SUMMARY.

No. of fraction.	Atomic weight.
1	90.80
2	91.25
3	90.85
4	89.65
5	88.80
6	88.45
7	88.00

As can be seen, Fraction 1 gave an atomic weight less than Fraction 2. This was due to the fact that the decomposition was carried too far and therefore the basic nitrate obtained was somewhat colloidal and also the fused nitrate was not entirely soluble in water.

C. Fractionation by Means of Boiling with Sodium Hydroxide.

A concentrated nitrate solution containing yttrium and erbium was boiled, and a sufficient quantity of sodium hydroxide added to precipitate about one-fifth the rare earth material present. This was boiled for a short time and then allowed to stand over night in order that the basic nitrate might crystallize out. In this way three fractions were obtained and the fourth precipitated with oxalic acid. These were purified as before and the equivalents determined.

SUMMARY.

No. of fraction.	Atomic weight.
1	90.30
2	89.90
3	88.75
4	88.30

Conclusions.

The best method found thus far for separating yttrium efficiently from the other earths is by means of fractional precipitation with sodium nitrite. This gives a larger yield, a more rapid separation and is less expensive than either the phosphate or chromate method. This method is, however, not very effective for separating terbium from yttrium.

CONTRIBUTION TO THE CHEMISTRY OF GOLD. II. AUTO-REDUCTION AS A FACTOR IN THE PRECIPITATION OF METALLIC GOLD.

BY VICTOR LENHER.

Received April 27, 1914.

In the various studies which have been made on the precipitation of gold from solution, attention has been directed for the most part to the action of various *reducing* agents on gold solutions. The general chemical inactivity of gold enables us to deposit the metal in elementary form by most of the metals, the metallic sulfides, ferrous salts, various organic compounds, and, in fact, in the ordinary sense of the word, gold compounds are readily reduced to metal by the mildest of reducing agents.

On the other hand, very little attention has been directed to the precipitation of gold in the metallic condition by oxidizing agents. A few isolated cases of the "auto-reduction" of gold from its compounds by certain oxidizing agents have been recorded, but the general principle of the auto-reduction of gold compounds has not received systematic study from the standpoint of the deposition of gold.

It has been known for a long time that hydrogen peroxide, when brought in contact with oxide of gold or oxide of silver, will reduce either of these metallic oxides to metal, water and oxygen being formed simultaneously.

$$Au_2O_3 + 3H_2O_2 = 2Au + 3H_2O + 3O_2.$$

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

In a similar manner, gold solutions in contact with hydrogen peroxide yield metallic gold, oxygen being evolved at the same time. This reaction of hydrogen peroxide with gold compounds takes place in either acid or alkaline solution. Sodium peroxide and sodium perborate precipitate metallic gold immediately from gold solutions. Barium peroxide and calcium peroxide act toward gold solutions in exactly the same way, precipitating metallic gold at once. These compounds are perhaps closely related to hydrogen peroxide and, as a consequence, act similarly toward gold solutions. Osmium tetroxide, or the so-called osmic acid (OsO_4), when dissolved in water will not reduce gold solutions, but when the free acid is neutralized, or when the solution is made alkaline with sodium hydroxide, sodium carbonate or calcium carbonate, metallic gold is precipitated. The higher oxides of nickel and cobalt, prepared by the action of an alkaline hypobromite on solutions of nickel and cobalt chloride, when brought in contact with a solution of gold which has been rendered alkaline, precipitate metallic gold.

Lead peroxide as well as red lead precipitate metallic gold from either neutral or alkaline gold solutions.

Ceric oxide, prepared in the hydrated form by rendering ceric chloride alkaline, precipitates metallic gold at once from a gold solution which has been rendered alkaline.

The compounds of manganese present interesting deportment along this same general line of auto-reduction. Manganese dioxide, prepared by the action of bromine on a manganese acetate solution, precipitates gold from its solution either under slightly acid, neutral, or alkaline conditions. Potassium permanganate, on being allowed to stand for some time with auric chloride, causes metallic gold to be precipitated along with manganese dioxide.

The minerals pyrolusite, wad, braunite and manganite, when brought in contact with a gold solution, which is either acid, alkaline, or neutral, slowly cause gold to deposit.

