THE SOLVENT EFFECT OF FERRIC AND CUPRIC SALT SOLUTIONS UPON GOLD.

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While analyzing a sample of gold bullion, containing considerable tin (25 per cent.), some very interesting irregularities were observed. The precipitation of the gold by oxalic acid was not desirable on account of its extreme slowness, forty-eight hours being necessary to complete the precipitation (Fresenius, p. 328, ed. 1890). Again, the oxalic acid in the filtrate must be completely destroyed before the tin can be precipitated by hydrogen sulphide.[1] This requires an evaporation with sulphuric acid, a tedious and disagreeable operation.[2]

To separate the gold from the tin, precipitation by ferrous sulphate appeared to be the most favorable method. The precipitated gold, however, was purple in color and contained tin. When sufficient hydrochloric acid had been added to keep the tin in solution, the precipitation of the gold was not complete. The question arose then, whether or not the gold was soluble in the stannic salts, or in ferric salts, in the presence of so much hydrochloric acid. Preliminary determination showed that gold is soluble in hydrochloric acid solutions of ferric and stannic salts.

Comey's "Dictionary of Solubilities" gives the bare statement that gold is soluble in solutions of ferric and cupric salts without reference to the literature. Fresenius advises in precipitating gold with ferrous sulphate to "heat gently for a few hours, during the precipitation" and makes the statement, that there are "no inherent sources of error in this method."

It was planned, therefore, to study the solubility of gold in ferric salt

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[1] F. W. Clarke, *Chem. News*, 21, 124.

[2] F. P. Dewey, *Am. Chem. J.*, 1, 244.

solutions, to see what effect the concentration of salt and acid had upon the solubility; likewise, to find out what influence the temperature exerted upon the solubility and the effect of the presence of ferrous sulphate. The solvent action upon gold of cupric chloride solutions was also studied.

Materials.—The gold used was proof gold made by Mr. Eckfeldt, of the Philadelphia Mint, from pure electrolytic gold (999 fine). The latter was dissolved in aqua regia, diluted and allowed to stand for two weeks. The solution was decanted from any silver chloride, and potassium chloride and alcohol were added to precipitate any platinum. After standing two weeks the solution was decanted and precipitated with sulphurous acid. It was redissolved, the above steps repeated and final precipitation made by oxalic acid. The precipitated gold was melted in Beaufay crucibles under borax, and rolled into ribbons 0.009 inch thick. From this little pieces, one-eighth inch square, were taken and washed with alcohol.

The ferric iron salt used was C. P. iron alum, since it approximates the conditions which obtain in the precipitation of gold by ferrous sulphate, and as a ferrous salt, "pure" ferrous sulphate was used.

The copper salt used was C. P. cupric chloride.

The general method of procedure was as follows: The solution containing the desired amount of salt and acid was placed in a 1/4 liter Erlenmeyer flask. The neck of the latter was provided with a perforated cork carrying an air condensing tube fourteen inches long and one-half inch in diameter. The projecting end of the tube was closed with a small funnel and the latter covered with a watch-glass to prevent evaporation. The neck of each flask fitted into a hole in a thin board and was held in place by a slotted leather washer. The four flasks were then lowered into a constant-level bath of boiling water and retained at this temperature from thirty to forty-five minutes before adding the gold. A string was tied around the neck of the hot-water flask and the condensers of the Erlenmeyers to keep the latter from tilting when immersed two-thirds of their depth. The water in the bath was kept boiling briskly.

The solubility at lower temperature was also determined in 1/4 liter Erlenmeyer flasks, necks of which were closed with small funnels and watch-glasses to prevent evaporation. The flasks were kept on a steam plate. The solutions at definite intervals were poured into small beakers and covered with watch-glasses. The flasks were then filled twice with tap water and the gold washed into porcelain crucibles with distilled water by placing the crucible bottom up on the neck of the flask and quickly inverting. The washing was completed in the crucible. The solutions were returned to the flasks and these again placed in the bath. This has been found necessary at higher temperatures, since owing to its diminished solubility, gold separates out upon cooling.

The weighing of the gold was done on an assay balance sensitive to

1/200 of a milligram and in each experiment 250 milligrams of gold were taken.

Experimental Results.—Upon boiling 25 and 50 cc. of hydrochloric acid (sp. gr. 1.178) diluted to 125 cc. with 250 milligrams of gold for several hours, there was no loss in the weight of gold.

