and, as will be recalled, mercury seemed to show a greater tendency to wet Pyrex than it did soda-lime glass. That on two occasions a degree of wetting was noted when a soda glass was used can be accounted for by assuming that the specific conditions of washing and subsequent drying of the soda glass were such as to prevent any appreciable alkaline film formation. In the case of the capillary tubes, on the other hand, no marked wetting ever occurred in the capillaries because a longer period of time was required to remove the water from within these tubes than from surfaces outside, and this was favorable to the formation of alkaline films.

Summary

An attempt has been made to cause mercury to wet glass and quartz after their surfaces have been denuded of gas as far as it is possible with the present means at our command. The difficulty of this task appears to become greater as the alkaline content of the glass increases. Fairly good wetting can generally be obtained on quartz, while on Pyrex and soda-lime glass it is obtained only occasionally.

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LIESEGANG RINGS. III. THE EFFECT OF LIGHT AND HYDROGEN-ION CONCENTRATION ON THE FORMATION OF COLLOIDAL GOLD IN SILICIC ACID GEL. RHYTHMIC BANDS OF PURPLE OF CASSIUS

By Earl C. H. Davies

Received July 2, 1923

Introduction.—In a previous paper[1] the author showed that light has a pronounced influence on the tendency for colored bands of colloidal gold to form in silicic acid gel. It was the purpose of the present work to make a more exhaustive study of this light effect. The following factors were investigated: the effect of light of different wave lengths; the relation between band formation and hydrogen-ion concentration; the variation of band formation with kind of acid used in making the silicic acid gel; the effect of variation of oxalic acid concentration; the result of using different strengths of gold chloride solution; the result of replacing the oxalic acid by other reducing agents.

The Effect of Light of Different Wave Lengths.—For the first series of experiments, glass cylinders, 18 × 5 cm., were fitted with large corks holding 2.5cm. test-tubes, within which were smaller tubes, containing the gel in which diffusion was to take place. Some of the gel was protected by

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[1] Davies, This Journal, 44, 2700 (1922).

black glazed paper. Other tubes were protected by grids made by cutting horizontal, parallel slits 2mm. wide out of the black paper. These slits were 8 mm. apart. Other tubes were unprotected from the light rays, except by a total thickness of 5.1 mm. of nearly colorless glass, and the respective liquid, which was between the large test-tube and the wall of the cylinder. Tests were made in duplicate. Since the intensity of light varies inversely with the square of the distance, some samples were placed in the circumference of a circle of 30cm. radius at the center of which were 2 Edison Lamps "100 Watts, 115 Volts. P. S., 25 Mazda C." Other similar samples were put in the circumference of an outer concentric circle of 43.5cm. radius. Hence, the light intensity in the outer circle was to that in the inner circle as $(30)^2/(43.5)^2$ or about $^1/_2$. The cylinders in the inner circle were spaced in such a way that they did not shut off the light from the farther cylinders. Solutions were so chosen that the light transmitted was of the different wave lengths present in the visible spectrum. The outer cylinders contained, respectively, air, water, 1 *M* cobalt nitrate, 0.001 *M* potassium permanganate, 0.01 *M* potassium permanganate, 1 *M* copper sulfate, 1 *M* nickel nitrate, and 1 *M* potassium dichromate solutions.

The silicic acid gel was made by slowly adding 500 cc. of water glass (d., 1.16) to a mixture of 500 cc. of 2.975 *N* sulfuric acid and 40 cc. of 1% gold chloride solution. The mixture was filtered before use. The water glass was of such composition that, with congo red as indicator, it was 1.564 *N* at d., 1.16 and 0.585 *N* at d., 1.06. Three days were allowed for the gel to set in the test-tubes. Five cc. of saturated oxalic acid solution was then added to each tube.

The experiment was run for 3 weeks without disturbing the lights or tubes. At the end of this time in no case did I find any evidence of bands in the gel samples which had been protected by black paper. Neither were there bands in the tubes protected only by the potassium dichromate solution. In all other cases of tubes exposed continuously to light some gold was reduced to the colloidal condition. The tubes with only air and glass as absorbent had at the top a purple region 7mm. wide, fading to a light green. There were faint, light green, double bands at 4.6, 5.6, 6.4, 7.7, 8.3 and 9.5 cm., respectively, from the top. These bands slanted toward the light and tended to be double, due to the fact that two bulbs were used instead of a point source of light. They were caused by irregularity of light intensity. The tubes with the grids showed, at each opening, reduction similar to the comparable position in an open tube. Behind the dark portions of the grids the results were very similar to the dark tubes at comparable depths but there appeared some effect of light due to reflection. Tubes more distant from the light showed less color than those in the inner circle. The order of decreasing reduction, that is, of decreasing tendency to form colloidal gold, was found to be: air, inner circle; air, outer circle; water, inner; water, outer; 1 *M* cobalt nitrate;

0.001 *M* potassium permanganate; 0.01 *M* potassium permanganate; 1 *M* copper sulfate; 1 *M* nickel nitrate; 1 *M* potassium dichromate; and no light. However, 1 *M* potassium dichromate and black paper protected the gold equally well.

