Studies on Rhythmic Precipitates.

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Contents.

I. Introduction.

In 1896 Liesegang discovered that when silver nitrate solution was allowed to diffuse into a gel impregnated with a small quantity of potassium dichromate, the deposition of the silver chromate in the gel was not continuous but marked by gaps or empty spaces at regular intervals.(1) Percieving the importance of the phenomenon he studied this phenomenon systematically(2) which was then followed by many other investigators.(3) As the result of their investigations, it was observed that not only silver chromate but also some other scarsely soluble substances form rhythmic precipitates. It was ascertained, that in many precipitation reactions rhythmic bands are obtained, when two reactive substances are brought in contact with each other, by diffusing one of the substances into a solution of the other in a gel. Since then it attracted the interest of the investigators in the question: what mechanism the phenomenon is produced by? At first, Wilh. Ostwald proposed a theory to explain this phenomenon, which is known to-day as the "super-saturation theory".(4) Ever since many other theories were presented by different authors,(5) yet this phenomenon cannot be fully explained by these hitherto proposed theories.

The present author studied the rhythmic precipitates from various standpoints, the description of which is given in the following pages. A number of new examples were obtained in the course of study, and it was made clear that in several examples the rhythmic precipitates, which are considered hitherto as Liesegang phenomenon, are produced by the periodic changes of external conditions such as light or temperature. It has been studied on the effect of the varieties of gel, the electrolytes, the hydrogen ion concentration, the presence of impurities and other substances, the ageing of gel, the light and the temperature on the formation of rhythmic precipitates. It was also studied a general regularity with regard to the intervals of the bands.

II. Various Influences on the Formation of Rhythmic Precipitates.

The Influence of the Nature of Gel. Rhythmic precipitates are formed not only in a gel but also in places such as capillary tubes or narrow aperture between two glass plates where no gel is present. The formation of rhythmic precipitates in a gel will be described first.

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(1) Liesegang, *Naturw. Wochschr.*, **11** (1896), 353; *Photographisches Archiv*, (1896), 221.

(2) Liesegang, *Kolloid-Z.*, **2** (1998), 70; *Z. physik. Chem.*, **88** (1914), 1; "Chem. Reaktionen in Gallerten" Düsseldorf, (1898); "Geologische Diffusionen", Dresden, (1913).

(3) See Hedges, "Liesegang rings"; S. Veil, "Les Phénomènes Périodiques de la Chimie" Paris, (1934).

(4) *Z. physik. Chem.*, **23** (1897), 365; "Lehrbuch der Allgemeinen Chemie" II, 2, 777, Leipzig, (1911).

(5) Bradford, *Kolloid-Z.*, **30** (1922), 364; Chatterji and Dhar, *Kolloid-Z.*, **31** (1922), 15; *ibid.*, **37** (1925), 2, 89; Wo. Ostwald, *Kolloid-Z.*, **36** (Zsigmondy-Festschrift) (1925), 380; Holmes, *J. Am. Chem. Soc.*, **40** (1918), 1187; Fischer and Mclaughlin, *Kolloid-Z.*, **30** (1922), 13; Traube and Takehara, *Kolloid-Z.*, **35** (1924), 245; Michaleff, Nikiforoff and Schemjakin, *Kolloid-Z.*, **66** (1934), 197; Christiansen and Wulff, *Z. physik. Chem.*, B, **26** (1934), 187.

As Liesegang(1) had first found, the rhythmic precipitation of silver chromate is well developed in a gelatine jelly, but generally not in an agar-agar or in a silicic acid gel. This is known as a specific influence of a gel on the formation of rhythmic bands. Moreover, even though a gel is made of gelatine, the same results may not be obtained with various gelatines from different manufacturers.

The present author carried out three series of experiments. In the first series, five kinds of gelatines were used, two of which, being the products of our country, were purchased from Takeda Pure Chemicals & Co. and were denoted by A and B, while the others were also purchased from Takeda but manufactured by Coignet Père et Fils & Co. in Belgium and were denoted by A, D, and No. 1. In the gels which were made from these gelatines under entirely the same conditions, it was tried to make rhythmic precipitate of silver chromate. 3% gelatine solutions containing 0.1% potassium dichromate were made and introduced into test tubes (diameter about 10 mm.) to the height of 7 cm. After the gel set firmly, 5% silver nitrate solution was poured on it. The test tubes were kept in a dark room.