Table I gives the loss in weight of gold due to its solubility in a hydrochloric acid solution of iron alum at a temperature of 38–43°.

TABLE I.

Time.[1] Hours.	A. 1 g. Fe. 25 cc HCl. Mg. gold dissolved.	B. 1 g. Fe. 50 cc. HCl. Mg. gold dissolved.	C. 2 g. Fe. 25 cc. HCl. Mg. gold dissolved.	D. 2 g. Fe. 50 cc. HCl. Mg. gold dissolved.
16	1.00	1.30	1.08	1.47
22	1.12	1.55	1.20	1.81
40	1.52	2.15	1.82	2.75
46	1.71	2.34	2.02	2.95
64	1.96	3.10	2.60	3.79
72	2.12	3.30	2.83	4.05
89	2.32	3.65	3.22	4.65
100	2.40	3.76	3.38	4.81
113	2.45	3.95	3.51	5.12
124	2.60	4.09	3.63	5.39
161	2.78	4.36	3.95	5.96
185	2.90	4.49	4.11	6.22

The preceding results are graphically presented in Curve I.
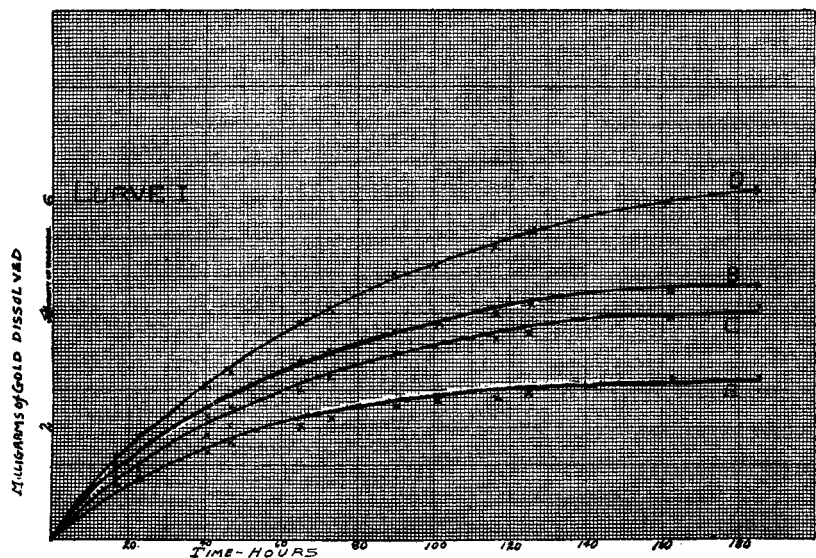
[1] These periods represent the actual time during which the gold was acted upon by the solutions. The process was necessarily interrupted for analytical control.

A contains 1 gram Fe as iron alum, 25 cc. HCl (sp. gr. 1.178)
B　　　"　　1　　"　　"　"　"　"　　"　50　"　　"　　("　"　1.178)
C　　　"　　2　　"　　"　"　"　"　　"　25　"　　"　　("　"　1.178)
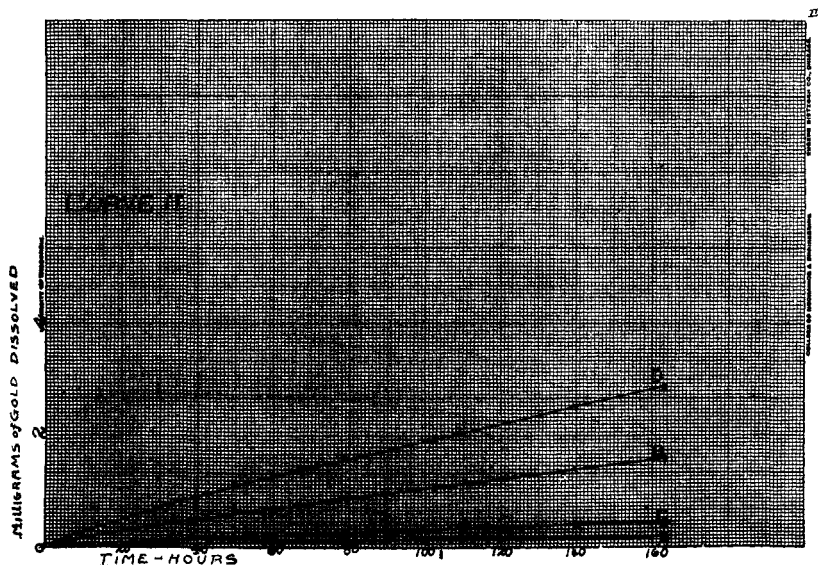D　　　"　　2　　"　　"　"　"　"　　"　50　"　　"　　("　"　1.178)

Total dilution 125 cc. at about 20°.

