

chloride to metal instantaneously. Many of the organic liquids which are immiscible with water, extract auric chloride from its aqueous solution.

3. It has not been possible to produce the aurous type of compounds by the use of an organic reducing agent.

4. Of the inorganic reducing substances sulfurous acid and arsenious oxide are the only ones studied which are capable of reducing auric to aurous gold, all others throw out metallic gold. Of these two, sulfurous acid is by far the more satisfactory reagent for reducing auric compounds to the aurous form. Its use is with the double auric chlorides, for in the absence of another salt, sulfurous acid reduces auric chloride directly to metallic gold, without apparent indication of production of the aurous state.

UNIVERSITY OF WISCONSIN, MADISON, WIS.

AUROUS CHLORIDE.

By MELVIN E. DIEMER.

Received March 27, 1913.

Although univalence is one of the factors which places gold in the first group of the periodic system, the derivatives of the valence of one have not received as much attention along certain lines as is desirable.

The most satisfactory work of recent times on aurous chloride has been conducted by Lengfeld¹ who heated auric chloride for some time at a temperature of 185°. He states that at this temperature it slowly dissociates into gold and chlorine.

A few years later experiments were made in the laboratory of Professor Lenher in which auric chloride was heated to 100° and the substance weighed at definite intervals of time, thereby determining the loss of chlorine. These results plotted graphically gave a continuous curve, which showed no break or indication of change from auric chloride to pure metallic gold, and at the time apparently indicated a questionable existence of aurous chloride.

The auric chloride used in the above experiments was prepared by dissolving metallic gold in aqua regia, and removing the excess of acid by evaporation. This was in reality HAuCl_4 with, beyond doubt, a considerable quantity of water.

This work was repeated by the author, using material prepared in a like manner, and the same results obtained. Furthermore, when the substance thus prepared was heated in an atmosphere of hydrochloric acid gas, there was no intermediate step apparent between auric chloride and metallic gold.

Further experiments along this line were undertaken and it was found that if the auric chloride was prepared in another manner, the result of

¹ *Am. Chem. J.*, 26, 324 (1901).

heating was quite different. To this end, gold was dissolved in aqua regia, the excess of acid removed by evaporation, and the residue heated in a current of dry chlorine gas, the temperature being maintained at 200° for one-half hour. This gave AuCl₃ free from hydrochloric acid and water, which when heated to 100° showed no loss in weight nor slightest indication of decomposition.

This anhydrous auric chloride when heated in an atmosphere of hydrochloric acid gas at a temperature of 190 to 200° evolved chlorine and assumed a yellowish white color, the new product undergoing no further change by prolonged heating at this temperature.

A weighed quantity of AuCl₃ prepared after the above method was heated at a constant temperature of 190° and the material weighed at definite intervals. By this means the relation of the loss of weight to the time of heating could be represented graphically, thus obtaining a criterion as to the nature of the substance formed—whether it was a mixture of gold and auric chloride or the chemical compound aurous chloride.

RESULTS.

	Weight of anhydrous AuCl ₃	3.3534
Time of heating (minutes).		Loss in weight (gram).
15		0.5981
30		0.7401
45		0.7736
60		0.7969
75		0.7991
90		0.8021
105		0.8045
	Loss of weight in 60 minutes (where rate of decomposition becomes constant).....	0.7969
	Calculated loss of chlorine (3.3534 grams AuCl ₃ to AuCl)...	0.7839

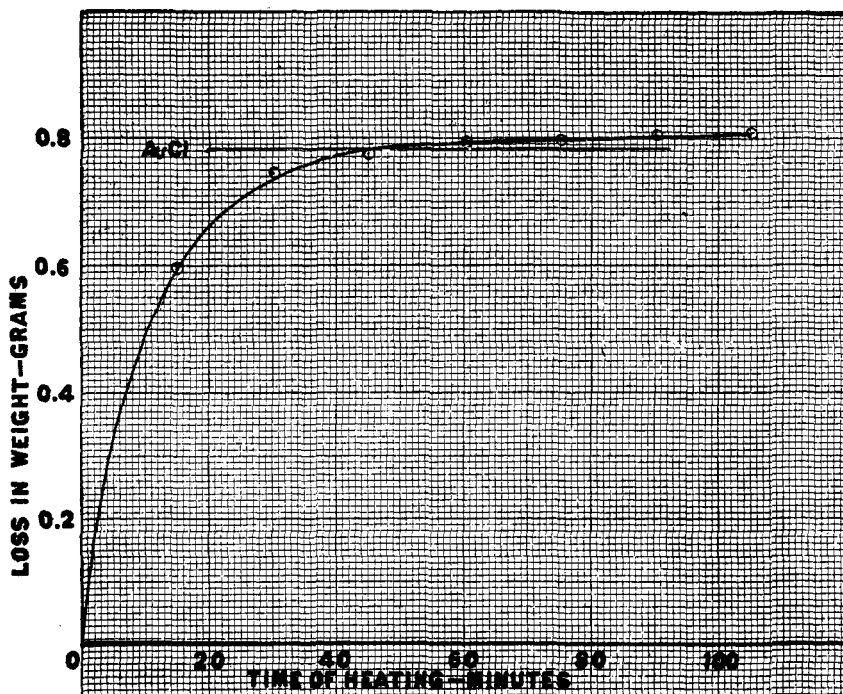
Inasmuch as the decided break in the curve plotted from these results falls at the point where the material is entirely converted to AuCl, the existence of a definite chemical compound is indicated. The small losses beyond this point are probably due to decomposition incurred by small quantities of aqueous vapor.

