TABLE II.

The Effects of Sodium and Potassium Bromides on the V. C. of Formamide.

Temperature —2.5°.

NaBr mols per liter.	Time per meter in seconds.	KBr mols per liter.	Time per meter in seconds.
0.15	996.0	0.15	852.0
0.10	819.0	0.10	718.0
0.05	550.0	0.05	481.0
0.025	441.0	0.025	436.0

From these experiments it is probable that the relative effect produced by dissolved substances on the V. C. of formamide is chiefly due to solvation in solution. Further, those substances which are solvated to the greatest extent in water are also solvated to the greatest extent in formamide.

Summary.

1. The velocity of crystallization of formamide has been determined at several temperatures.
2. Formamide is very susceptible to spontaneous crystallization even when but slightly undercooled.
3. The values for the V. C. of the pure liquids, water, formamide and benzene are numerically wide apart. An explanation why this should be so is offered.
4. The effect of dissolved substances on the V. C. of formamide is probably a solvation effect.
5. Substances which are hydrated most in aqueous solutions are also solvated most in solutions of formamide.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY, OBERLIN COLLEGE.]

EXPERIMENTS IN RHYTHMIC BANDING.

BY HARRY N. HOLMES.

Received May 10, 1918.

Rhythmic banding of precipitates was first observed and recorded by Liesegang, hence the name "Liesegang's rings." His original experiment dealt with the rhythmic precipitation of silver chromate in gelatin. A solution of silver nitrate was poured on a solid gel containing dilute potassium chromate. The precipitate of silver chromate formed was not continuous but marked by gaps or empty spaces at regular intervals.

Ostwald[1] held that the silver chromate of Liesegang's original experiment formed a supersaturated solution. When crystallization started at any given point the excess beyond that required for saturation migrated to the points where crystals were forming. By repetition of this process gaps and bands were produced.

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[1] *Z. phys. Chem.*, **23**, 365 (1897).

Bechold[1] advanced the theory that the precipitate of the bands is slightly soluble in products of the reaction and hence that new bands can form only in regions where the concentration of such products has sufficiently fallen off.

Bradford[2] holds that rhythmic banding is due to gradual adsorption of the solute in the gel by the growing precipitate.

Experimental.

Preparation of the Silicic Acid Gels.—Silicic acid gels were found to be the best for experiments in banding. A convenient procedure was the quick and thorough mixing of equal volumes of solutions of sodium silicate and the acid desired. A known amount of one of the substances reacting to form bands was added to this mixture before the gel set to a solid or the reacting substance was dissolved in the acid before addition of the water glass. After the solid gel had formed in a test-tube a solution of the other reacting substance was poured on top. This upper solution diffused downward into the gel reacting to form bands in some cases crystalline and in others apparently amorphous or microcrystalline.

An interesting and useful variation of this procedure was introduced by pouring the mixture of water glass and acid into a U-tube, just filling the bend. When the solid gel formed, the two reacting solutions were poured into the respective arms of the U-tube. This device permitted many variations in the concentrations of the reacting substances.

The particular water glass used in experiments described below was of such composition that when diluted to a density of 1.06 it neutralized an equal volume of 0.51 N acid, using methyl red as indicator. A solution of 1.06 density mixed with an equal volume of N acetic acid set to a solid gel in a few hours at room temperature; at higher temperatures the time of set was shortened. A mixture of equal volumes of 1.06 density water glass and 3 N sulfuric acid set in about one week; of 1.16 density water glass and 3 N sulfuric acid in one or two days; of 1.10 density water glass and 2 N nitric acid in two days; of 1.06 density water glass and 2 N hydrochloric acid in 5 days. A water glass of different composition should be diluted to a convenient density such as 1.06 and titrated against standard acid. Allowance can then be made in comparison with the times of set given above. These gels need not be dialyzed. In fact salts and sugars may be added with interesting effects on banding. For example, glucose greatly aided the sharp banding of mercuric iodide.

The mixtures of water glass and acid previously described contained an excess of acid. I found it convenient to use less acid than enough to react with all the sodium silicate, the resulting gels reacting more or less

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[1] *Z. phys. Chem.*, **52**, 185 (1905).