This series of experiments shows conclusively that light of short wave length is responsible for catalyzing the formation of colloidal gold in silicic acid gel, when the experiment is carried out according to the directions of H. N. Holmes.[2] When the diffusion takes place in the dark only the larger particles of yellow gold crystals are produced. The beautiful, multicolored zones obtained by Holmes were not true Liesegang bands, for the latter would be formed in the dark and their distance apart would increase going from the top to the bottom of the gel. I have obtained these same colored zones but only in changing light, when Holmes' directions were followed. In connection with these bands, in his book on colloidal chemistry, Bancroft[3] says, "He (Holmes) has put forward a theory of rhythmic banding which unfortunately does not account for the fact, recorded in the same paper, that colloidal gold gives three bands, red, purple and blue, before repeating." My present work plainly removes the only objection that Bancroft has offered to the theory advanced by Holmes. Whether Holmes' theory is general in its application is, of course, another matter.

Lecture or Laboratory Demonstration of the Effect of Light on Reduction of Gold.— To 25 cc. of 3 *N* hydrochloric acid add 2 cc. of a 1% solution of gold chloride. Shake this mixture while adding slowly 25 cc. of water glass (d., 1.16). Filter the liquid into 2 test-tubes and allow the gel to set for 3 days. Cover with black paper. Add to each tube 5 cc. of a saturated solution of oxalic acid. Place in a dark room and allow to diffuse for 3 weeks. Open a tube in bright sunlight and with a stopwatch record the time when color appears. When a tube is first opened only a few crystals of gold will be seen, but soon the color of colloidal gold will appear.

With such a tube I obtained a color flash in the upper part in 50 seconds. The time varies with light intensity. Hence the experiment may be used to measure the latter. The great rapidity, with which the color deepened, was very striking. After 3 minutes colloidal gold extended from a position 1.5 cm. from the top to the bottom of the tube. In the zone from 1.5 to 1.8 cm. it was a beautiful red; in the zone from 9.6–12 cm. the color shaded to purple. When 3 *N* sulfuric acid is used instead of the hydrochloric acid, the diffusion should not be allowed to continue for so long a time. Striking results may be obtained from the gel made with 3 *N* sulfuric acid by exposing it to light for a few minutes on the third day, and then each week until diffusion has reached the bottom of the tube. In this way the colored zones will be separated by nearly colorless ones.

Relation between Band Formation and Hydrogen-Ion Concentration.— This relation was studied in two ways, one direct, and the other more indirect. I used 76 tubes of gel for this phase of the work. Results, in Table I, are confined to shielded and open tubes. To make the gel, 6 cc. of 1% gold chloride solution were added to 75 cc. of the acid. To this

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[2] Holmes, This Journal, 40, 1190 (1918).

[3] Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1st ed., p. 259.

mixture were then added 75 cc. of filtered water-glass solution, and the product was quickly poured into test-tubes. After 3 days, gels with 0.67 N acidity were satisfactory. With the gels of lower hydrogen-ion concentrations setting occurred in less than 2 minutes.

TABLE I

RELATION BETWEEN HYDROGEN ION AND COLOR OF COLLOIDAL GOLD[4]