Aurous chloride prepared in this manner is decomposed by water, even moist air quickly causing the separation of metallic gold, hence, in its preparation moisture must be rigidly excluded. When boiled with water, complete decomposition is effected, the products being in the following quantitative ratio:

	Gram.
Weight of gold separated as metal.....	0.5916
Weight of gold taken in solution as AuCl ₃	0.2959

This gives the ratio—Au : AuCl₃ :: 2 : 1 and the reaction 3AuCl = 2Au + AuCl₃.

Aurous chloride is soluble in ammonium hydroxide in a manner similar to silver chloride, and when such a solution is acidified with hydrochloric acid a white crystalline substance is precipitated which cannot be dried,



CURVE 1

owing to its instability. By rapid manipulation it may, however, be removed from the solution and the ratio of constituents determined. Following is an analysis:

	Au.	NH ₃ .	Cl.
Found.....	79.30%	6.91%	13.74%
Calculated for AuNH ₃ Cl.....	79.00	6.80	14.20

This same substance can be prepared by a different procedure described later.

When the ammoniacal solution of aurous chloride is treated with a strong solution of sodium or potassium hydroxide, a white flocculent precipitate separates, which, owing to its extreme instability, darkens within a few minutes. The partially decomposed substance when gently heated explodes violently. This compound, like the preceding may be prepared by another method.

When heated in an atmosphere of nitric oxide or carbon monoxide, auric chloride is decomposed with the separation of metallic gold. The

reaction with carbon monoxide is of especial interest, inasmuch as phosgene is formed in which auric chloride is volatil to a considerable extent.

It is readily observed from these experiments that the foremost factor in the preparation of aurous chloride is the exclusion of water. Absolutely anhydrous auric chloride must be used, and the same heated in an atmosphere free from aqueous vapor. It is possible to prepare AuCl by heating AuCl₃ in dry air, but the product is decidedly impure, being contaminated with quantities of metallic gold. When one employs an atmosphere of hydrochloric acid gas, this marked dissociation is obviated, and when a temperature of 190° to 200° is maintained, a very pure product is obtained.

Preparation of Aurous Chloride by Partial Reduction of Auric Chloride.

When a solution of auric chloride (or hydrochlorauric acid) is treated with sulfur dioxide, it is commonly noticed that the solution bleaches to a certain extent before the separation of metallic gold, but this bleaching cannot be carried to the extent of a colorless solution without simultaneous partial decomposition.

This is true of solutions containing auric chloride alone, but if we add to such a solution a quantity of sodium, potassium, ammonium, calcium, or magnesium chloride, the yellow color of the auric salt can be entirely removed by sulfur dioxide, and the colorless solution thus obtained remains for quite a period without the separation of metallic gold.

By means of a standard solution of sulfur dioxide added from a buret, such mixed chloride solutions may be titrated, and inasmuch as the coloration imparted by auric chloride is about as delicate as that of iodine in solution, the end point obtained gives about the same degree of accuracy as an iodine titration with thiosulfate without the addition of starch.

Therefore, if standard sulfur dioxide water be employed in titrating solutions containing known amounts of auric chloride in the presence of one of the chlorides before mentioned, the degree of reduction incurred may be definitely ascertained.

The results obtained by such a procedure are as follows:

	No. 1.	No. 2.
Weight of Au ₂ O ₃ in solution as AuCl ₃	0.06887	0.06887
Reduction incurred in the production of a colorless solution by means of SO ₂ , calculated as grams O ₂	0.00496	0.00500
Calculated reduction of the auric present to aurous (as grams O ₂)	0.00498	0.00498

While the above ratio indicates the production of the aurous state, it was considered expedient to determine the variation of the single potential of the element in solutions of auric chloride to which had been added varying amounts of sulfur dioxide.

