutions, and selenium dioxide is readily soluble in water. The precipitate that he obtained must have been silver selenite. Sendersen's experiment of heating the solution in contact with the selenium in a closed tube was repeated; no difference could be detected in the outcome of the reaction, and no blue coloration was observed.

Experiment 1.—0.1012 gram of selenium in a solution of silver nitrate for eight days gave 0.2513 gram of precipitate, the theory requiring 0.2497 gram.

Experiment 2.—0.1047 gram of selenium in a solution of silver chloride containing 0.4320 gram of silver, gave 0.2550 gram of precipitate, the calculated for silver selenide being 0.2590 gram.

Experiment 3.—0.1012 gram of selenium in a solution of silver nitrate containing 2.4157 grams of silver gave 0.2468 gram of precipitate, the theory for silver selenide being 0.2497 gram. After the removal of the precipitate the solution contained 2.2370 grams of silver which would make the precipitate contain 0.1785 gram of silver and 0.0683 gram of selenium, the calculated amounts for

0.2468 gram of silver selenide being 0.0666 gram of selenium and 0.1802 gram of silver.

The precipitate obtained in Experiment 2 was treated with a solution of gold chloride and reduced it nearly as well as does elementary selenium. The fact that both the telluride and the selenide of silver reduce gold chloride suggested an investigation of the action of the sulphide of silver on solutions of silver and gold. Silver sulphide was prepared by passing hydrogen sulphide into a solution of silver nitrate made alkaline with ammonia, the precipitate washed, dried in an air-bath and then washed with carbon bisulphide to remove any excess of sulphur. A sample of silver sulphide prepared in this way was boiled with a solution of silver nitrate for seven days and the solution tested for sulphur without any trace being found to be present. The silver sulphide reduced gold chloride solution to metal, readily on warming but only slightly in the cold.

CONCLUSIONS.

Tellurium reduces a gold chloride solution completely to metallic gold either in the warm or in the cold and the only difficulties so far as quantitative precipitation is concerned are mechanical ones. The action of tellurium on silver salts in solution is to reduce them with formation of the telluride of silver, which is still a reducing agent as it throws gold out from solution. The behavior of the product obtained is, in all respects, similar to that of the telluride of silver obtained by the reduction of silver tellurite and to that of the native mineral itself.

The action of selenium is similar to that of tellurium but is not as energetic. Selenium reduces silver solutions in the cold, but has no action on gold solutions unless heated nearly to boiling, the action then being fairly rapid and complete. With silver solutions selenium forms silver selenide which resembles silver telluride in being a reducing agent to solutions of gold salts, both of them being similar to the sulphide of silver in this respect.