

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, WEST VIRGINIA UNIVERSITY]

## LIESENGANG RINGS. I. SILVER CHROMATE IN GELATIN AND COLLOIDAL GOLD IN SILICIC ACID GEL

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## Introduction

It is generally agreed that while the present theories regarding Liesegang rings may cover the broad features of this phenomenon they are quite inadequate to explain its many details, complexities and variations. To study this phenomenon further, I have in the first place investigated the effect of gravity on the formation of bands of silver chromate in gelatin. In the second place, I have studied the formation of rhythmic bands of colloidal gold in silicic acid gel, since this presents an ideal opportunity for following changes in the sizes of the particles.

## Silver Chromate Bands in Gelatin

**Effect of Gravity.**—An aqueous solution of silver nitrate was made containing 8.5 g. in 100 cc. The gel contained 4 g. of powdered gelatin, 0.12 g. of potassium dichromate, and 120 g. of water. The gelatin was boiled with the water and the dichromate for a few minutes on a water-bath until solution had taken place, and the solution was then filtered into tubes. After it had solidified (standing over-night) and had been left in

TABLE I  
RATE OF DIFFUSION AT 0°

Tube	Time in days									
	7	14	18	20	25	27	32	34	39	46
	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.
A right	6.40	9.00								
A left	6.40	9.00								
A' right	6.40	8.75								
A' left	6.40	8.75								
B	6.40	9.25	10.60	11.27	gelatin frozen					
B'	6.40	9.25	10.60	11.29	12.62	13.10	14.35	14.80	16.25	16.5
C upper	6.40	8.68								
C' upper	6.40	9.04								
C lower	5.97	8.16								
C' lower	5.97	8.40								
D	5.76	8.60	9.80		10.80		13.17		14.65	
D'	5.76	8.60	Gelatin frozen							

the ice-room at 0° for about 2 hours, the tubes were arranged as follows: A and A' were horizontal with silver nitrate contact at both ends; B and B' were horizontal with silver nitrate contact at one end; C and C' were vertical with silver nitrate contact at both ends; D and D' were vertical

with silver nitrate contact at the lower ends; E and E' were vertical with silver nitrate contact at upper ends.<sup>1</sup>

The results given in Table I show that diffusion is slowest when it operates against gravity (Tube D), and that hydrostatic pressure may partially counterbalance gravity (Tube C, lower).

After the 18th day the tubes were removed from the ice-room while observations were made at room temperatures and with varying light, either artificial or sunlight. Hence the results previous to the 18th day are most satisfactory. After that elapsed time all tubes were removed for the same length of time and subjected to practically the same light and heat conditions.

**Preliminary Bands.**—It seems from observations so far recorded that in the case of silver chromate in gelatin the method of ring formation is: first, the silver nitrate diffuses into the gelatin and gives what seems to be an opaque region which in reality consists of small opaque bands. These preliminary bands have not been observed in the earlier stages of diffusion. Tube B' at 13.5 to 15 cm. from the surface of entrance of the silver nitrate had 28 bands. Tube D had 16 bands at 12.8 to 13.8 cm. from the point of the beginning of the silver nitrate penetration. Tube E' had 26 opaque bands at 10.5 to 11.5 cm. from the surface. From this point it appears that there is a tendency for the opaque bands to be closer together in the earlier stages of diffusion and to be farther apart as the distance from the surface of initial diffusion increases. It is, therefore, not unlikely that this formation of preliminary bands extends to all portions of the tube, but that the bands are at first so close that they seem to merge.

In the case of silver chromate in gelatin the reaction as carried out in a test-tube would be,  $K_2Cr_2O_7 + H_2O + 4AgNO_3 = 2KNO_3 + 2Ag_2CrO_4 + 2HNO_3$ . We are not dealing simply with silver chromate, and it is a well-known fact that electrolytes have a profound effect on gels. They not only influence the rate of imbibition of water but also tend to produce peptization. As the gelatin gel ordinarily used is not as dilute as possible we know that it is capable of absorbing more water. The presence of nitric acid would disturb the layer of gelatin where it is produced. There is a similar change in rate of imbibition when a base is one of the products. The potassium nitrate and nitric acid have the greatest concentration at the layer of reaction between the potassium dichromate and silver nitrate. From microscopic observations it appears that at least at 0° some of the potassium nitrate is crystallized simultaneously with the small particles of silver chromate. The nitric acid is more soluble and hence, according to Fick's law, diffuses faster than the potassium nitrate because it is potentially more concentrated.