[2] *Biochem. J.*, **10**, 169 (1905).

alkaline. For example, a mixture of equal volumes of 1.06 density water glass and 0.5 *N* acetic acid (or any acid) was slightly basic and set in two or three minutes. This type of gel permitted a study of basic salts and many reactions impossible in an acid gel.

Mercuric Iodide.—A tube of silicic acid gel (from mixing equal volumes of 1.06 density water glass and *N* acetic acid) was made 0.1 *N* with respect to potassium iodide and covered with 0.5 *N* mercuric chloride. In a few days bands of red crystalline mercuric iodide began to appear. These bands were not sharply marked for the first cm. or two below the surface of the gel but below that depth were excellent. In some tubes there were 40 bands rather sharply marked in a distance of 8 cm. The spaces between the thin disks contained many scattered crystals.

In a U-tube with a gel filling the bend, 0.5 *N* mercuric chloride in one arm and 0.1 *N* potassium iodide in the other, the sharp red bands of mercuric iodide followed the curve like ranks of soldiers pivoting in regular formation. The excess of mercuric chloride diffusing into the gel reacted with the red mercuric iodide forming a soluble colorless double salt, leaving the gel somewhat clearer where the red bands had been. This gave the appearance of shadow bands following in the rear.

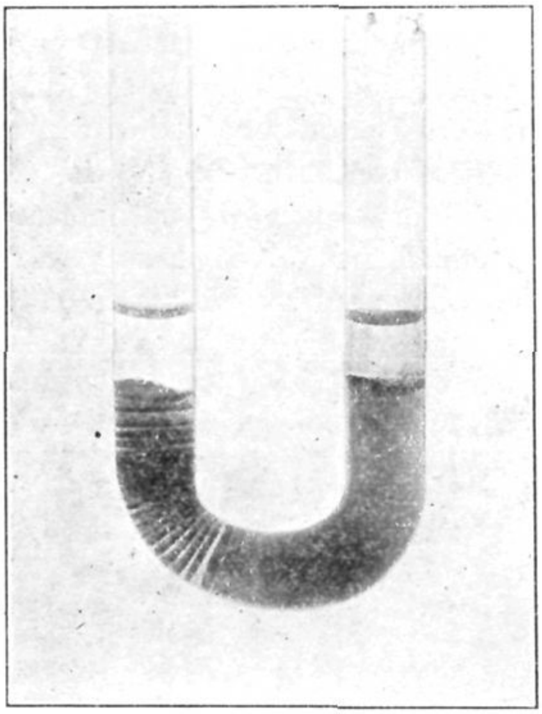

Fig. 1.—Mercuric iodide banding in a silicic acid gel.

The presence of glucose in the gel made the bands very much sharper. Sodium chloride, on the other hand, diminished the tendency to band and in sufficient concentration prevented it altogether. In a gel of the composition described above but containing an added 10% of sodium chloride, the mercuric iodide formed, not in the usual red needles, but in much larger crystalline aggregates and very few bands appeared. The crystals were scattered in an irregular way. The addition of sodium chloride to the amount of 25% of the weight of the gel caused the appearance of still larger widely scattered crystalline aggregates. Neither needles nor bands were in evidence. Since a gel made from sodium silicate and hydrochloric acid contains considerable soluble chloride no sharp banding of mercuric chloride could be expected under such conditions. This may explain why earlier investigators in this field failed to record the beautiful examples of banding possible with mercuric iodide.

It is worthy of note that when mercuric nitrate was substituted for mercuric chloride still finer banding was obtained. This may be due to the absence of chlorides or in part to the fact that mercuric chloride is less ionized than mercuric nitrate.