In Japanese gelatine A no distinct rhythmic bands were formed but at the transition zone from the fine brick-red precipitates to the relatively coarse dark violet precipitates, some faint bands were seen. In Japanese gelatine B, 8～9 distinct bands were found under a continuous zone of brick-red precipitate, beneath which a layer was formed of uniformly scattered dark violet precipitate, and in the lower part of the test tube there were 6 violet bands which consisted of relatively coarse precipitate. On the other hand, in all other three gelatines, which were made in Belgium, the typical rhythmic precipitate of brick-red silver chromate was well developed. In gelatine A of Coignet, 25 bands were formed. In this case, the intervals between two succeeding bands were the shortest among the three examples. In gelatine No. 1. of Coignet, 21 bands were formed. In gelatine D of Coignet, 20 bands were formed and the intervals between them were the longest among these three.

The second series of experiment were conducted in the same manner, with seven samples of photographic gelatines, A, B, and C for the manufacture of positive cinematographic film and A, B, C and D for negative film. These photographic gelatines were placed at the author's disposal by the kindness of Fuji Photo Film Co. Ltd. The conditions were entirely the same as those of the first series. The results were as follows. In gelatine A for positive film, 15 bands were recognised, though seven of which were very faint. In gelatine B for positive film, 26 bands were formed, the lower the position of the band formed in the gel was, the smaller the diameter of the disc of band. The density of the band formation was large. In gelatine C for positive film, 26 distinct bands were formed, and in this case also, the lower the position of the band the smaller the diameter of the disc. In gelatin A for negative film, 12 bands were formed, though all were faint, four of them were especially very faint. In gelatine B for negative film, 30 bands were formed. The band was too dense and a part of the banded precipitate was blurred. The banding was the same type with gelatine B for positive film. In gelatine C for negative film 15 bands were formed, seven of which being very faint. The appearance of this rhythmic precipitate was similar to that in gelatine A for positive film. In gelatine D for negative film, 17 bands were formed, the typical rhythmic precipitate being well developed.

In the third series, an attempt was made to make bands of magnesium hydroxide in these photographic gelatines. In this case, the specific influence of gelatines was more or less indistinct. In gelatine A for positive film, 2 bands and a band of saturn structure were formed. In gelatine B for positive film, 2 bands and a ring were formed. In gelatine C for positive film, 2 bands and a ring were formed. In gelatine A for negative film also, 2 bands and a ring were formed, but in this case the intervals between the bands were somewhat larger than the cases of gelatine B and C for positive film. In gelatine B for negative film, 2 bands and a ring were formed, the intervals between them were the same as in the cases of gelatine B and C for positive film. In gelatine C for negative film, 2 bands and a band of saturn structure were formed and in gelatine D for negative film, 3 bands were formed. The differences of bands in the case of magnesium hydroxide caused by the varieties of gelatine were somewhat obscure but recognisable.

Thus the different gelatines give entirely diverse results. It seems that these effects may be chiefly referred to the hydrogen ion concentration of the gel and to the impurities contained in gelatine. Liesegang(6) concluded that the specific influences of gelatines on the formation of rhythmic precipitates are referred to the content of gelatose, a hydrolytic product of gelatine.

By the author's experiment, however, it was recognised that the influence of the difference of gelatose content is not so large, for the banding was scarcely influenced by the addition of a small quantity of gelatose to the gel. Accordingly, the influence of the species of gelatines is not referred only to the gelatose content.

