

ART. XXXIX.—*On Colloidal Gold: Adsorption Phenomena and Allotropy*; by J. C. BLAKE.

[Contributions from the Kent Chemical Lab. of Yale University—CXX.]

RED and blue colloidal gold solutions have long been known,* the red being changed to blue by the action of electrolytes. Hence, in order to study all of the concurrent phenomena, it is necessary to begin with a red solution. All of the red solutions heretofore described, however, have either contained objectionable impurities, like the acids of phosphorus, or have been very dilute and hard to prepare in stable form with constant properties. I have found that a concentrated red gold solution, free from all these objections, may be prepared by pouring into acetylene water containing ether an ethereal solution of gold chloride dried at 170°. The resulting garnet-colored solution of colloidal gold is exceedingly stable, though quite strongly acid. It is scarcely turbid in ordinary light, but gives the Tyndall effect when a beam of light is thrown into it with a lens. This solution has been investigated with regard to the adsorption phenomena of the gold when precipitated by electrolytes, an investigation attended by some interesting observations on the apparent allotropy of gold.

It should be remembered that Linder and Picton† and Whitney and Ober,‡ working with colloidal solutions of arsenious sulphide, have found that when such solutions are coagulated by electrolytes, part of the basic radical of the electrolyte is retained by the coagulum, with the liberation of the corresponding amount of free acid in the filtrate. The base thus retained by the coagulum cannot be washed out with water. Since the suspended particles of which the colloidal solutions are made up are known to be negatively electrified, whereas the basic radicals or ions carry a positive charge, the question arises whether the basic radical retained by the coagulated colloid may not be held by reason of the mutual neutralization of these charges, with the formation of a chemical compound or pseudo-chemical compound, thus perhaps affording an indication of the nature of chemical union and proving that the phenomena of the permanent suspension of solid particles in liquids and their subsequent precipitation by electrolytes are essentially electrical, as is assumed in Whetham's§ hypothesis. It was thought that the

* Faraday, Phil. Trans., cxlvii, 145; Pogg. Ann., ci, 313. Zsigmondy, Lieb. Ann., ccci, 29, 361; Zeit. phys. Chem., xxiii, 63.

† Jour. Chem. Soc., lxvii, 63.

‡ Jour. Am. Chem. Soc., xxiii, 842.

§ Jour. of Physiol., xxiv, 288; Phil. Mag., xlvi, 474.

results to be obtained with colloidal gold solutions would be especially interesting in this connection, both because of the great improbability of ordinary chemical union between the gold and the basic radicals, and because of the ease and thoroughness with which the precipitated gold could be washed.

Red colloidal solutions of gold prepared according to the method just described were precipitated by solutions of barium compounds, and the coagulum was analyzed for gold, barium, and carbon, derived from the acetylene. Except when otherwise stated, all the filtrations and weighings were made on asbestos felt contained in a perforated platinum crucible. The mixed coagulum, either washed or unwashed, was ignited in a porcelain crucible and then treated with aqua regia in small amount either at the ordinary temperature or on the steam bath, the carbon being nearly all dissolved in the latter case. After dilution, the undissolved carbon was filtered off, washed, dried at 200°, weighed and ignited. The gold was determined as the metal in the filtrate from the carbon by precipitation with magnesium ribbon. The barium was precipitated as sulphate in the filtrate from the gold and weighed after standing twelve hours on the steam bath.

It was found that if the colloidal gold solution contained a little unreduced gold chloride, the coagulum was coherent, spongy, opaque, insoluble in water, and reflected brownish yellow light. If, however, the gold chloride had been completely reduced, the coagulum was blue-black, non-coherent, readily soluble in pure water to a blue colloidal solution, the color being due to transmitted light.

I. *The Spongy Form of Gold.*

In the following experiments the gold chloride used in preparing the colloidal gold solution was not quite all reduced, and the colloidal gold, precipitated with a solution of a barium salt, came down in the spongy form. The coagulum was either washed in succession with the amounts of water given in the table, the included liquid being finally pressed out of the spongy precipitate as much as possible, or the coagulum was not washed, but merely dried between filter papers. For purposes of comparison the amounts of the barium compounds (calculated as hydroxide) which were present in 0.5^{cm}³ of the supernatant liquid are also given in the table.

TABLE I.