The solvent action of cupric chloride solutions of varied concentrations upon gold at a temperature of 38–43° is shown in the following table:

TABLE II.

Time.[1] Hours.	A. 1 g. Cu. 25 cc. HCl. Mg. gold dissolved.	B. 1 g. Cu. 50 cc. HCl. Mg. gold dissolved.	C. 2 g. Cu. 25 cc. HCl. Mg. gold dissolved.	D. 2 g. Cu. 50 cc. HCl. Mg. gold dissolved.
19	0.03	0.26	0.05	0.39
25	0.09	0.36	0.05	0.54
43	0.10	0.54	0.14	0.94
49½	0.12	0.61	0.15	1.07
66½	0.11	0.76	0.17	1.40
78	0.14	0.87	0.22	1.58
91	0.14	0.92	0.24	1.75
102	0.16	1.02	0.27	1.90
139	0.18	1.34	0.32	2.45
163	0.23	1.60	0.39	2.84

These data are graphically presented in Curve II.

[1] These periods represent the actual time during which the gold was acted upon by the solutions. The process was necessarily interrupted for analytical control.

A contains 1 gram Cu as chloride, 25 cc. HCl (sp. gr. 1.178)
B   "   1   "   "   "   "   50   "   "   ("   "   1.178)
C   "   2   "   "   "   "   25   "   "   ("   "   1.178)
D   "   2   "   "   "   "   50   "   "   ("   "   1.178)

Total dilution 125 cc. at about 20°.

From these two tables, one sees a regular change in solubility with a change in concentration of acid or salt. In case of ferric alum, by doubling the concentration of the acid, the solubility is increased by the factor 1.5 as is shown by the ratios B/A and D/C. By doubling the concentration of the salt, the solubility of the gold is increased by the factor 1.4 as shown by the ratios C/A and D/B.

Similarly by doubling the concentration of the acid, the solubility of gold in cupric chloride solutions is increased *seven* times. By doubling the concentration of the cupric salt, the solubility factor is only raised 1.7 times. From these facts, the conclusion may be drawn that in the solvent action of cupric salts upon gold, the presence or absence of hydrochloric acid is of the greatest importance, while for ferric alum solutions, variations in concentration of salt and of acid cause almost equal change in the solubility of gold.

Upon placing solutions of varying concentration of ferric iron and hydrochloric acid in the water bath and determining the solvent action at the temperature of boiling water, we have the following solubilities at 98–100°.
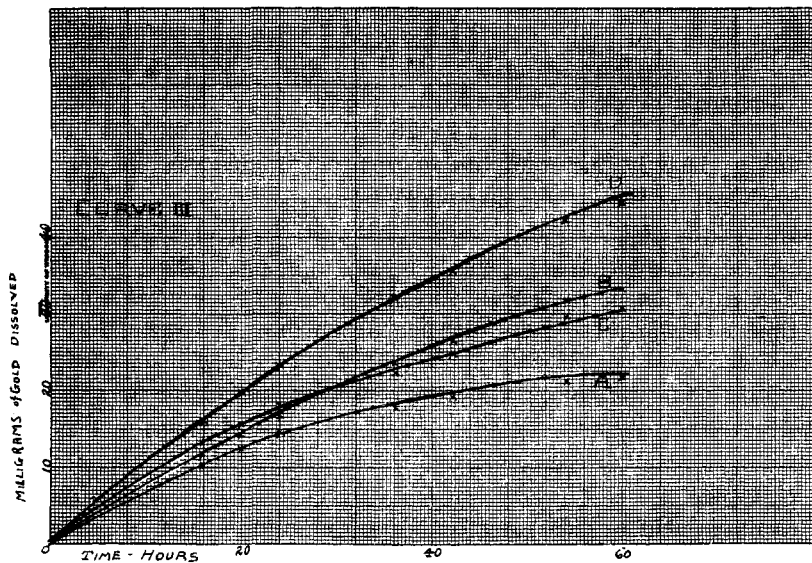
TABLE III.