Acid	Acidity of mixture N	After standing in the dark 4 days	28 Cm. from lights	Exposed to sunlight after 3 days in dark
HNO_3	0.67	Very light blue to 2 cm.	Some blue to 2.1 cm.	In 50 sec. blue zone started at 4.3 cm. and reached 5.7 cm. in less than 5 min.
HNO_3	0.045	Slight purple to 7.5 cm.	Purple to 8 cm.	In 1 min. 5 sec. a blue zone appeared between 6.4 and 7.4 cm.
HNO_3	0.012[a]	Very light purple	Green to violet	In 1 min. 40 sec. a light blue zone appeared at 5.7 cm.
HCl	0.664	A few yellow crystals	Green, brown, yellow	In 43 sec. purple began at 0.7 cm. Final colors, blue, red, blue. Very pretty.
HCl	0.034	Slight purple to 7.3 cm.	Purple to 8 cm.	Not observed in sunlight on third day.
HCl	0.012[a]	Slight purple to 6 cm.	Violet light, brown	In 28 sec. a purple zone came at 3.7–4.9 cm. In 3 min. 45 sec. light purple at 6.2–7.7 cm.
H_2SO_4	0.67	Gold crystals	Light blue, green, yellow	In 7 min. 30 sec. with carbon arc light, old rose red at 3.7–4.7 cm.
H_2SO_4	0.012[a]	Violet to 6.7 cm.	Blue, violet, brown	In 40 sec. a purple blue zone appeared at 5.6–6.8 cm.
H_2SO_4	0.021[a]	Slight purple to 6.7 cm.	Purple to 8 cm.	In 2 min. 28 sec. a distinct blue zone appeared at 6.6–7.2 cm.
$HC_2H_3O_2$	0.67	Slight blue to 2.2 cm.	Slight green, blue to 2.1 cm.	In 28 sec. a purple zone began at 4 cm. After 3 min. 45 sec. it had extended to 4.7 cm.
$HC_2H_3O_2$	0.047	Violet to 7.3 cm.	Purple to 8 cm.	No change in 10 minutes.
$HC_2H_3O_2$	0.012[a]	Wine color to 6.2 cm.	Wine color Very pretty	No change in 10 minutes. Very pretty.

[a] Basic.

Conclusion in Regard to Hydrogen-effect in the Dark.—With the acids used, and at the concentration of these experiments, the decreasing order of hydrogen-ion concentration is nitric, hydrochloric, sulfuric, and acetic acids. The nitric and hydrochloric acids furnish nearly the same hydrogen-ion concentration. In keeping with this, I found that, with the final concentration of 0.67 N nitric and hydrochloric, scarcely any reduction took place in the dark. With sulfuric acid the reduction was to yellow

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[4] Red gold indicates small particles and hence also small "pockets." Blue gold indicates larger particles, and green still larger ones. A saturated solution of oxalic acid was used above the gel as the reducing agent.

crystals, and no colloid was formed in the dark. With acetic acid, in the dark, the reduction took place sufficiently rapidly to give the purple colloid. Similarly, when we consider the decreasing hydrogen-ion concentrations for each of the several acids, we find that there is a regular tendency for the reduction in the dark to take place more rapidly in the more basic gels. Take, for example, the concentrations of acetic acid recorded in Table I. With a final normality of 0.67, a slight blue developed to 2.2 cm. from the top. With a final acid normality of 0.047 the violet color extended to 7.3 cm. With the 0.012 *N* basic gel a wine color developed. So, also, in the other cases in the dark the most rapid reduction and hence the smallest colloidal particles occur where hydrogen-ion concentration is lowest.

In the Light.—When diffusion takes place in continuous, uniform light, we have the same relation between hydrogen-ion concentration and rapidity of reduction as we have in the dark. The difference is that in all cases the light hastens reduction, but it does not disturb the regularity of the hydrogen-ion relation. For example, in the case of acetic acid at 0.67 *N* a slight green-blue was developed, showing that relatively large particles were present and hence reduction had occurred in large "pockets." With 0.047 *N* acidity the color is purple. With 0.012 *N* basic the color is like that of wine.

Hence, it appears from this series of experiments that where the hydrogen-ion concentration is relatively low we have reduction in small "pockets." I have spoken of this as "rapid" reduction. The effect of the light is comparable to a rapid decrease of hydrogen-ion concentration.

Besides the experiments recorded, I performed a series in which the final normality of the sulfuric acid in the gel was 2.1. With such a large hydrogen-ion concentration there was slightly more reduction to colloidal gold than with the 0.67 *N* sulfuric acid; but, when exposed to the light, gels made with this acid gave very little further reduction, whereas a check tube of 0.67 *N* excess acid gave reduction in the light in 42 seconds. Hence, we are driven to the conclusion that the influence of light shows up best at a final hydrogen-ion concentration of less than 2.1 *N* and approximately 0.67 *N*.