Gold.—To 25 cc. of a mixture of equal volumes of 1.16 density water glass and 3 *N* sulfuric acid was added one cc. of 1% gold chloride. The solid gel formed in a day or two and was then covered with a saturated solution of oxalic acid (about 8%). As the oxalic acid diffused into the gel the gold chloride was reduced. A wonderfully beautiful series of colored bands of colloidal gold developed with sparkling golden crystals scattered throughout the gel. The upper layer of the first bands was red, the next blue and the next green. A comparatively clear gap below this series was followed by another red-blue-green zone. Usually after the first few rainbows the red was omitted. A dozen or more such complex bands in an ordinary test-tube were not uncommon, the upper bands measuring about one cm. in depth.

These concentrations of the gold chloride and the oxalic acid were varied somewhat with no improvement in results. If, however, the gel was made from 1.06 density water glass and 3 *N* sulfuric acid (setting in about one week) no bands of colored colloidal gold appeared—or only traces of them—but great numbers of gleaming yellow crystals of gold formed throughout the gel—strikingly beautiful in a beam of sunlight.

These bands have been obtained before, but I found the use of sulfuric acid in making the gel a very great improvement. Using hydrochloric acid, the colored bands were quite inferior. With acetic acid instead of sulfuric no bands appeared, but the gel was colored uniformly with violet-blue colloidal gold. However, loading an acetic acid gel with considerable sodium sulfate developed a few shadowy bands. Evidently the influence of sulfates was a factor of importance.

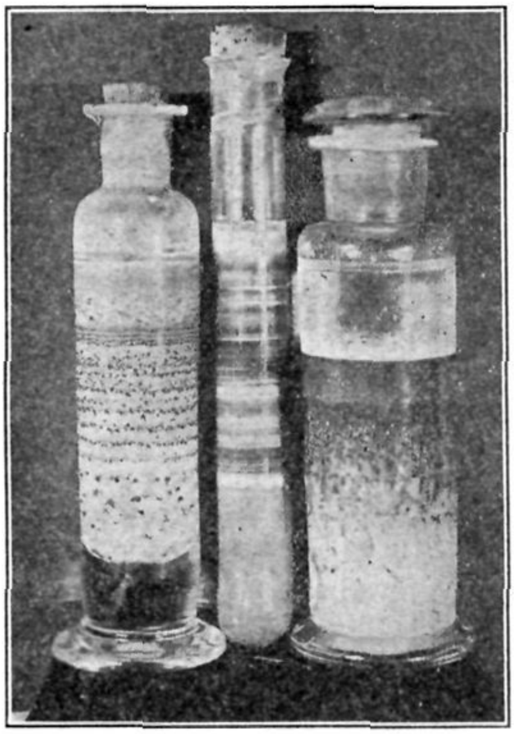

Fig. 2.—Basic mercuric chloride bands. The silicic acid gel on the left contains a slight excess of base, the one on the right a greater excess and the one in the middle contains glucose.

Basic Mercuric Chloride. — Very striking bands made up of brown-black crystals were formed when a 0.5 *N* solution of mercuric chloride diffused into a silicic acid gel of slightly basic reaction. With a gel from mixing equal volumes of 1.06 density water glass and 0.5 *N* acetic acid the best bands were observed. In gels containing a greater excess of base the separate crystals were smaller and the bands more compact. Nitric acid was substituted for acetic with excellent results. In some cases the gaps between the bands were quite free from crystals, but this was not commonly true. A slightly basic gel containing glucose, when covered with mercuric chloride solution, yielded a gray mass of closely packed bands, over 100 in a distance of 8 cm.

Copper Chromate.—The banding of copper chromate in a silicic acid gel of very slightly basic reaction affords the best material for a detailed study of the phenomenon. Gold banding is often more beautiful but the remarkable sharpness of the layers of copper chromate and the perfect clearness of the gaps excel all other examples.

A gel from mixing equal volumes of 1.06 density water glass and 0.5 *N* acetic acid was made 0.1 *N* with respect to potassium chromate (before solidifying) and was later covered with 0.5 *N* copper sulfate. In a day or two bands of apparently amorphous copper chromate formed. The first layer was often rather deep, one cm. or more, then a clear gap with no trace of a precipitate of copper chromate, below that a much thinner band, more gaps and bands, the gaps widening steadily. These relative distances varied not only with the initial concentrations of the reacting solutions but also with the volumes of the potassium chromate solution in the gel and the copper sulfate solution above. It is, of course, apparent that these relative volumes greatly influenced the rates of decrease in the initial concentrations. The distances were also influenced by the substitution of other acids for acetic in making the gel. The first deep band at the top always showed more or less distinct marks of smaller bands merging rather hazily into one. In reality, then, the bands steadily increased in thickness from the first as did the width of the gaps.