Time. Hours.	A. 1 g. Fe. 25 cc. HCl. Mg. gold dissolved.	B. 1 g. Fe. 50 cc. HCl. Mg. gold dissolved.	C. 2 g. Fe. 25 cc. HCl. Mg. gold dissolved.	D. 2 g. Fe. 50 cc. HCl. Mg. gold dissolved.
1	1.13	0.78	1.15	1.27
2	1.99	1.74	2.56	2.86
4	3.46	3.31	4.55	5.06
16	10.09	11.37	13.15	15.56
20	12.20	13.72	15.59	19.41
24	14.37	16.49	17.96	23.29
36	17.38	23.27	22.07	31.73
42	18.79	26.30	24.62	35.29
54	20.94	31.39	29.49	42.11
59½	21.64	33.12	30.64	44.43

A contains 1 gram Fe as iron alum, 25 cc. HCl
B   "   1   "   "   "   "   "   50   "   "
C   "   2   "   "   "   "   "   25   "   "
D   "   2   "   "   "   "   "   50   "   "

Total dilution 125 cc. at about 20°.

This solubility is graphically presented in Curve III.

Upon cooling, the solutions of ferric alum deposited fine spangles of gold. After standing for four days, the gold was filtered off, ignited and weighed with the following results: A = 13.29 mg. gold; B = 13.57 mg.; C = 16.47 mg.; D = 25.05 mg.

The solvent action of cupric chloride solutions on gold at a temperature of 98–100° is as follows:

TABLE IV.

Time. Hours.	A. 1 g. Cu. 25 cc. HCl. Mg. gold dissolved.	B. 1 g. Cu. 50 cc. HCl. Mg. gold dissolved.	C. 2 g. Cu. 25 cc. HCl. Mg. gold dissolved.	D. 2 g. Cu. 50 cc. HCl. Mg. gold dissolved.
1	0.15	0.34	0.17	0.46
4	0.55	1.23	0.55	1.35
16	1.34	5.00	2.12	8.80
20	1.63	6.52	2.78	11.86
26	2.17	9.13	3.59	15.70
38	3.13	13.98	5.07	23.14
43	3.61	16.54	5.77	26.62
48	4.07	19.26	6.26	30.80
60	4.82	26.37	7.47	39.09

A contains 1 gram Cu as cupric chloride, 25 cc. HCl.
B   "   1   "   "   "   "   "   50   "   "
C   "   2   "   "   "   "   "   25   "   "
D   "   2   "   "   "   "   "   50   "   "

Total dilution 125 cc.

This solubility is graphically presented in Curve IV.

For a solution of ferric alum containing one gram of iron per 125 cc., doubling the concentration of hydrochloric acid increased the quantity of gold dissolved 1.53 times and where the iron solution contained 2 grams of iron per 125 cc. the solubility of gold was increased 1.46 times by doubling the concentration of acid. In like manner, when the concentration of hydrochloric acid is kept the same and the concentration of the iron doubled, the quantity of gold dissolved is increased; thus, where 25 cc. of strong hydrochloric acid were used, doubling the iron alum concentration increased the solubility of the gold 1.41 times; where 50 cc. of strong acid were used, doubling the iron concentration gave a slightly smaller effect, the solubility of gold being increased 1.34 times.
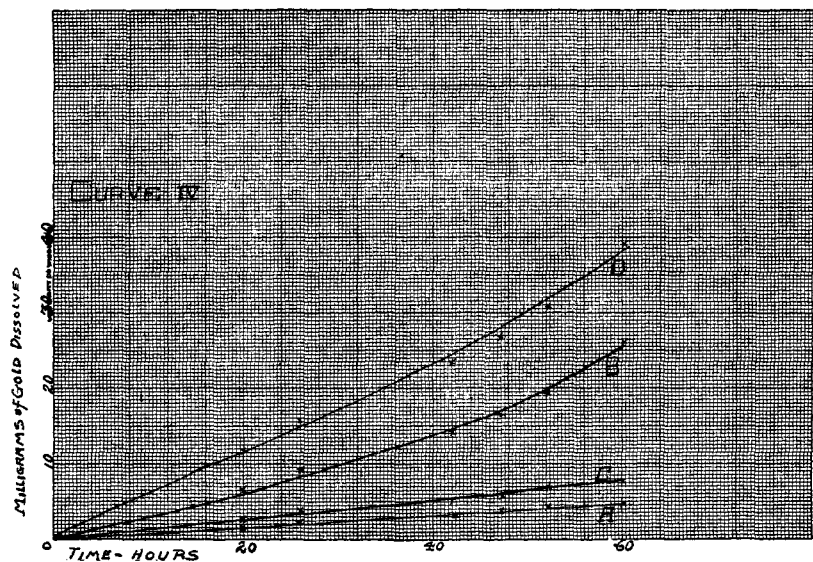
With cupric salts, however, this regular increase in the solubility of gold, due to increasing the concentration of acid and of cupric salt, is more pronounced than for acid solutions of iron salts. Doubling the concentration of acid increases the quantity of gold dissolved 5.47 times where 1 gram of copper as cupric chloride per 125 cc. was used; where 2 grams of copper per 125 cc. were taken, doubling the acid concentration increased the solubility of the gold 5.23 times.

