

nate, $Au_2(SeO_4)_3$. Analysis of the salt showed that it agrees with this formula. The gold leaf was replaced by small pieces of gold, and it was found that the latter dissolve nearly as readily as the leaf and at about the same temperature. In most respects the action is similar to that of sulphuric acid on copper, although no such complicated products arise as mentioned by Baskerville¹ in the study of this reaction.

The selenate has been obtained as very small yellow crystals. It is soluble in hot concentrated selenic acid, forming a reddish-yellow solution, and separates on cooling. It is insoluble in water, and can be completely separated from selenic acid by dilution, when it appears as a yellow precipitate. It is soluble in sulphuric acid and in nitric acid. Hydrochloric acid decomposes the salt with evolution of chlorine, forming auric chloride and selenious acid. It is decomposed by heat below redness, metallic gold being obtained. On exposure to the light, auric selenate is decomposed, becoming dark green then bronze colored. It is worthy of note that all the members of the subgroup B in the first group of the periodic system, dissolve in selenic acid with evolution of selenium dioxide and formation of the corresponding selenate. Silver dissolves in selenic acid when the latter is hot and concentrated, the selenate being produced and selenium dioxide being evolved. Copper also acts in a similar manner. During the solution of gold in selenic acid, selenium dioxide is produced, being evolved as fumes, and is also invariably found in the solution after the reaction. Moreover in the reaction of selenic acid on gold we have for the first time the solution of gold in a simple oxygen acid.

UNIVERSITY OF WISCONSIN,
MADISON, WIS.

NATURALLY OCCURRING TELLURIDE OF GOLD.²

BY VICTOR LENHER.

Received January 6, 1902.

THE occurrence of gold in nature, according to the commonly accepted view, is either as native gold or as telluride. It is generally conceded that gold exists in pyrite or other sulphide ores uncombined and in the elementary condition. This, broadly speaking, is the manner in which gold is considered to exist in nature. No mineral containing gold as one of its constituents,

¹ Baskerville: This Journal, 17, 904.

² Read at the Philadelphia meeting of the American Chemical Society.

and no chemical compound of gold is known in nature with the possible exception of the so-called "tellurides" or the tellurides of gold.

It is the purpose of this paper to describe a series of experiments which have been conducted with the view of throwing some light on the constitution of the naturally occurring tellurides.

The peculiar combinations of gold and tellurium which occur in nature have a more or less definite and more or less indefinite character, both from the standpoint of the chemical mineralogist and of the crystallographer. The recorded analyses of the telluride minerals show considerable variation from a constant composition.

One of the best defined compounds of gold and tellurium occurring in nature, and the compound which contains the nearest to pure tellurium and gold has been called "calaverite."

Calaverite is a silver-white mineral, frequently possessing striated faces, containing in composition from 55.8 to 57.6 per cent. tellurium, 40.6 to 42.7 per cent. gold, and smaller quantities of silver, 0.40 to 3.0 per cent. The theoretical requirements for AuTe_2 are 56.32 per cent. tellurium and 43.68 per cent. gold. This mineral contains more gold and less silver than the other tellurides. This combination of gold and tellurium appears to present some definite characteristics of a mineral. The recent work of Penfield and Ford¹ seems to throw some doubt on the definiteness of its crystallographic constants. In this valuable paper, measurements of crystal faces are given, which show either monoclinic or triclinic symmetry.

Sylvanite, one of the most common tellurides of Colorado and West Australia, occurs in brilliant white twinned crystals which are frequently distributed over the faces of rocks in such a manner as to resemble Arabic writings; hence, it has been called "graphic tellurium." This mineral contains about 60 per cent. tellurium, 16 per cent. gold, and 14 per cent. silver. Other tellurides, which are well defined, are krennerite and petzite.

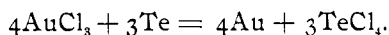
Finally, from the recorded analyses of native tellurium, gold is not infrequently found to be present.