Certain rhythmic precipitate is formed in gelatine, in agar-agar, or in silicic acid gel, irrespective of the species of the medium, or even in the complete absence of gel. For example, the rhythmic precipitate of calcium phosphate is the case. It is well known that calcium phosphate forms rhythmic precipitate in gelatine, in agar-agar or in the complete absence of gel. The author could obtain the rhythmic bands of this substance also in silicic acid gel.(7)

On the other hand, it is well known that silver chromate gives a typical rhythmic precipitate in gelatine jelly but not in agar-agar or in silicic acid gel. Bradford(8) obtained silver chromate bands in an agar-agar gel which contained somewhat large quantity of potassium citrate with potassium dichromate. Hatschek(9) had succeeded in obtaining the bands of silver chromate in a silicic acid gel, which was prepared by the unusual method, based on the fact that silicic acid is gelatinised on mixing

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(6) Liesegang, *Kolloid-Z.*, **2** (1907), 70.

(7) Isemura, this Bulletin, **13** (1938), 493.

(8) Bradford, "Alexander's Colloid Chemistry, Theoretical and Applied" Vol. I, 790, New York (1926).

(9) Hatschek, *Kolloid-Z.*, **38** (1926), 151.

a solution of sodium silicate with somewhat large quantity of a solution of potassium dichromate.

As reported in a previous communication,(10) the present author had also succeeded in obtaining more distinct rhythmic bands of silver chromate in a silicic acid gel which was prepared by the usual procedure. A sol was prepared by mixing a solution of sodium silicate with some acids and then potassium dichromate was added. After the gel set firmly, a strong silver nitrate solution was put on it and let diffuse into the gel. Silver chromate bands in a silicic acid gel were thus obtained. In this case, hydrogen ion concentration of the gel plays an important rôle, and the range of pH where the rhythmic precipitates are made, is very narrow. So, it was believed by many investigators, that silver chromate cannot be obtained in bands in silicic acid gel and they insisted upon the non-formation of bands as being the specific effect of gel. The rhythmic precipitates of the same substance are produced in various jellies by modifying the conditions in certain degree.

Lead chromate does not form rhythmic bands in an ordinary silicic acid gel, but forms bands in the presence of some glucose in the gel.(11) Lead iodide in a silicic acid gel does not form rhythmic precipitate in an ordinary condition and fern-like fronds grow down into the gel, mixed with many hexagonal plates. But it was found in rare cases that the rhythmic precipitate of this substance occurred accidentally. When the crystal became relatively small, the rhythmic precipitate was generally formed. The increase of the concentration of inner and outer electrolytes is favourable for making the deposited crystals small. In order to make sure of the formation of the rhythmic precipitate of lead iodide a third substance has to be added, which makes the crystals of lead iodide very small. Citrate and tartrate fit for this purpose. The typical rhythmic bands of lead iodide in a silicic acid gel were obtained by the presence of a small quantity of citrate or tartrate.(12) These results will be described later in detail.

It seems from the above-mentioned results that the nature of gel has a great influence on the formation of periodic precipitate but rhythmic bands are produced in any gel when we modify the condition appropriately. Generally the precipitates formed in gelatine are especially small in size. The precipitates formed in silicic acid gel on the contrary, are often well-developed crystals, and the bands are often blurred by the growth of too large crystals which came in contact with each other.

The presence of a gel is favourable in many cases but not always necessary for the formation of bands. This was already shown by Dreaper(13) and others.(14) In their experiments rhythmic precipitation was observed in a capillary tube of in a narrow aperture between two glass plates and the formed rhythmic bands are always microscopic. We can recognise from these facts, that the gel has an important signifi-

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(10) Isemura, this Bulletin, **13** (1938), 489

(11) Isemura, *ibid*, **8** (1933), 11.

(12) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 58.

(13) Dreaper, *Kolloid-Z.*, **14** (1914), 163.

(14) Wo. Ostwald, *Kolloid-Z.*, **40** (1926), 144; Notboom, *ibid.*, **32** (1923), 247; Morse, *J. Phys. Chem.*, **34** (1930) 1554; Ghosh, *J. Indian Chem. Soc.*, **7** (1930), 509.

cance to prevent the disturbances caused by heat convection or by mechanical shocks. If the reactions are undertaken in a viscous fluid and mechanical shock is prevented and the sudden change of temperature is avoided, then rhythmic bands may be produced in an ordinary test tube in the absence of jelly. When the density of the precipitate produced by such reaction in the viscous fluid is large, the precipitate settles down by gravity so that the bands blur.