The Variation of Band Formation with the Kind of Acid Used.—Hydrochloric acid and nitric acid give gels which behave quite similarly, but that from hydrochloric acid is better where the light effect on the gel is to be studied. In comparing similar hydrogen-ion concentrations it seems that the gel made with sulfuric acid shows a greater tendency for the reduction of gold than does that made with hydrochloric acid. Such differences are due to the presence of different salts which have an influence on the rate of peptization and hydration and hence help to govern

TABLE II

REDUCTION OF GOLD IN SILICIC ACID GEL WITH REDUCING AGENTS OTHER THAN OXALIC ACID

Acid	Substance in gel[a]	Substance above gel	Results in continuous[b] light, 4 days	Results in dark	At 42 cm. from Balopticon lens
H_2SO_4	1% $AuCl_3$	10% phenylhydrazine, in alcohol	Green, yellow,[c] over 25 plates	Cryst. Au, 30 plates	In 10 sec. light red color at 1.0–5.6 cm.
HCl	1% $AuCl_3$		No colloidal Au, or band	Cryst. Au, 10 plates	In 9 sec. light red color at 0.0–5.7 cm.
H_2SO_4	10% $AuCl_3$		Brown, black, 50+ plates	Brown, black, 50+ plates	In a few sec. very light red at 3.8–4.8 cm.
HCl	10% $AuCl_3$		Colorless, 50+ plates	Colorless, 50+ plates	In 2 min. 10 sec. red, black
H_2SO_4	0.25% phenylhydrazine, in alcohol	10% $AuCl_3$, mottled	Dark brown, mottled many plates	Brown, mottled many plates	No change in 15 min.
HCl	0.25% phenylhydrazine in alcohol	10% $AuCl_3$	Green, brown, many plates	Green, yellow	More black in 10 sec.
H_2SO_4	1% $AuCl_3$	40% HCHO	Similar to orig. gel	Very few Au cryst.	Very slight red before 5 min.
HCl	1% $AuCl_3$	40% HCHO	Similar to orig. gel	No change	No change in 6 min.
H_2SO_4	10% $AuCl_3$	40% HCHO	Few Au cryst.	Few Au cryst.	No change in 6 min.
HCl	10% $AuCl_3$	40% HCHO	No change	No change	No change in 6 min.
H_2SO_4	0.25% formaldehyde	10% $AuCl_3$	Yellow, no reduction	Yellow, very slight pink	In 25 sec. pink became more intense
HCl	0.25% formaldehyde	10% $AuCl_3$	Yellow, no reduction	Yellow, no reduction	No change in 13 min.
H_2SO_4	0.1% glucose	10% $AuCl_3$	Light red, brown, regular bands[d]	Light red, brown, regular bands[d]	Little change in 12 min.
HCl	0.1% glucose	10% $AuCl_3$	Yellow, no reduction	Yellow, no reduction	No change in 9 min.
H_2SO_4	0.1% $AuCl_3$[a]	10% $SnCl_2$, + 0.1% $SnCl_4$	Blue, purple	Blue, purple	Little change in 11 min
HCl	0.1% $AuCl_3$		Liesegang bands, "purple of Cassius"	Liesegang bands, "purple of Cassius"	No change in 10 min.
H_2SO_4	10% $AuCl_3$		Brown, yellow	Brown	In 55 sec. top of brown turned black
HCl	10% $AuCl_3$		Brown, to deep purple bands[e]	Brown, to deep purple bands[e]	No change in 6 min.
H_2SO_4	0.25% $SnCl_2$-$SnCl_4$ mixt.	10% $AuCl_3$	Light to dark brown	Light to dark brown	No change in 8 min.
HCl	0.25% $SnCl_2$-$SnCl_4$ mixt.	10% $AuCl_3$	Top 2 cm. clear yellow, lower portion brown, with bands[f]	Top 2 cm. clear yellow, lower portion brown, with bands[f]	No change in 5 min.

[a] 1 cc. for every 25 cc. of mixture, except with glucose where 0.1% means the percentage of solid glucose in the gel.

[b] Later observations, after 3 weeks, on the duplicate tubes, showed that the results at 4 days were typical of the longer period.

[c] These were present in all tubes in which phenylhydrazine was used. They were cleavage planes, of varying sizes up to 4.2 by 1.5 cm.

[d] These bands were light, reddish-brown, about 1 mm. wide. They were, starting

the size of the "pockets." However, the kind of acid is of far less importance than the concentration of hydrogen-ion present.

The Effect of Variation of the Concentration of Oxalic Acid.—My experiments show that in the case of the gel made with sulfuric acid the strength of oxalic acid solution may vary between saturated and $^1/_4$ saturated, and perhaps may be even less, without effecting any great change in results. However, it is to be recommended that a saturated solution of oxalic acid be used.

The Results Obtained with Different Strengths of Gold Chloride Solution.—In Table II results are recorded of the effects of different reducing agents diffusing into gels, containing 1 cc. of 1 to 10% gold chloride in each 26 cc. There seems to be no advantage in having the gel contain more than 0.04% by weight, of gold chloride, while 0.4% gold chloride seems too concentrated for use.