Vol. of gold sol. cm ³ .	Precipitant.	Wash water cm ³ .	Mixed coagulum, ignited. gm.	Gold found. gm.	Ba(OH) ₂ found. gm.	Calc. amt. of Ba(OH) ₂ in 0.5 cm ³ supernatant liquid. gm.	Error of analysis. gm.
550	50 cm ³ $\frac{n}{10}$ —Ba(NO ₃) ₂	{ 300 50	0.4151	0.4151	0.0000	0.0003	0.0000
1200	n —BaCl ₂	{ 500 100 100	2.2668	-----*	0.0020	0.0033	-----
610	10 cm ³ $\frac{n}{10}$ —BaCl ₂	{ Not washed. Dried between filter papers. }	0.7569	0.7566	0.0000	0.0001	0.0003—
610	100 cm ³ n —BaCl ₂	{ filter papers. }	0.6499	0.6417	0.0066	0.0060	0.0016—†

From the foregoing results it is plain that very little of the barium compound is held by the gold under these conditions, and that the traces thus retained cannot readily be washed out—a condition agreeing exactly with what would be expected if the barium were held as nitrate or chloride dissolved in the liquid mechanically retained by the spongy gold. The obvious physical properties of this spongy gold proved to be identical with those of the gold thrown out from strong solutions of gold compounds by ferrous sulphate or oxalic acid, which is known to be crystalline.‡

II. *The Blue Form of Gold.*

In the following experiments the gold chloride used in preparing the colloidal gold solution was all reduced, and the colloidal gold, precipitated with a solution of a barium compound, came down in the non-coherent blue form. In the experiments given under A (p. 386), the coagulum was washed successively by decantation with the given amounts of hot water without the use of a filter, part of the finely-divided gold thus temporarily re-suspended being washed away. In the experiments given under B, the coagulum was thrown upon an ashless filter (or asbestos felt) held in a large platinum cone, the mother liquor was exhausted by suction, and the barium compound held by the unwashed gold and the filter was determined.

* Gold lost by explosion, presumably owing to the formation of a hydride during reduction by magnesium.

† This error becomes 0.0003—if the barium held by the gold be calculated as the chloride.

‡ Roscoe and Schoeffer, *Treatise on Chemistry*, 1898, ii, p. 399.

By comparing the amounts of the barium compounds thus found with the amounts of the barium compounds held by the filter in blank experiments similarly conducted, and with the amounts of the barium compounds held by 1^{cm}³ of the supernatant liquid, a very fair estimate of the amount of the barium compounds held by the gold can be arrived at. In these experiments the amounts of carbon left with the gold after ignition, not readily dissolved in the subsequent treatment with *aqua regia*, first became noticeable, indicating that in the former experiments most of the carbon had been lost by decantation. In the experiments given under C (p. 387), a freshly prepared solution of barium hydroxide, containing about 20^g^m per liter, was used as the precipitant, the supernatant liquid being still slightly acid; while in the experiments given under D, the barium hydroxide was added to alkaline reaction. The wash-water was neutral to litmus.

The results of Table II (pp. 386, 387) show that as long as the solution is even slightly acid only insignificant amounts of barium are held by the gold, whether washed or unwashed. Other colloidal (blue) gold solutions, prepared by the action of hydrazine hydrate on a water solution of gold chloride, in which the free acid was nearly neutralized by the hydrazine hydrate before the gold was precipitated by barium chloride, gave similar results. When the supernatant liquid becomes alkaline, on the other hand, the amount of barium retained by the gold becomes appreciable. It is probable that none of this amount was due to the presence of barium carbonate, although there was doubtless some barium chloride (formed by the reaction) present with the hydroxide in experiment (12) of the table, owing to the insolubility of the chloride in alcohol. There is, however, no reason to suppose that the amount of barium hydroxide retained by the gold precipitated from alkaline solution is greater than that which would have been retained, owing to the well-known tenacity of free alkalis for solid substances, by any finely-divided insoluble substance under similar conditions of concentration.* In fact, the absence of adsorption phenomena in acid solution and the presence of such phenomena in alkaline solution is in full accord with Van Bemmelen's functional equation for absorption from solution by porous solids

$$C''_{\text{KOH}} = f(C'_{\text{K}_2\text{SO}_4}, C'_{\text{SO}_3})$$

where C''_{KOH} is the concentration of the base in the liquid retained by the solid, and C' represents the concentrations of the given substances in the supernatant liquid. C'' increases as $C'_{\text{K}_2\text{SO}_4}$ increases, and decreases as C'_{SO_3} increases.

* Cf. Van Bemmelen, *Zeit. anorg. Chem.*, xxiii, 364.