In some colour reactions, however, bands are preserved for a long time. For example, the reaction which is known as Lunge's reaction for nitrate ion, gives often rhythmic bands when the system is kept from disturbances. A dilute potassium nitrate solution is gently run down the side of a test tube on a diphenylamine solution in concentrated sulphuric acid, and the tube is allowed to stand for several days. Blue rhythmic bands, are formed in sulphuric acid. Similar rhythmic colourings were observed in some other colour reactions. Reaction between an aqueous solution of egg albumin and a solution of α-naphthol or thymol in sulphuric acid, which is called Molisch's reaction for sugar in protein, gives violet or red-brown bands. The reaction of an aqueous solution of egg albumin with a solution of glyoxylic acid in sulphuric acid, that is known as the Hopkins and Cole's reaction for protein, gives blue violet rhythmic colouring in the entire absence of disturbance. Fig. 1 shows the rhythmic colouring of the reaction of protein with α-naphthol and thymol. The left photograph is obtained by the reaction of protein with thymol and the right by the reaction with α-naphthol. When we carefully protect the test tubes from shocks and sudden change of temperature, we can preserve these bands for a long period.

The Influence of Inner Electrolyte and its Concentration. The range of the concentration of inner and outer electrolytes for the formation of the Liesegang rings is rather narrow. Accordingly, it gives the general appearance that the formation of rhythmic precipitate is limited to some special substances. In the author's opinion, however, the formation of periodic precipitate is a general phenomenon.

The concentration of inner electrolyte has especially a profound influence on the formation of bands. The concentration of electrolyte beyond a certain limit is necessary for the formation of bands. The increase of the concentration of inner electrolyte beyond this limit makes the banding more dense. The distance from the top of the gel to the first separted band becomes large with the increase of the concentration of inner electrolyte. On the other hand, if the concentration exceeds certain upper limit, bands can no more be obtained.

The increase of the concentration of inner electrolyte hinders the diffusion of outer electrolyte into a gel, while the inner electrolyte diffuses in the opposite direction, so that there remains little reactant at the bottom of the test tube. Consequently, the distance between the last formed band and the top of the gel becomes short when the bands deposit closely each other. The relation between the density of bands and the change of concentration of inner electrolyte was shown in the previous communications.(15) Some of the results are given in the following tables.

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(15) Isemura, *J. Chem. Soc. Japan,* **58** (1937), 301, 629.

Table 1.
Bands of Silver Carbonate.

Conc. of sodium carbonate (inner electrolyte) (%)	Number of bands
0.25	continuous precip.
0.23	continuous precip.
0.20	10
0.15	5
0.12	4
0.10	3
0.08	0
0.06	0

Gelatine 2.8%.
Outer electrolyte: silver nitrate 5%.
Temperature: 5°C.

Table 2.
Bands of Silver Carbonate.

Conc. of ammonium carbonate (inner electrolyte) (%)	Number of bands
2.3	13
1.4	15
0.9	12
0.6	9
0.5	8
0.4	7
0.3	5
0.2	6
0.1	3

Gelatine 2.8%.
Outer electrolyte: silver nitrate 5%.
Temperature 5°C.

Table 3. Bands of Silver Iodate.

Conc. of silver nitrate (inner electrolyte) (%)	Total number of bands	Number of bands *
0.17	20	15
0.13	22	14
0.09	22	13
0.07	22	12
0.04	10	3

Gelatine 2.8%. Outer electrolyte: potassium iodate 5%. Temperature: 5°C.

The asterisk denotes the number of bands formed from 10 to 40 mm. from the contact surface of the diffusing solution and gel. (The same in Tables 3, 5, 7, 12, 14, 16).

Table 4. Bands of Silver Arsenite.

Conc. of sodium arsenite (inner electrolyte) (%)	Total number of bands	Number of bands **
1.8	28	16
1.0	29	18
0.7	27	19
0.3	26	18
0.2	20	17
0.1	14	11

Gelatine 2.5%. Outer electrolyte: silver nitrate 5%. Temperature: 10°C.