The Effects of Replacing the Oxalic Acid by other Reducing Agents.—136 Tubes of gel were made up in many different ways. The conditions governing the use of continuous light, grids, and control of the operations in the dark were observed also in these cases. The sulfuric acid used was 2.975 *N* and the hydrochloric acid was 2.967 *N*. The water glass was d. 1.16 and was 1.584 *N*. To 75 cc. of the acid was added 6 cc. of the gold chloride solution or the reducing agent (in the cases where the gold chloride was placed above the reducer); 75 cc. of filtered water glass (d., 1.16) was then added and the mixture constantly and vigorously shaken, and poured into 15mm. test-tubes to set. Three days were allowed for setting; after which some of the tubes were covered with grids or dark paper and all were put in the dark room at the same distance from the light, as described earlier in this paper. Illumination was continuous for three weeks.

Conclusion in Regard to Reducing Agents other than Oxalic Acid.—The most interesting set of experiments was with the formation of purple of Cassius. Formaldehyde and phenylhydrazine in alcohol are not suitable for this type of experiment. The results obtained when a 10% gold chloride solution diffused into a silica gel made with sulfuric acid and containing 0.1% glucose were remarkable in that regular bands were obtained but they were equally spaced, whereas the true Liesegang rings are

at the top, at 3.7, 4.1, 4.45, 4.8, 5.1, 5.4, 5.7, 6.0, 6.25, 6.5, 6.8, 7.3, 7.7, 8.0 and 8.3 cm., respectively.

[e] In the upper part of the tube the color was so intense that the bands were indistinct. In the lower part the purple bands were sharp. At 8 cm. they were 2.5 mm. apart, and they were true Liesegang bands.

[f] This was peculiar in that the concentrated $AuCl_3$ solution seemed to have dissolved the brown precipitate in the upper 2 cm. region. The bands in the brown portion were true Liesegang bands, but were difficult to see on account of the nature of the precipitate. At 4 cm. from the top, they were 1.5 mm., and at 9.7 cm. they were 5 mm. apart.

developed farther and farther apart. I shall refer to this striking phenomenon in a later paper.

Rhythmic Bands of Purple of Cassius.—Narrow but distinct rhythmic bands of purple of Cassius are obtained as follows. To 12.5 cc. of 3 *N* hydrochloric acid add 1 cc. of 1% gold chloride solution. Shake the mixture vigorously while adding 12.5 cc. of water glass (d., 1.16). Allow the liquid to set in a test-tube for 3 days. Add 3 cc. of a mixture made from the equivalent of 10 g. of anhydrous stannous chloride and 0.1 g. of anhydrous stannic chloride in 90 g. of water. This mixture is turbid and, therefore, must be shaken vigorously before it is used. During the diffusion, the turbidity entirely disappears. When heavier bands are desired they may be obtained by using more concentrated solutions of gold chloride up to 10%; but when these more concentrated solutions are used the zones between the bands are not so free from residue.

Summary

1. Experiments have been performed which show that gels made with silicic acid and gold chloride are remarkably affected by light and that it is the light of short wave length which functions thus.

2. The results obtained remove Bancroft's objection to Holmes' diffusion theory of Liesegang band formation.

3. Another series of experiments has shown that there is a distinct relation between hydrogen-ion concentration and the size of "pockets" in which the gold is formed.

4. Directions are given for a striking lecture or laboratory experiment to show the influence of light on reduction.

5. Purple of Cassius was obtained in true Liesegang bands.

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[CONTRIBUTION FROM THE EPPLEY LABORATORY]

THE TEMPERATURE COEFFICIENTS OF UNSATURATED WESTON CELLS

BY WARREN C. VOSBURGH AND MARION EPPLEY

RECEIVED JULY 3, 1923

The unsaturated Weston cell, although not a true standard cell, is widely used as a secondary standard of electromotive force because of its low temperature coefficient. Jaeger[1] stated that the electromotive force of a cell of this type with a cadmium sulfate solution saturated at 4° as the electrolyte could be regarded as practically constant at all ordinary temperatures. Dearlove[2] found a temperature coefficient —0.00003 volts

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[1] Jaeger, "Die Normalelemente," Wilhelm Knapp, Halle a.S., **1902**, p. 86.

[2] Dearlove, *Electrician*, **31**, 645 (1893). Dearlove does not state the concentration of cadmium sulfate in the electrolyte of his cells but the electromotive forces indicate that it was smaller than that of a solution saturated at 4°.