In the investigation of the tellurides, the author has been extremely fortunate in having had placed at his disposal the fine collection of tellurides of the University of Wisconsin, through

¹ *Am. J. Sci.*, p. 225, September, 1901.

the courtesy of Professor W. H. Hobbs, of the department of mineralogy.

In some investigations now being carried out by Hall and Lenher, on the action of metallic tellurium on gold and silver salts, it has been observed that tellurium quantitatively precipitates gold from solution in the ratio of $4\text{Au} : 3\text{Te}$, according to the equation



When a solution of chloride of gold is added to metallic tellurium, metallic gold is deposited, tellurium tetrachloride passing into solution. The reaction is accelerated by heating the solution, and time is a considerable factor as far as quantitative results are concerned. If proper precautions are observed and the gold salt is in excess, the above ratio will be obeyed.

Likewise, when tellurium is introduced into a silver solution, similar results are obtained. The reaction, as thus far studied, appears not to be as sharp as with gold, nor as complete; nevertheless, our results have demonstrated that from a silver solution, no matter whether an aqueous solution of fused silver nitrate, ammoniacal silver nitrate, or ammoniacal silver chloride be used, metallic silver is obtained.

The action of elementary selenium on gold solutions has also been studied, and the results obtained show that selenium acts as a reducing agent to gold salts, throwing the metal out of solution.

When these facts had been ascertained, the natural tellurides were tested to determine their behavior to chloride of gold. Sixteen specimens of the minerals from different sources were tested, and in each case, when the telluride mineral was brought into contact with a chloride of gold solution, metallic gold was obtained. The minerals examined were:

One specimen calaverite, Abe Lincoln Mine, Cripple Creek, Colorado.

One specimen calaverite, Little May Mine, Cripple Creek, Colorado.

One specimen calaverite, Porcupine Mine, Cripple Creek, Colo.

Five specimens calaverite, Gold Coin Mine, Victor, Colorado.

One specimen sylvanite, Battle Creek Monument, Cripple Creek, Colorado.

Two specimens sylvanite, Magnolia, Boulder County, Colorado.

One specimen sylvanite, Offenbanya, Hungary.

One specimen coloradoite, West Australia.

Two specimens kalgoorlite, West Australia.

One specimen nagyagite, Nagyag, Austria.

All of these minerals precipitated metallic gold from the solution of chloride, and when only a small quantity of gold solution was used, the latter was bleached from yellow to completely colorless.

The question naturally arises at this point, whether a chemical compound can precipitate one of its constituents in such a manner as shown in this reaction. An attempt was then made to prepare telluride of gold artificially with a view of studying its composition and properties.

In the elaborate research of Brauner¹ on the atomic weight of tellurium, an attempt was made to synthesize telluride of gold. He obtained "crystalline polytellurides (alloys of gold and tellurium) of a silvery lustre," but not definite in composition. Au_2Te is the nearest approximation to a definite formula. Brauner's work has been repeated by me. Gold mixed with an excess of tellurium was placed in a porcelain boat and heated to redness in a current of carbonic acid. Under these conditions, tellurium distils on heating, and the amount given off is entirely dependent on the temperature and length of heating. After conducting this experiment for six hours, the material remaining in the boat had a golden appearance. On removing this substance, which appeared in globules, from the boat, it was found to consist of an outer shell or crust of gold, covering a white alloy-like substance. Inasmuch as this white body, on being brought in contact with chloride of gold solution, precipitates metallic gold, it is hardly likely that it is a definite chemical compound.