** denotes the number of bands formed 30 to 60 mm apart from the contact surface of the gel and the diffusing electrolyte. (The same in Tables 4 8, 13, 17).

Table 5. Bands of Lead Iodate.

Conc. of potassium iodate (inner electrolyte) (%)	Number of bands*
2.0	23***
1.8	25
1.6	23
1.4	22
1.2	20
1.0	20
0.8	19
0.6	17
0.4	14
0.1	8

Gelatine 2%. Outer electrolyte: lead acetate 0.5 mol.
Temperature: 15°C.

*** A continuous precipitate was formed to a point of 12 mm. from the contact surface and the bands could not be counted in the part 10 to 12 mm. apart from the surface.

In these cases, the effects of concentration of inner electrolyte were investigated keeping other conditions in same. Experiments were conducted in test-tubes the inner diameter of which being 1.2 cm. and the length, 11 cm. These test tubes were filled with the gel to the height of 6.5 cm. Fig. 2 shows the effect of concentration of inner electrolyte in the case of silver carbonate bands. These photographs correspond to the third to seventh experiments shown in Table 1.

The influence of the concentration of inner electrolyte was studied subsequently with barium chromate, lead carbonate in gelatine, lead carbonate, cobalt sulphide, ferric ferrocyanide, cobalt phosphate, copper iodate, copper carbonate and bismuth chromate bandings in silicic acid gels. These experimental results will be described later in details.

The appearance of the rhythmic precipitate of a certain substance, produced by the action of the various salts as the inner electrolyte, differs profoundly according to the kind of salt. For instance, when we make silver carbonate bands in gelatin, we can use ammonium carbonate as well as sodium carbonate. But the appearance of the obtained rhythmic bands is quite different in these cases. In the case of ammonium carbonate the bands are obtained for relatively wide range of the concentration of inner electrolyte, namely $0.1 \sim 2.3\%$, while in the case of sodium carbonate the range of concentration is rather narrow. Moreover the bands of silver carbonate which were made by using sodium carbonate as the inner electrolyte looked like tablets and were separated from each other with considerable intervals. The bands which were made by using ammonium carbonate, grew relatively close as seen in Table 2 and each band was often incomplete and had the appearance of a net-work or an assemblance of fragments of crescent-shaped precipitate. It seems that the influence of the varieties of inner electrolyte is referred to the effect of the soluble reaction products, such as sodium nitrate or ammonium nitrate, on the solubility and growth of the precipitate.

The Influence of Outer Electrolyte and its Concentration. On the formation of rhythmic precipitate it is necessary that the outer electrolyte diffuses into the gel. So the concentration of the outer electrolyte must be high. At least it must be hypertonic to that of the inner electrolyte. The effect of the concentration of the outer electrolyte on the formation of periodic bands is similar in many cases. The higher the concentration is, the larger the number of bands becomes. The larger the ratio of concentration of outer electrolyte to that of inner electrolyte becomes, the closer the intervals between the bands, generally become. So, if the conditions, excepting the concentration of the outer electrolyte are maintained constant, it is obvious that the higher the concentration is, the larger the number of the formed bands and the smaller the intervals between the bands become. The importance of the concentration as to whether bands are formed or not, is smaller in this case than in the case of inner electrolyte, that is the range of concentration that can form rhythmic bands is very wide. But too concentrated solution is often unfavourable for the rhythmic banding. If the concentration becomes too high, the bands stand too close together, so a part of precipitate appears only like a column of precipitate and has not a periodic structure. At the same time, if too concentrated solution of outer electrolyte was used, it often peptised the gel. For example, when silver chromate bands are made in gelatine, too concentrated silver nitrate solution peptises the gelatine at the contact surface of the gel with the solution. For these reasons, the concentration of outer electrolyte is somewhat restricted, but in general, the concentration of outer electrolyte for the rhythmic banding has a relatively small significance. The results of the experiments on the influence of the concentration of outer electrolyte, were also shown in the previous communication.⁽¹⁵⁾ Some of the results are given in the following tables.

Table 6.