<sup>1</sup> Data for E and E' were not given in Table I because the silver nitrate had not the same strength as that used in the other tubes.

It is to this unequal rate of diffusion that we attribute the preliminary bands. The groups of silver chromate-potassium nitrate "crystals" are gradually broken up as the potassium nitrate diffuses away and the silver chromate particles become larger because of the oncoming silver nitrate. Hence the small bands lose their identity and the larger band is formed. Below the small band the silver nitrate and nitric acid and some potassium nitrate are diffusing into the potassium dichromate. Of course, the potassium dichromate is diffusing "up" but because of its low concentration the rate of diffusion is low.

### Colloidal Gold in Silicic Acid Gel

**Light a Factor in Formation of Rythmic Bands.**—To ascertain the effect of periodic illumination in the production of bands, I have carried out the following experiments using colloidal gold in silicic acid at the concentrations suggested by H. N. Holmes,<sup>2</sup> who apparently carried out his experiments in changing light.

Tubes gave no bands either at 0° or at room temperatures when covered, light-tight, with black paper and placed in a dark room even after 9 days. Instead, the gold precipitated in sparkling yellow particles. A band of about 1.5 cm. width was formed in these tubes by removing the black paper and exposing them to the light from a projection lantern for an hour. The band did not start as a fine line and then gradually grow; rather, it began as a faint color throughout the entire region, becoming gradually more intense by longer exposure to the light until it reached a maximum at which all the gold adsorbed by the fibrils in this region had been precipitated. The color was lighter at the top of the band and most intense near the bottom. Below the colored zone, yellow crystals of gold could be seen for a distance of 8 to 9 mm.

Second, slits were cut in the black paper in such a way as to expose 2 mm. cover 8 mm., expose 2 mm., etc., throughout the length of a tube. This tube was placed in the dark room at a distance of 14 cm. from an 80-watt, 110-volt Mazda light. Slightly green colloidal bands developed at the openings after 9 days, and at each opening there were distinct yellow bands of gold crystals.

Third, a similar tube which had been in the dark at 0° for 6 days showed no bands at the openings. When this tube was exposed to the strong light of the projection lantern for a few minutes, bands developed at 2 of the openings in the same region as in the case of a tube which had been handled exactly similarly except that it had no protection from the light of the lantern. Between these openings the bands did not form, although the tube was in the strong light for 1 hour. This tube was then put in the dark for 7 more days at 0°. The black slit paper was then entirely removed and the tube put in front of the lantern for 3 hours. There was a

<sup>2</sup> Holmes, *THIS JOURNAL*, **40**, 187 (1918).

slight blue color developed in the 8mm. zone between these 2 bands. From the faint color of this blue it was apparent that the light is not the only factor in promoting the band formation of the gold. There must also be proper concentrations of the oxalic acid and the gold chloride. The sodium sulfate is not included because it is presumably uniformly distributed.

Hence it seems that the molecular gold adsorbed by the walls is in some way at first protected from immediate precipitation by the oxalic acid. It is probably oriented.<sup>3</sup> After a time such gold is gradually precipitated in the dark, but not in bands. At some other concentrations bands may be obtained in the dark; but so far I have observed no tendency for the gold to form in bands in silicic acid except under more or less periodic light changes. For example, E. Küster<sup>4</sup> found under certain conditions, in the case of bands of silver chromate in gelatin, that when the silver nitrate had diffused into the gelatin in the dark there was an evenly distributed precipitate, but when the diffusion area was exposed to light rhythmically, that is, alternate exposure (25 minutes) and darkness (45 minutes) the precipitate took the characteristic ring formation. I have obtained just as good bands of silver chromate in the dark as in the light, both at 0° and at room temperature of about 20°.

**Two-phase Character of Silicic Acid Gel.**—It seems that the “protected” gold chloride, which we have assumed to be adsorbed by the more solid portion of the gel cells, gradually diffuses away and is precipitated if the band is not started by the light, or the peptizing and imbibition action of the products of reaction. It is because of this migration and precipitation that the null spaces are formed.