This was carried out using solutions of known auric chloride content, in the presence of a quantity of a certain chloride (NaCl , KCl , NH_4Cl , CaCl_2 , MgCl_2), and to this mixture adding definite volumes of a standard solution of sulfur dioxide. After each addition of the latter the single potential of gold in the solution was determined. Throughout the experiments the concentration of all substances in solution was kept constant so that the observations made are in no way due to concentration effects.

The following are the results obtained from the determination of the single potential of gold in an auric chloride solution containing sodium chloride, at various stages of its reduction by means of sulfur dioxide:

Auric chloride solution (0.00307 gram Au per cc.).....	20.0 cc.
Sodium chloride solution (4 N).....	50.0 cc.
Sulfur dioxide water (O_2 factor = 0.000497 gram per cc.) required to bleach 20.0 cc. AuCl_3 solution.....	10.0 cc.
Reduction incurred (as gram O_2)	{ (1) Found by experiment..... 0.00497 gram. (2) Calculated for formation of aurous from auric..... 0.00498 gram
Potential of calomel electrode.....	
Galvanometer reading of standard cell (1.01875 v.).....	511.0

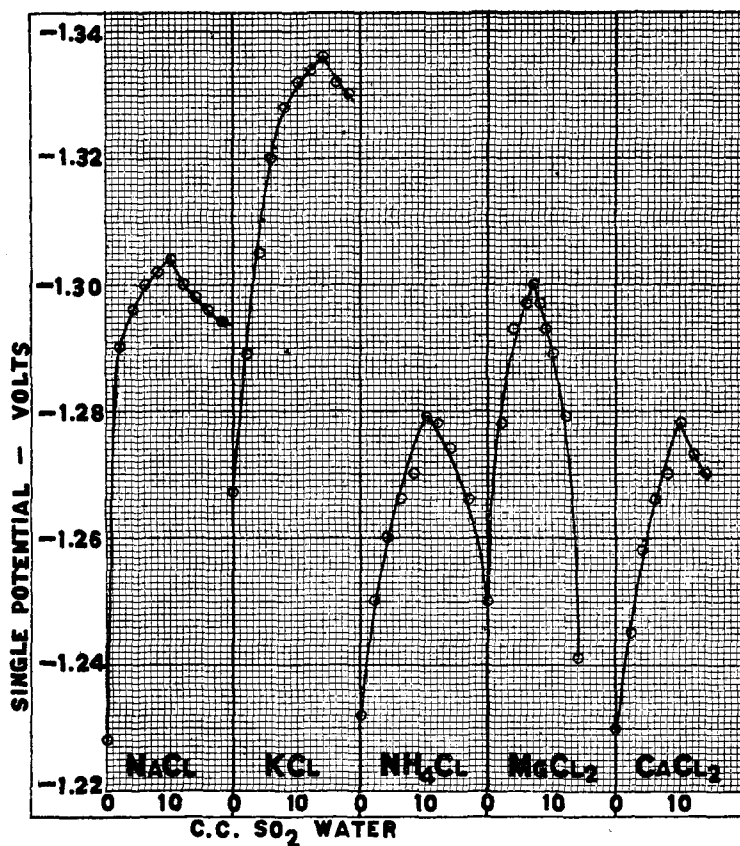
No.	SO_2 water. Cc.	AuCl_3 solution. Cc.	Water. Cc.	NaCl solution. Cc.	Galvan. reading.	Single potential. Volts(-).
1	0.0	10.0	10.0	5.0	335	1.228
2	2.0	12.0	..	6.0	366	1.290
3	4.0	14.0	..	7.0	369	1.296
4	6.0	16.0	..	8.0	371	1.300
5	8.0	18.0	..	9.0	372	1.302
6	10.0 ¹	20.0 ¹	..	10.0	373	1.304
7	12.0	22.0	..	11.0	371	1.300
8	14.0	24.0	..	12.0	370	1.298
9	16.0	26.0	..	13.0	369	1.296
10	18.0	28.0	..	14.0	368	1.294
11	20.0	30.0	..	15.0	367	1.292
12	22.0	32.0	..	16.0	366	1.290
13	24.0	34.0	..	17.0	364	1.286
14	26.0	36.0	..	18.0	363	1.284
15	28.0	38.0	..	19.0	362	1.282
16	30.0	40.0	..	20.0	361	1.280
17	32.0	42.0	..	21.0	360	1.278
18	34.0	44.0	..	22.0	358	1.274
19	36.0	46.0	..	23.0	356	1.270
20	38.0	48.0	..	24.0	353	1.264
21	40.0	50.0	..	25.0	345	1.248
			Dropped to		125	0.808

It will be noted from this table that the maximum single potential electromotive force is reached when the degree of reduction corresponds

¹ Colorless solution.

to the formation of a colorless solution, which as we have seen is identical with the production of an aurous compound. This phenomenon is certainly indicative of the existence of a definite chemical compound.