Bands of Silver Carbonate.

Conc. of silver nitrate (outer electrolyte) (%)	Number of bands
20	9
15	8
10	7
5	6

Gelatine 2.8%.
Inner electrolyte:
sodium carbonate 0.17%.
Temperature 5°C.

Table 7. Bands of Silver Iodate.

Conc. of potassium iodate (outer electrolyte (%)	Total number of bands	Number of bands*
Saturated solution	22	13
5.0	21	12
4.0	17	9
3.0	13	6
2.0	12	2

Gelatine 2.8%.
Inner electrolyte: silver nitrate 0.1%.
Temperature 5°C.

Table 8. Bands of Silver Arsenite.

Conc. of silver nitrate (outer electrolyte) (%)	Number of bands**
15	15
10	26
5	15

Gelatine 2.5%.
Inner electrolyte:
sodium arsenite 0.67%.
Temperature: 10°C.

When a 15% silver nitrate solution was added the formed continuous precipitate came down to a distance of 43 mm. from the surface of the gel. Therefore, the bands decreased in number, but in reality they stood close by in the highest degree.

Table 9. Bands of Lead Iodate.

Conc. of lead acetate (outer electrolyte) (mol.)	Number of bands*
1.00	22
0.75	21
0.50	20
0.25	18

Gelatine 2.0%.
Inner electrolyte:
potassium iodate 1.2%.
Temperature: 15°C.

Fig. 3 shows the change of the closeness with the concentration of outer electrolyte in the case of silver carbonate bands.

The influence of the concentration of outer electrolyte was subsequently studied with lead carbonate, copper iodate, and cobalt sulphide bandings in silicic acid gels. In the case of calcium phosphate bands in the silicic acid gel, some peculiar results were obtained. While the concentration of outer electrolyte is relatively low, the general rule—the higher the concentration is, the larger the number of bands formed becomes or the smaller the intervals between the bands become—holds in this case also. But if the concentration exceeds a certain limit, the influence is scarcely observed as shown in Table 10. The rhythmic precipitates which were obtained by the diffusion of calcium chloride, the concentration of which were beyond a certain limit, are entirely identical(16).

Table 10. Calcium phosphate in silicic acid gel.

Conc. of calcium chloride (outer electrolyte) (%)	Number of bands	
30	8	These three coincide and showed no difference.
25	8	
20	8	
15	8	The bands were close in proportion to the concentration of outer electrolyte.
10	8	
5	7	

Inner electrolyte: sodium phosphate 0.5%.

As described in the foregoing paragraphs, bands of different appearance are obtained under the same experimental conditions when the

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(16) Isemura, this Bulletin, **13** (1938), 493.

species of the inner electrolyte are different. Similarly, different bands are obtained, when the species of outer electrolyte differs. This is proved in the cases, for example, of the formation of periodic precipitates of lead iodate in gelatine, where lead nitrate and lead acetate solutions of the same concentration are used as the outer electrolyte respectively. When lead nitrate is used, the bands are thinner and their number is larger and the intervals between them become shorter than the case of lead acetate. Fig. 4 shows such a case, the left being obtained by diffusion of lead nitrate and the right by lead acetate. The bands stood so close in the case of lead nitrate, that scarcely any strata were discriminated in the upper part of the figure. This fact is not to be referred to the difference of the diffusibility of lead nitrate and lead acetate. It must preferrably be referred to the influence of the solubility of the précipitate in the formed soluble salts such as potassium nitrate and potassium acetate. Because, the effects of the temperature or the concentration of gel, which affect considerably the diffusibility, give smaller difference of bandings than the effect of the outer electrolyte. Even when a half concentrated solution of lead nitrate to that of lead acetate is used still closer the bands are formed than those formed by the diffusion of the lead acetate solution.

Rhythmic precipitates of bismuth chromate in silicic acid gel, obtained by diffusing bismuth nitrate and bismuth chloride have quite different appearances. In this case, the acid which is used to prepare the gel has also some effects on the bands. So this case will be treated later again.