When in the dark or in mild light there is a rather broad band which forms at the top of the silicic acid layer. This band was in some cases reddish-purple in transmitted light and yellow in reflected light. Below this there were sparkling yellow crystals of gold. These latter precede the usual bands. Observed with a powerful Tyndall cone it is seen that the particles of gold are most numerous just beneath the band. They become relatively fewer until they cease to appear at a distance of about 8 to 9 mm. Then a band begins to form in the region already best filled with the larger particles of gold. The band owes its formation to the condensation of the molecular gold to the size of colloidal particles. Much of the gold has already been precipitated as microscopic particles. Hence in the formation of these bands there comes a time when there is a considerable accumulation of the products of reaction, hydrochloric and carbonic acids. Also the concentration of the gold chloride becomes quite small due to the previous precipitation of the microscopic particles. The

<sup>3</sup> For discussion of the subject of molecular orientation see Harkins, Davies and Clark, *THIS JOURNAL*, 39, 541 (1917).

<sup>4</sup> Küster, *Kolloid-Z.*, 13, 192 (1913).

whole experiment behaves as would be expected if the gold chloride were held in the gel in two ways. First, some of it is most free to move and forms the larger particles. Second, the accumulation of the products of reaction affects the "protective" coating on the other gold chloride molecules so that they are attacked by the oxalic acid. It would seem that these colloidal particles which form the bands must likewise be protected by the gel, as they remain unaffected by further diffusion of the electrolytes. This is what might be expected if we had films of the solid gel and pockets of the amorphous gel. W. Moeller<sup>5</sup> has observed such a formation in the case of gelatin, where he finds fibrils of  $\alpha$ -gelatin imbedded in amorphous  $\beta$ -gelatin.

However, the structure of the gel is not the only factor. Many experiments on band formation have been performed where gel was replaced by solids, as sand, sulfur, etc. There is also in these cases a possibility that an oriented adsorption of one of the reacting substances by the solid plays an important part. Some of the precipitate is, in nearly all cases, of a preliminary nature. It may be scattered, as in the case of gold, or in preliminary bands, as in the case of silver chromate in gelatin. These preliminary particles may sometimes be later partially converted into colloids by the excess of electrolytes but in the case of gold there seems to be no such tendency. The gold originally precipitated as blue remains blue, the red remains red. This shows that it is formed in protective coats of the gel. Otherwise we might expect the red particles to enlarge gradually and become blue as more of the diffusion takes place. The molecular gold in the fibrils forms the bands. The gold chloride in the amorphous portion of the gel forms the granules.

In all the bands of gold observed, the red has formed first where it has formed at all. In the region in which it is formed we have relatively large concentrations of oxalic acid as compared with the small amount of adsorbed gold. After a red band, the blue forms. Under this same red band relatively large amounts of the yellow gold have been observed for a distance of 8 to 9 mm. beyond it. Hence, where the blue bands form there are relatively large amounts of the products of reaction, hydrochloric and carbonic acids, with relatively high concentration of adsorbed molecular gold. Under the latter conditions we should have greater tendency for absorption of the oxalic acid with more of the "protected" molecular gold collecting in each "protected" colloidal particle.

**Effect of Temperature.**—Upon a study of the literature on Liesegang ring formation one is impressed by the small attention paid to the effect of temperature. Experiments have nearly always been carried out at room temperatures. Yet it is recognized that the elasticity of gels<sup>6</sup> is directly

<sup>5</sup> Moeller, *Kolloid-Z.*, 19, 205-213 (1916).

<sup>6</sup> See Hatschek, *ibid.*, 14, 115-22 (1914).

related to the formation of Liesegang rings. In the present experiments with silver chromate in gelatin, the bands were closer when made at  $0^{\circ}$  than when formed at room temperatures. Particularly in the case of gelatin should studies be made at different and regulated temperatures. Thus the ordinary gelatin gels melt between  $25^{\circ}$  and  $29^{\circ}$ , depending upon the concentration. When working at room temperatures with a 4% gelatin gel (m. p. about  $26^{\circ}$ ), we are very close to the limit of non-elasticity. When we lower the temperature to  $0^{\circ}$  we have lowered the distance from the melting point by several hundred per cent. Therefore, we have greatly affected the elasticity and may expect marked influence on ring formation. At lower temperatures, the rate of diffusion is also lessened. It is doubtful whether as low a temperature as  $0^{\circ}$  is desirable but it is certainly advisable to work at a uniform temperature not too close to the melting point of the gel. With the silicic acid there is not the difficulty of melting at higher temperatures. In fact it seems best many times to work at higher temperatures; but here also conditions of light and heat should be carefully regulated if the observations are to be more than qualitative.