Hence, it appears that adsorption phenomena are not pronouncedly concerned, if at all, in the color changes brought about in red gold solutions by electrolytes, or in the subsequent precipitation of the blue or of the spongy gold. Some interesting results might be obtained in this connection by working with neutral red gold solutions, such as might have been prepared by dialysing the ones here described; but it is difficult to see how any such results could be intelligible unless differentiated by a series of parallel experiments from the effects due to the hydrolysis of neutral salts and absorption of the basic radical by porous solids. If these two effects are identical, as suggested by Whitney and Ober, then Whetham's hypothesis can receive no support from the results to be obtained with them.

The "blue gold" precipitated in these experiments is amorphous and has a dark bronze appearance when viewed in reflected light. The three apparently allotropic forms of gold here noted, named according to the colors most readily observed, as in the case of silver,* are the following:

Form of gold.	Color in reflected light.	Color in transmitted light.
"Yellow gold"	Golden	Blue
"Blue gold"	Dark bronze	Blue
"Red gold"	Light golden†	Red

* This Journal [4], xvi, 282 (1903).

† Well seen in the Tyndall effect.

TABLE II.
 A. *Coagulum washed.*

No.	Vol. of gold solution cm ³ .	Precipitant.	Treatment of moist coagulum.	Coagulum, ignited, gm.	Gold found, gm.	Carbon found, gm.	Ba(OH) ₂ found, gm.	Calc. amt. of Ba(OH) ₂ in supernatant liquid, gm.	Ba(OH) ₂ in blank, (aver'ges) gm.	Error of analysis, gm.
1	600	100 cm ³ <i>n</i> -BaCl ₂	<i>Water.</i> { 500 100 1000 150 20 500 100 100 }	0.3216*	0.3200	-----	0.0013	0.5 cm ³ 0.0071	-----	0.0003—
2	1400	100 cm ³ <i>n</i> -BaCl ₂	{ 1000 150 20 }	0.5691	0.5690	-----	0.0003	0.0030	-----	0.0002+
3	1100	50 cm ³ 2 <i>n</i> -BaCl ₂	{ 500 100 100 }	0.8439†	0.8435	-----	0.0004	0.0037	-----	0.0000

 B. *Coagulum unwashed.*

No.	Vol. of gold solution cm ³ .	Precipitant.	Treatment of moist coagulum.	Coagulum, ignited, gm.	Gold found, gm.	Carbon found, gm.	Ba(OH) ₂ found, gm.	Calc. amt. of Ba(OH) ₂ in supernatant liquid, gm.	Ba(OH) ₂ in blank, (aver'ges) gm.	Error of analysis, gm.
4	760	25 cm ³ <i>n</i> -BaCl ₂	{ Collected on asbestos felt without washing.	0.9271	-----	Considerable	0.0009	1 cm ³ 0.0003	0.0005	-----
5	880	25 cm ³ <i>n</i> -BaCl ₂	{ Collected on filter paper without washing.	0.8875	-----	amounts.	0.0027	0.0024	0.0023	-----
6	1000	25 cm ³ <i>n</i> -BaCl ₂	{ Collected on filter paper without washing.	0.3520	0.3503	Dissolved with the gold, by digestion.	0.0002	0.0002	0.0005	0.0015—†
7	980	25 cm ³ <i>n</i> -BaCl ₂	{ Collected on filter paper without washing.	1.3239	1.3161	0.0027	0.0037	0.0022	0.0023	0.0013—†

* Loss above 80° = 0.0032 gm.

† Loss above 120° = 0.0027 gm.

‡ Attributed to carbon dissolved by the *aqua regia*.

TABLE II—Continued.
C. $Ba(OH)_2$ not in excess.

No.	Vol. of gold solution, cm ³ .	Precipitant.	Treatment of moist coagulum.	Coagu- lum. ignited, grm.	Gold found, grm.	Carbon found, grm.	Ba(OH) ₂ found, grm.	Calc. amt. of Ba(OH) ₂ in supernatant liquid, grm.	Error of analysis, grm.
8	1000	25 cm ³ Ba(OH) ₂ sol.	Water. { 500 200 100	0.1465	0.1463	0.0003	0.0002	0.5 cm ³ 0.0003	0.0003 +

D. $Ba(OH)_2$ in excess.

10	1000	50 cm ³ Ba(OH) ₂ sol.	{ 500 100 100	0.2545	0.2524	0.0006	0.0019	0.5 cm ³ 0.0005	0.0004 +
1000	100 cm ³ Ba(OH) ₂ sol.	{ 100 100 100 5	0.8447	0.8306	—————	0.0168	0.0010	0.0027 + †	

* Gold lost by explosion.

† This error becomes 0.0009 + if the barium held by the gold was present as the oxide after ignition, protected from the carbon dioxide of the air by the surrounding gold. Cf. Gmelin-Kraut, Anorg. Chem. II (1), 259.