In a typical gel made as above the depth of the first solid band or group of bands was 8 mm., the first definite gap 2.5 mm., the second band 2.5 mm., the next gap 7.5 mm., the next band 2 mm., the next gap 15 mm., and

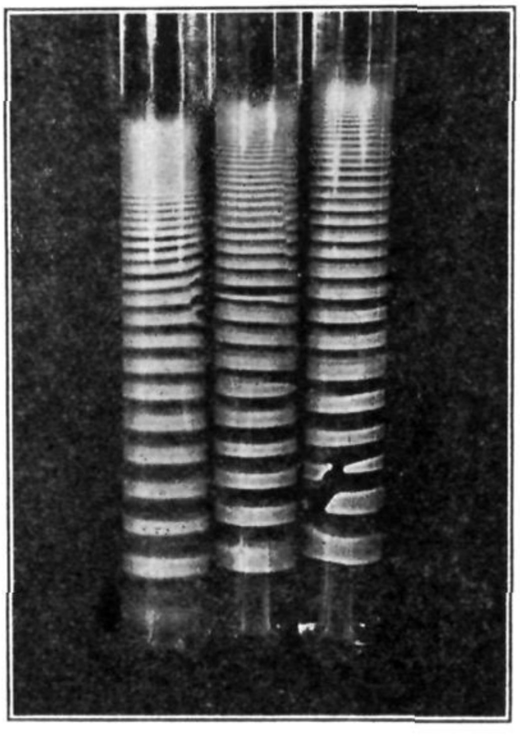

Fig. 3.—Copper chromate bands. The silicic acid gels, slightly basic, were made with sulphuric, hydrochloric and nitric acids, reading from left to right.

the next band 7 mm. In general, the best results were obtained by using 0.5 *N* copper sulfate and 0.1 *N* potassium chromate. With a saturated solution of copper sulfate there was no banding, merely a vague precipitation zone of copper chromate. But even this applied only to the ordinary test-tube used. In a very long column of gel covered with a relatively small amount of saturated copper sulfate solution the copper salt solution must become more dilute as it diffuses to greater depths and finally reaches a suitable concentration for sharp banding.

Making the gels by substituting 0.5 *N* hydrochloric or sulfuric or nitric acid for the 0.5 *N* acetic acid described above produced a striking change in the banding. The gaps were more nearly equal and none of greater depth than 3 mm. With bands, many of which were 4 or 5 mm. in thickness, an ordinary test-tube contained as many as 28 in a distance of 8 cm. The results with these 3 types of gel differed very little except that the gaps in the sulfuric acid gel were not clear.

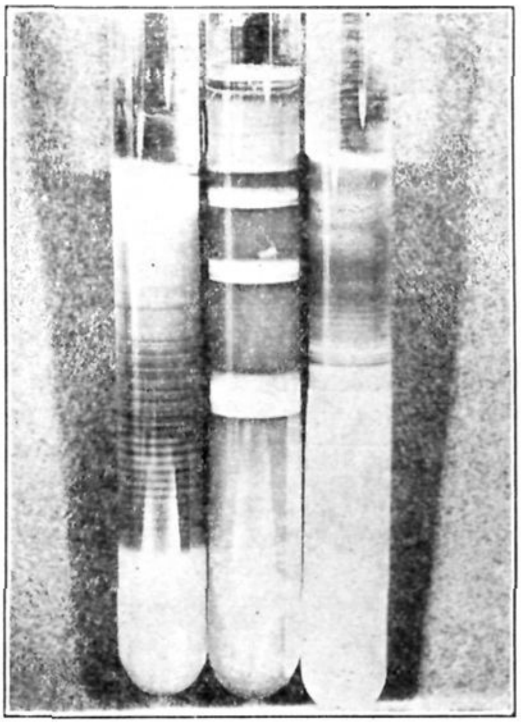

Fig. 4.—Copper chromate bands. The silicic acid gel in the middle tube contains a slight excess of base, the other two are more basic.