It should be borne in mind that we are here discussing ratios and that the quantity of copper salt in solution exerts a marked influence upon the quantity of gold dissolved. By doubling the concentration of cupric salt, the solubility of gold in acid solutions (containing 25 cc. of strong hydrochloric acid per 125 cc.) is increased 1.55 times, and for solutions

where 50 cc. of strong hydrochloric acid were used, the solubility of gold was increased 1.48 times.

If we now look at the effect the increase of temperature had upon the solubility of gold, we find some interesting facts. The amount of gold, in the case of the iron salt (Tables III and I), dissolved in 59.5 hours at 98–100°, divided by the corresponding amount of gold dissolved in solutions of the same salt of the same concentration in 64 hours at 38–43° (nearest determination without interpolating), we get $21.64/1.96 = 11.04$, $33.12/3.10 = 10.7$, $30.64/2.60 = 11.07$, $44.43/3.79 = 11.7$.

In the case of the copper salt, the amount of gold dissolved in 48 hours at 98–100°, divided by the amount of gold dissolved in solutions of the same concentration for 49.5 hours at 38–43° (nearest determination without interpolating), we get $4.07/0.12 = 34$, $19.26/0.61 = 32$, $6.26/0.15 = 41.8$, $30.80/1.07 = 29$. From these relations it is seen that the solvent ac ion of these salts increases regularly with the temperature, and in the case of the copper salt, this increase in solubility is about three times the increase found for the iron salt. The increase in solubility due to raising the temperature seems to be independent of the concentration of the solvent.

This study was discontinued for a time to observe the effect of ferrous salt upon the solvent action of ferric salts. Accordingly, solutions of iron alum containing 1 gram of iron with varying quantities of hydrochloric acid were made up to the desired volume (less the volume of ferrous sulphate solution to be added). These solutions were poured into the flasks and the latter immersed in boiling water and kept there for 30–40
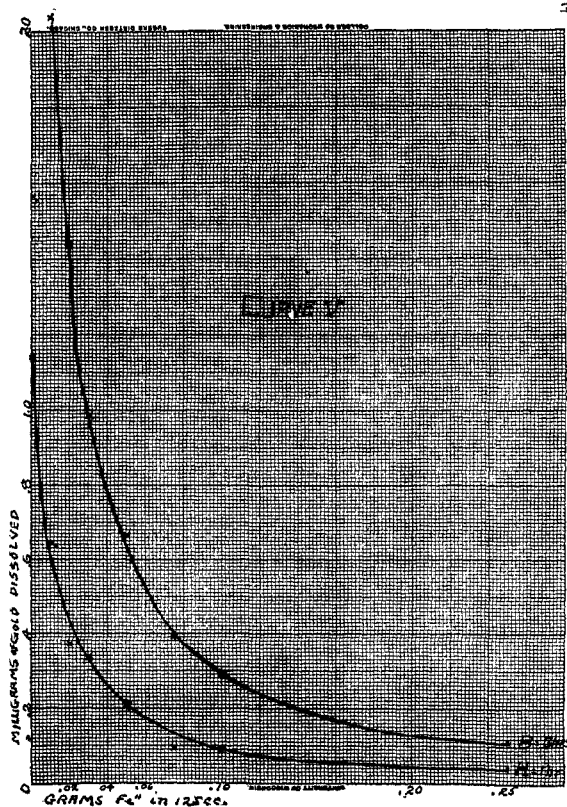
minutes. Five or ten minutes before adding the gold, the required amount of ferrous sulphate solution was added and subsequently 250 mg. of gold. At the expiration of an hour, these solutions were decanted from the gold into a beaker and covered with a watch-glass to prevent oxidation. After washing, igniting and weighing, the gold was returned to the flasks in the water bath for another period of two hours. On account of the oxidation of the ferrous sulphate, it was not thought advisable, under the present crude conditions, t) carry on the determinations for more than three hours, as the results would be valueless. The amount of ferrous iron present before and after the experiment was determined by titration with potassium bichromate solution.