Recently Brokaw[1] has shown that manganese salts, when made alkaline, or even manganese carbonate will precipitate gold from solution. The direction of the reaction between manganous salts and gold chloride is considered by Brokaw to be largely due to hydrolysis of gold chloride solutions, although the equations, as given, show that gold chloride and manganous salts react in neutral solution to form manganese dioxide and metallic gold. All of the reactions recorded by Brokaw have been studied and corroborated. That manganese can be of considerable importance in the deposition of gold is unquestionably true, and its function may be that which Brokaw has suggested; but, in addition, manganese may play the role of a reducing agent, acting solely through auto-reduction.

Auric compounds, as is well known, are easily reduced to metallic gold, and, hence, can be considered as oxidizing agents and can, obviously, oxidize manganous hydroxide to manganese dioxide. It can therefore be considered that the mutual precipitation of gold and manganese dioxide by calcite, as cited by Brokaw, is simply the neutralization of the excess of acid, whereupon the oxidation of the manganese by the gold solution results in the precipitation of both manganese dioxide and metallic gold.

That this is the direction of the reaction is evidenced by the duplication of the phenomenon by replacing manganese salts with cerium compounds. Cerous hydroxide precipitates metallic gold in alkaline solution; the cerium being at the same time oxidized to cerium dioxide. Similarly, when a piece of calcite is introduced into a solution of cerium chloride and gold chloride, as the free acid is neutralized by the calcium carbonate a deposit of cerium dioxide containing metallic gold begins to form on the calcite.

The presence of gold in the manganese deposits, which observation has been studied by Emmons,[2] may be due to the fact that manganese is a significant agent in the superficial transportation of gold; but such is by no means necessarily the case. Two distinctly different kinds of reactions may be going on. In one case a chloride solution, containing free acid on coming in contact with an oxidized manganese deposit will produce free chlorine, or its equivalent. This chlorine solution can then dissolve gold and cause the production of a gold bearing manganese solution, which, so long as it contains considerable free acid, is quite permanent; but, when, it comes in contact with any neutralizing agency, for example, a limestone, metallic gold and manganese dioxide would be at once precipitated. This accords with experiments which have been reproduced in the laboratory, and which do not, as indicated by Emmons, require such a reducing agent

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[1] *J. Eng. Ind. Chem.*, 5, 560 (1913).

[2] Emmons, *Trans. Am. Inst. Min. Eng.*, 1910, 768.

as ferrous sulfate or other reducing agents as indicated by Wells,[1] to produce a precipitate. On the other hand, the gold present in the manganese deposits adjacent to other gold deposits may be due wholely to the fact that gold solutions in contact with manganese dioxide yield metallic gold, by virtue of the principle of auto-reduction shown by other peroxides with gold solutions.

The auto-reduction of gold solutions to metallic gold has apparently, thus far, not been considered as an important geological factor in the secondary deposition of gold, but it is doubtless possible that in many instances one can conceive of the oxygen of the air as being the real agent which causes the gold to be reduced in presence of a manganese or similar compound which acts as a catalytic agent.

UNIVERSITY OF WISCONSIN,
MADISON, WIS.

THE VOLUMETRIC DETERMINATION OF TITANIUM AND CHROMIUM BY MEANS OF A MODIFIED REDUCTOR.

BY C. VAN BRUNT.

Received May 4, 1914.

Shimer and Shimer[2] have described a modification of the method of Newton[3] for the determination of titanium, in which the reduction by boiling with zinc in a flask is supplanted by the use of a Jones reductor. The authors found that the ordinary form of this familiar apparatus, as used in the determination of iron, does not give complete reduction—a fact which the present writer can corroborate. They accordingly substituted a much longer and narrower tube, which modification had the desired effect.

The proposed method seemed to offer a way of escape from the tedious methods in vogue. These must include the original Newton method which, though for most purposes preferable to the gravimetric, is still lacking, mainly because of the slow disappearance of the last portions of the zinc, and the difficulty of preventing, with certainty, during this stage, the partial reoxidation of the very sensitive hot titanous solution.

But in practice in this laboratory, the Shimer reductor filled with 20-mesh zinc has been found to offer little, if any, advantage in point of time, because of the extremely slow passage of the solution through the long, thin tube. The difficulty of preventing reoxidation was present here also.

This latter point, however, was successfully met by the simple device of letting the titanous solution run directly from the reductor into an excess of ferric solution previously placed in the receiving vessel. An ex-

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[1] *Trans. Am. Inst. Min. Eng.*, **1910**, 793.

[2] *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, **1**, 445.

[3] *Am. J. Sci.*, [4] **25**, 130, 343.