In a similar manner the single potential of gold in auric chloride solutions containing other chlorides was determined. These included the chlorides of potassium, ammonium, magnesium and calcium.



CURVE 2

In all of these curves the same order of phenomenon is shown, namely, a decided break at exactly the point where the degree of reduction corresponds to the formation of an aurous compound. Furthermore, this is the only break shown between the auric condition and complete reduction to metal. Hence, it may be concluded that auric chloride under these conditions shows reduction definitely to aurous chloride as an intermediate reduction stage.

Further study of these solutions shows that they are in reality more

stable in some respects than the auric. It requires considerable excess of sulfur dioxide to cause precipitation of metal, and with oxalic acid, which if boiled with a solution of auric chloride alone, soon causes precipitation, it is almost impossible to affect complete reduction to metal.

The exact amount of a chloride necessary to prevent the precipitation of metallic gold during the process of reduction from auric to aurous is somewhat difficult to determine, inasmuch as the stability of these solutions seems to depend to a large extent upon the concentration of the particular chloride present. Thus, when the aurous solution is saturated with sodium chloride, it is much more stable than when only a small amount is present.

To this end solutions of potassium, sodium, ammonium and calcium chlorides were used containing known amounts per cubic centimeter, and by means of these it was determined what quantity was necessary for the production of a colorless solution when a known amount of auric chloride was reduced to aurous in its presence. This required that the colorless stage be attained before the separation of metal.

With sodium, potassium, and ammonium chlorides, the smallest amount which would allow decoloration of the auric chloride by means of sulfur dioxide without simultaneous partial precipitation of the gold was one molecule of the chloride to one molecule of auric chloride. In the case of calcium chloride, about forty molecules were required to each molecule of auric chloride.

In these extreme cases with the small amount of alkali chloride present, although the solutions were completely decolorized, metallic gold separated within a few minutes.

These experiments lead one to believe that in these solutions (with the exception of calcium chloride) the aurous gold exists as a compound of the type $\text{AuCl} \cdot \text{NaCl}$, which in itself is unstable, but in the presence of a large amount of some other chloride becomes more stable, the concentration retarding the dissociation of the aurous chloride into metallic gold and auric chloride.

When decomposition of these double aurous compounds takes place, the solution becomes yellow, due to the formation of auric chloride, and metallic gold is simultaneously precipitated.

These solutions of aurous chloride in the presence of various other chlorides offer us a means of study hitherto unknown, namely, a soluble salt of aurous gold by which other aurous compounds may be prepared. For example, when one of these solutions is made ammoniacal and then acidified with hydrochloric acid, a white crystalline compound is precipitated having the same composition as that described on p. 554. Also, if to the ammoniacal solution strong caustic alkali is added, a white unstable compound is formed.

This investigation was undertaken at the suggestion of Professor Lenher, and the author takes this opportunity to express his gratitude for the many gracious and helpful suggestions tendered throughout the course of the work.

UNIVERSITY OF WISCONSIN, MADISON, WIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

YTTRIUM SODIUM SULFATE.

BY C. JAMES AND H. C. HOLDEN.

Received March 3, 1913.

The separation of the cerium and yttrium earths is usually effected by adding potassium or sodium sulfate to a sulfate solution of the rare earths, the whole being thoroughly stirred and allowed to stand for some time. Some writers state that potassium sulfate is the better, while others recommend sodium sulfate. The authors, who always employ sodium sulfate, at first obtained varying results, which led to the investigation of the system yttrium sulfate, sodium sulfate and water.

At an early stage of the work, it was found that sodium hydroxide was not an ideal reagent for the quantitative precipitation of yttrium, since the results came a little high and did not check well. The work upon the sebacates¹ showed that ammonium sebacate was well adapted for this purpose.

Twenty-four bottles of 100 cc. capacity were made up containing varying amounts of yttrium sulfate, sodium sulfate and water. The greatest amount of yttrium sulfate added to any one was nine grams. It was found that even eight grams were too much when added to bottles of greater concentration. The bottles were sealed and placed in a thermostat on November 25, 1911. They were rotated at 25° until March 29, 1912, when the first analyses were made. From the results obtained, it was evident that the system was not yet in equilibrium, and accordingly the bottles were re-sealed and returned to the thermostat. From about the middle of June to the first of September, the bottles were allowed to stand at ordinary temperatures. At the latter date the rotation was recommenced and allowed to proceed until January 18, 1913. At this time the bottles were again opened and the solutions submitted to analysis. Even after this extra period it was found that four bottles were, apparently, still in a metastable condition, as can be readily seen from an observation of the curve.

It might be interesting to mention that, when the mixtures were first placed in the thermostat, the solid phase disappeared in most of the bottles; and that they remained perfectly clear for some weeks, after which the double salt was very slowly deposited.

¹ THIS JOURNAL, 34, 772.