Working with acetic acid as at first discussed, the effect of increased alkalinity was studied. Making a gel from equal volumes of 1.09 density water glass (as compared with the usual 1.06 density) and 0.5 *N* acetic acid the copper chromate bands were much closer together, greatly resembling an agate. Thirty in a distance of 3 cm. were obtained. With a gel from 1.15 density water glass and 0.5 *N* acetic acid the bands were still more compact. It is evident that an increase in the excess of sodium silicate with its resulting alkalinity brings the bands of copper chromate closer together.

Addition of sugar to the usual gels made the bands thinner. Urea had the opposite effect. The influence of gravity was shown by corking tubes and inverting. The bands were irregular and made up of crescent-shaped fragments. It is noteworthy that the final condition of many tubes showed the blue of the copper sulfate in all the clear gaps—even below the last band.

Cuprous Oxide.—Closely packed bands of the yellow and red forms of cuprous oxide were obtained after a few months when glucose as a reducing agent was added to a mixture of equal volumes 1.08 density water glass and 0.5 N acetic acid and the resulting gel covered with 0.5 N copper sulfate. The yellow bands appeared first and later turned red. Near the surface of the gel blue cupric hydroxide was observed. With the U-tube method and 1% hydroxylamine hydrochloride as the reducing agent the above reduction finally resulted in tetrahedrons of metallic copper.

Copper Ferrocyanide.—Regular bands of copper ferrocyanide very close together were formed when a slightly basic gel made by mixing equal volumes of 1.06 density water glass and 0.5 N acetic acid was made 0.05 N with respect to potassium ferrocyanide and covered with 0.5 N copper sulfate. Variations in the concentration of the potassium ferrocyanide or the alkalinity of the gel produced variations in the thickness of the bands. They commonly varied from 2 to 4 mm. Although sharply defined there were no clear gaps, the bands almost merging into each other.

Basic Lead Iodide.—With a very basic gel from 1.06 density water glass and an equal volume of 0.3 N acetic acid in the band of a U-tube the arms were filled with 0.25 N lead acetate and 0.1 N potassium iodide, respectively. After some time ten well-marked bands were counted in one cm. of the curve.

Theory and Discussion.

The experimental evidence given above justifies the advancement of a more detailed theory of rhythmic banding. For the clearest illustration consider the copper chromate banding.

The gel (a silicic acid gel of slightly basic reaction) contains a dilute solution of a chromate and above it in the tube a solution of a copper salt. The copper ions diffuse into the gel, meet the chromate ions and form a layer of insoluble copper chromate at the surface of the gel. The chromate ions immediately below this precipitation zone diffuse into this region now depleted of chromate ions and meet the advancing copper ions thus thickening the layer of copper chromate. According to Fick's law of diffusion the rate of diffusion is greatest where the difference in concentration of the chromate ions in two contiguous layers is greatest, that is, just below the front of this thickening band of copper chromate. As a result the region near the band decreases in concentration of the chromate ions faster than does the space below. Finally the copper ions have to advance some distance beyond the band to find such a concentration of chromate ions that the solubility product of copper chromate may be exceeded and a new band formed. This repeats again and again. Of course if the copper ions were retarded sufficiently there would be time for the concentration of the chromate ions again to become uniform throughout the remaining clear gel and no gap would occur. Hence if the diffusion of the copper ions is retarded by any means the clear gaps decrease in depth—the bands are closer together. If copper ferrocyanide bands are formed in similar manner they almost merge after the first layer reaches a thickness of a few cm. Yet they are distinct and agate-like. A precipitate of copper ferrocyanide greatly retards the diffusion of the ions that form it, hence we have here the proper condition to reduce the clear gaps to a minimum depth.[1]

In practice the best medium for banding was found to be a silicic acid gel, yet I secured distinct banding of mercuric iodide in gels of manganese arsenate and ferric arsenate. In one experiment I obtained good banding of silver dichromate in loosely packed flowers of sulfur. From these and other experiments it is evident that a gel is not absolutely necessary. Morse and Pierce[2] as well as Dreaper[3] secured stratification in single capillary tubes without the aid of a gel.