The following are the results in tabulated form:

TABLE V.—EFFECT OF FERROUS SULPHATE UPON THE SOLUBILITY OF GOLD.

HCl, cc.	Fe. (Start). G.	Au dissolved.		Fe. (End). G.
		1 hr. Mg.	3 hrs. Mg.	
25	0.25	0.04	0.11	......[1]
50	0.25	0.02	0.04	......
25	0.1	0.09	0.29	......
50	0.1	0.05	0.30	......
25	0.075	0.09	0.39	0.0680
50	0.075	0.19	0.60	0.0571
25	0.05	0.21	0.66	0.0489
50	0.05	0.26	0.69	0.0398
25	0.03	0.34	0.98	0.0297
50	0.03	0.34	1.16	0.0207
25	0.02	....	1.39	0.0197
50	0.02	0.37	1.34	0.0116
25	0.01	0.64	2.16	0.0100
50	0.01	0.60	1.78	0.0051

From these results it will be seen that gold is soluble in ferric salts even in the presence of considerable ferrous salts and that apparently the solvent action of ferric salts upon gold varies inversely with the concentration of the ferrous salts present. Plotting the values for one hour on Curve V we have a regular curve expressing the effect upon the solubility of gold produced by a change in the concentration of the ferrous salts present. With increased concentration of acid there is an increased oxidation of the ferrous iron present.

Summary.

Gold is soluble in hydrochloric acid solutions of iron alum and of cupric chloride.

With increased concentration of acid or salt we have definitely increased rates of solubility and apparently definitely increased limit of solubility in the case of a salt of iron.

[1] Not determined.

The rate of solubility increases more with an increase in concentration of acid than with an increase in concentration of the salt. Particularly is this so in the case f copper salt.

With an increase in temperature from 38–43° to 98–100°, the rate of solubility increases eleven times in the case of iron. With the same increase in temperature the rate of solubility in cupric chloride solutions increases thirty-two times.

By doubling the concentration of acid at 38–43° the solvent action of cupric chloride solutions is increased seven times; at 98–100° it is increased five times.

The solvent action of ferric salt takes place even in the presence of ferrous salt and decreases with increase in concentration of the ferrous salt. In this case then, the precipitation of gold by ferrous sulphate would not be complete even in the presence of considerable ferrous salt. With increased concentration of ferric salt obtained by oxidation of ferrous sulphate by the gold chloride we would approach a balanced reaction.

It is advisable in the precipitation of gold by ferrous sulphate to use a rather large excess of ferrous sulphate, and if the precipitation takes place from a hot solution to allow the solution to cool down before filtering, since the solvent action of ferric salts is much more pronounced at the higher temperatures.

In the case of copper chloride, the solubility of gold apparently does not approach a limit. The amount of gold dissolved is proportional to the time, and there is apparently no decrease with time in the amount dissolved as in the case of iron salt. Can it be that the cupric chloride at the higher temperature is decomposed into chlorine and cuprous chloride which is reoxidized by the air and the hydrochloric acid present as in the Deacon process, and that the greatly increased solubility and constant rate of solution is due to the generation of minute quantities of chlorine? If there is an increased solubility without decomposition, as in the case of the ferric chloride solution[1] we would expect the gold to be deposited upon cooling. Since the cupric chloride solution of gold at 98–100° upon cooling and standing four days did *not* deposit gold, this fact might be taken as indicative of such decomposition.

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[1] The solution of gold obtained by boiling for two days, an iron alum solution (2 g. of Fe + 50 cc. of HCl dil. 125 cc.) with gold does not give any evidence of ferrous iron present on testing with potassium ferricyanide solution; yet on cooling, there is deposited from the solution fine spangles of gold.