Contrary to the effects of the concentration of outer electrolyte previously described, there are a number of cases in which, when the concentration of outer electrolyte increases, the intervals between the bands increase and the bands become more distinct. This is the case of gold banding. Indeed, gold bands are not formed as a true "Liesegang phenomenon" but as a reflex of the rhythms of external conditions. This will be described in the later part.

According to Lincoln and Hillyer,⁽¹⁷⁾ if the ratio of the concentrations of outer and inner electrolyte is constant, the same distribution of the layers of rhythmic precipitate is obtained, providing that the gel concentration and the temperature are constant. By the decrease of the concentration of inner electrolyte the formation of precipitate becomes slower, and on the other hand, by the decrease of that of outer electrolyte, it diffuses more slowly, so the influences of the decrease of the concentration of both inner and outer electrolyte become relatively small, for both affect oppositely. But it seems that both influences are not completely compensated by each other. The present author studied this fact by using the bands of silver chromate in gelatine and calcium phosphate in silicic acid gel. These rhythmic precipitates, however, did not obey the above rule. So, it seems that the fact pointed out by Lincoln and Hillyer has no generality.

Interchange of Inner and Outer Electrolytes. When a rhythmic precipitate obtained by the interaction of two substances in a gel, either

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(17) Lincoln and Hillyer, *J. Phys. Chem.*, **38** (1934), 907.

of the two may well become an inner electrolyte or an outer electrolyte. In many experiments by various authors, in which silver chromate bands are made in gelatine, potassium dichromate is usually dissolved in gelatine as an inner electrolyte and silver nitrate is allowed to diffuse into the gel. But, inversely, by diffusion of potassium dichromate into the gelatine containing silver nitrate, we can also obtain the rhythmic precipitate of silver chromate.

Accordingly, the interchange of inner and outer electrolytes has no concern with the formation of rhythmic precipitate as a general rule.

It is often impossible to add salts of heavy metals to the silicic acid gel, for silicic acid is partially coagulated. On the other hand, when silver carbonate bands are formed in gelatine containing ammonium carbonate by the diffusion of silver nitrate, a rhythmic precipitate which often consists of crescent-shaped bands is obtained. When the bands are formed reversely in gelatine containing silver nitrate as an inner electrolyte, we shall meet an interesting fact. At first silver carbonate bands have formed, but with the progress of diffusion to the lower part of the gel, the upper bands successively re-dissolved by the formation of a more soluble double or complex salt with the excess of diffusing ammonium carbonate. Owing to the deposition of precipitate in gel, the gel is broken at these parts of deposition. Later, being separated, these parts do not cohere again. There remain rhythmic cracks.

When lead iodide bands in a silicic acid gel are formed by the diffusion of potassium iodide into a gel containing lead acetate, well-developed rhythmic bands are obtained, although a part of lead iodide re-dissolve, forming a soluble complex salt at the top of the gel. But inversely, if lead acetate diffuses into a gel containing potassium iodide, lead iodide is formed at first, but it is immediately converted into a white double salt with successively coming lead acetate. In this case the bands are not so distinct.

In some cases the rhythmic bands of quite different appearances are obtained by the interchange of the inner and outer electrolytes. This is the case with rhythmic bands of silver iodate in gelatine. When a gel containing potassium iodate was covered with silver nitrate solution a rhythmic precipitate is obtained as shown in Fig. 5, the bands of which consist of flocculent clusters of crystals. On the contrary, when a gel containing silver nitrate was covered with the potassium iodate solution the formed rhythmic precipitate is very peculiar in shape, showing a greatly different form from any rhythmic precipitates which the author had ever seen. Fig. 6 shows this rhythmic precipitate. In this case, the structure is rather complicated, thus, band consisting of scattered coarse crystals, thin band consisting of very small crystals and relatively thick band consisting of coarse crystals and empty interspace were repeatedly observed.

The Influence of the Concentration of Gel. The concentration of gel has a remarkable influence on rhythmic precipitate. In many cases, if the concentrations of inner and outer electrolyte are kept constant, the number of formed bands decreases and the intervals between them increase with the increase of gel concentration. The distance from the top of the gel to the last formed band also decreases, in general, with the concentration of the gel. The influence of gel concentration had been investigated on the rhythmic precipitates of silver carbonate, silver iodate, silver arsenite and lead iodate in gelatine gels. The results are shown in the following tables (Table 11–15).