The permeability of the gel as influenced by the presence of various salts, and sugars, for example, is an important factor in rhythmic banding. With mercuric iodide in a silicic acid gel the presence of sufficient sodium chloride entirely prevented the arrangement of the crystals in bands. On the other hand, glucose in a similar gel greatly favored the banding of mercuric iodide. In another experiment glucose produced a great increase in the number of bands of basic mercuric chloride. This marked influence of some salts gives importance to the selection of the acid used in making the gel. Hydrochloric acid is a poor choice when experimenting with mercuric iodide banding.

Silicic acid gels made by using sulfuric acid instead of acetic or other acids exerted a strikingly favorable influence on the banding of reduced gold yielding beautiful colored layers of colloidal particles.

Haschek's observation[4] that the gaps between bands of lead iodide contained the same precipitate in a different degree of dispersity and therefore less visible hardly applies to the gaps between layers of copper chromate. Under proper conditions these gaps—sometimes two cm. in depth—were absolutely clear and free from copper chromate precipitate. After a series of copper chromate bands formed the excess of copper sulfate between the layers was often evident from the clear blue color. A later addition of a saturated solution of copper sulfate on top of the gel did not produce any new bands in the old gaps.

Not all bands are made up of dense layers. A notable exception is basic mercuric chloride in a very slightly basic gel. The gleaming, feather-like crystals of this salt were sometimes rather widely scattered yet ar-

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[1] W. H. Chapin showed me a tube, over one meter long, containing many distinct bands of ammonium chloride. Ammonia had diffused from one end and hydrogen chloride from the other. No gel was used. Air took the place of a gel.

[2] *Z. phys. Chem.*, 45, 589 (1903).

[3] *Kolloid Z.*, 14, 163 (1914).

[4] *Ibid.*, 14, 115 (1914).

ranged in distinct layers. Rarely were the gaps between these bands free from crystals.

Liesegang[1] insists that silver chromate bands in gelatin only when definite small quantities of acid are present. The great field opened by the use of basic gels leaves to this observation a rather limited application.

Davis,[2] in securing bands of colloidal mercury, argues that there must have been supersaturation with this same colloid. In this connection my experiments with bands of colloidal gold might be studied. Throughout the red-blue-green bands of colloidal gold and the gaps as well were countless, gleaming, yellow crystals of gold.

Liesegang's "dead space" experiment[3] confirms the theory advanced in this paper. He filled a glass tube (open at both ends) with gelatin containing 10% of sodium chloride. This tube was then immersed in a solution of silver nitrate which diffused into the gel from both ends of the tube precipitating silver chloride in two bands. However, these two bands of silver chloride did not meet in the middle of the tube. A clear dead space remaining in the center of the tube contained no sodium chloride at all. The salt originally there had diffused away in opposite directions. A dead space was not formed when a gel containing a non-diffusing substance such as albumin was immersed in metaphosphoric acid.

Those who do not accept the theory I have advanced will, at least, find in the experimental evidence new and superior methods for investigating the problem.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

THERMAL DECOMPOSITION OF CERTAIN INORGANIC TRINITRIDES.

BY ARTHUR R. HITCH.

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Anticipating a later investigation of the atomic weight of nitrogen, and searching for a more satisfactory method than the proposed electrolysis of silver trinitride in anhydrous liquid ammonia, the author conceived the idea that it might be possible to decompose silver trinitride smoothly by subjecting it to constant heat for some time, just below the exploding point of the compound. Preliminary experiments along this line gave such promising results that it was considered more important to proceed with the study of a number of other inorganic trinitrides,

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[1] *Z. phys. Chem.*, **88**, 1 (1914).

[2] THIS JOURNAL, **39**, 1312 (1917).

[3] *Z. angew. Chem.*, **23**, 2124 (1910).