**Conclusion.**—The oriented adsorption in the gel or porous solid of the reacting substances as well as the products of reaction have not received the attention which they deserve. On looking through the literature we find that the concepts, which existed prior to our knowledge of colloids, are carried over to explain facts which are clearly related to the phenomena of colloidalilty. Thus we read statements to the effect that "the ions diffuse toward each other until the solubility product is exceeded." It is not clear how this, applies to the formation of bands which consist altogether of colloidal particles. The colloidal conception would be that a number of molecules, in some cases about 100 as for the usual colloidal silver, are congregated into a particle of rather definite size. If too many of the molecules collect on one "crystal" we have the usual precipitate (in our case the yellow crystals of gold). Hence it is necessary to regulate the number of these gold molecules which are reduced in a "protective" coating or pocket of the gel. Thus we are not surprised that light, heat, peptizing electrolytes and the rate of diffusion all play important roles in regulating the formation of bands and the size of particles in those bands, and in case of colloidal gold the color which The Svedberg<sup>7</sup> has shown, is directly related to the size of particles.

**Forecast.**—It seems possible to predict that subsequent experiments will show that in many cases of Liesegang rings which occur in nature light will be found to be an important factor. This is because of the natural periodicity of sunlight. Diffusion takes place at night with perhaps chemical reactions. Then in the daytime the combined action of the light and the products of the reactions is to cause a band to form where the con-

<sup>7</sup> Ostwald, "Theoretical and Applied Colloid Chemistry," 1st ed., 1917, p. 60.

centrations and the nature of the diffusion medium are suitable. Further experiments will be made, especially with silicic acid gel to determine the effect of light as a factor.

**"Preliminary" bands** of silver chromate were observed after the diffusion in gelatin had extended 10 to 12 cm. at 0°. The presence of these is attributed to the unequal rate of diffusion of the products of reaction. About 3 of these preliminary bands gradually form the nucleus of the final band; 26 such bands were observed in a space of 1 cm. These "preliminary" bands gradually lose their identity as the silver chromate is carried to the final band by the excess of silver nitrate.

**Light** is one of the most important variables in making rhythmic bands of gold in silicic acid. At the concentrations used no bands were formed in the dark at either 0° or room temperatures. Periodic variations of strong light and darkness produce bands in those regions in which there is still adsorbed molecular gold, excess of acid and suitable amounts of the by-products of the reaction. These by-products make precipitation in bands possible because they influence the tendency toward imbibition and peptization so that the gold is precipitated in "pockets" just large enough to give a colloidal dispersion. There is no fundamental difference between the bands of blue gold and those of red. Any combination of conditions which tend to precipitate the gold from the "fibrils" in relatively large "pockets" will produce blue bands. The red bands are made when the pockets are not so large. Rhythmic bands of silver chromate form in gelatin in the dark at 0° and at room temperatures.

**Silic acid gel is a 2-phase system;** the gold chloride is held in the gel in two ways. Some of it is most free to move and forms the larger yellow crystals before the bands begin to appear. The remainder of the gold chloride seems to be more "protected" by the gel. Oriented adsorption takes place at the interface between "fibrils" of  $\alpha$ -gel and the amorphous  $\beta$ -gel. This oriented adsorption may set up a temporarily "passive" state even where the adsorbed substance is not actually coated by a film of the gel. Such orientation can occur when solids such as alundum and sulfur are the mediums in which Liesegang rings are made.

At room temperatures gelatin gel is near its point of minimum elasticity. More experiments should be carried out with it at lower and uniform temperatures.

### Summary

Gravity decreases the rate of diffusion upward during the formation of Liesegang rings of silver chromate in gelatin dichromate.

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