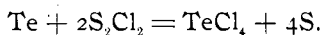
Another series of experiments was conducted with a view of preparing telluride of gold in the wet way. Hydrogen telluride generated by the action of dilute hydrochloric acid on aluminum telluride, was conducted into a solution of chloride of gold; a golden colored precipitate was formed. This precipitate was collected and carefully analyzed, and was found to be pure gold. The experiment was repeated, precipitating first only a part of the gold, then adding an excess of hydrogen telluride and precipitating completely. These fractions were separately analyzed, and in all cases the precipitates formed by the action of hydrogen telluride on gold solutions were found, by actual weight, to be

¹ *J. Chem. Soc.*, **55**, 391.

pure gold, and in no precipitate could even a trace of tellurium be detected. According to these results, hydrogen telluride does not form telluride of gold, or at all events, telluride of gold has not appeared thus far in the wet way. All attempts which have been made thus far for the preparation of artificial telluride of gold have been unsuccessful.

At this point, it might be well to add that an attempt to precipitate gold and tellurium together has been unsuccessful. To a solution containing 0.1089 gram gold and 0.1404 gram tellurium as chlorides, sulphur dioxide was added, with the hope that possibly the compound AuTe_2 might be precipitated. The result was first a precipitation of gold followed by tellurium. Had any tellurium come down at first, on coming in contact with the gold in solution, it would have precipitated the latter. The entire precipitate was collected, dried, and fused in carbon dioxide. It gave a white alloy which precipitated gold from a solution of gold chloride.

Recent work¹ on the action of sulphur monochloride on metallic tellurium has shown that when these two substances come in contact, tellurium tetrachloride is formed, and being insoluble in chloride of sulphur, separates in white needle-like crystals. The action is represented by the equation



The free sulphur formed as indicated in the reaction goes into solution in the excess of sulphur chloride.

The entire series of naturally occurring tellurides when subjected to the action of sulphur monochloride lost their tellurium, leaving gold as a residue, and in a number of cases the tellurium immediately separated as crystals of tetrachloride.

Another reaction of these minerals, which perhaps has not as much significance from the chemical standpoint, is that with nitric acid. When the minerals are treated with nitric acid, the tellurium and silver dissolve, leaving the gold as a residue.

SUMMARY.

1. Metallic tellurium quantitatively precipitates gold from solution. A similar reaction takes place with silver, though possibly not so completely. Selenium acts as a reducing agent with solutions of these metals, but is not as strong a reducing agent as tellurium.

¹ This Journal, 24, 188.

The tellurides of nature act towards gold solutions unlike a chemical compound of gold and tellurium, in that they throw gold out of solution.

It is not infrequent to find specimens of native gold in the same mine with the tellurides. The author has observed yellow or golden incrustations as a superficial coating on natural crystals of calaverite and sylvanite, while immediately under this coating the silver-white telluride was found; when this white material was brought into contact with gold chloride, metal was obtained.

Professor C. R. Van Hise informs the author that he has seen many beautiful specimens of gold from Cripple Creek which are pseudomorphs after the tellurides, showing both the crystalline form and striations of the original mineral.

2. Thus far the attempts to prepare telluride of gold artificially either in the wet way or the dry way have been unsuccessful.

3. It is possible to extract the tellurium from these minerals, leaving the noble metal as a residue.

CONCLUSIONS.

In view of the facts above ascertained, much doubt seems to be cast as to whether the tellurides are definite chemical compounds. The fact that they all precipitate metallic gold from solution, and lose their tellurium with such reagents as sulphur chloride, are points which are difficult to reconcile with a chemical compound.

The observation that hydrogen telluride in contact with gold solutions instead of forming telluride of gold, acts as a reducing agent, throwing out pure gold, may also be regarded as significant, and as well the fact that the body of inconstant composition containing tellurium and gold, obtained at high temperatures, reduces gold chloride, appears to place the telluride minerals in a very doubtful light as chemical compounds.

UNIVERSITY OF WISCONSIN,
MADISON, WIS.

SOME COMPOUNDS OF PYRIDINE.

BY J. ARTHUR HAYES.

Received January 6, 1902.

WHEN some compounds of the metals with the halogens, in solution of that halogen acid, are brought in contact with the halogen acid compound of pyridine, addition-products