Table 11.

Bands of Silver Carbonate.

Conc. of gelatine (%)	Number of bands
5.0	2
4.0	4
3.0	5
2.0	9

Inner electrolyte: sodium carbonate 0.17%.
Outer electrolyte: silver nitrate 5%.
Temperature: 5°C.

Table 12.

Bands of Silver Iodate.

Conc. of gelatine (%)	Total number of bands	Number of bands*
5.0	21	12
4.0	23	13
3.0	25	12
2.8	25	13
1.5	25	14

Inner electrolyte: silver nitrate 0.13%.
Outer electrolyte: potassium iodate 5%.
Temperature: 5°C.

Table 13. Bands of Silver Arsenite.

Conc. of gelatine (%)	Number of bands**
4.4	16
3.5	17
3.1	18
2.7	19
2.3	21

Inner electrolyte: sodium arsenite 0.67%.
Outer electrolyte: silver nitrate 5%.
Temperature: 10°C.

Table 14. Bands of Lead Iodate.

Conc. of gelatine (%)	Number of bands
6.0	16
4.8	18
3.0	20
2.0	23

Inner electrolyte: potassium iodate 1.6%.
Outer electrolyte: lead acetate 0.5 mol.
Temperature: 15°C.

Fig. 7 shows the effect of the concentration of gel in the case of silver carbonate bands in gelatine. The intervals between bands increase and the number of formed bands decreases with the concentration of gel. The influence of gel concentration was first investigated quantitatively by Popp(18) with rhythmic precipitate of magnesium hydroxide in gelatine. According to her experiment, the band itself and the intervals between bands increased with gel concentration, but the number of bands formed was unchanged. In a concentrated gel, the diffusion proceeds slowly and the gel acts to prevent the separation of precipitates. The above results seemed to show that the increase of gel concentration forced to decrease the diffusion velocity and to increase the action which prevents considerably the separation of precipitates.

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(18) K. Popp, *Kolloid-Z.*, **36** (1925), 208.

There is an exceptional rhythmic precipitate that gives a reverse result to the above mentioned general rule. This is the case of silver chromate in gelatine. The results are shown in Table 15. In this case the number of bands increases and the intervals between bands decrease by the increase of gel concentration.

Table 15.

Bands of Silver Chromate.

Conc. of gelatine (%)	Number of bands
10.0	35
7.5	31
5.0	27
2 5	19

Inner electrolyte: potassium dichromate 0.13%.
Outer electrolyte: silver nitrate 30%.
Room temperature.

Indeed, there is a significance in the existence of gel for the prevension of the disturbance caused by convection and removing unfavourable effects caused by shocks. Rhythmic precipitate is generally obtainable either in dilute or concentrated gel. For the quickness of diffusion of outer electrolyte it is convenient to use a dilute gel which has the "form-stability" beyond a certain limit. In some special cases, however, it is better to use the concentrated gel, for it favours the accumulation of the precipitate. One of the example of this case is the gold banding in silicic acid gel. Gold bands are well developed in the gel which is prepared by mixing equal volumes of a 1.16 density water glass solution and a 3 N solution of sulphuric acid, but only faint bands are obtained in the gel prepared by mixing a solution of water glass ($d = 1.06$) and a 0.5 N sulphuric acid.

The Influence of Light. Experiments have been done on the rhythmic precipitates of various examples in the light and dark place, and it has been known that, in general, the rhythmic bands appear in light as well as in dark. But in one of the previous communication,(19) the author has reported that the light has a profound influence on certain rhythmic precipitate such as that of silver chromate in gelatine jelly. Light has an effect only on the photo-sensitive systems such as chromate-gelatine and an essential significance on the diurnally formed system.

Küster(20) stated that no band of silver chromate was obtained in the dark, while Davies(21) obtained good bands. Blair(22) reported that the bands formed in complete darkness show irregularity. The experiment carried out by the present author are as follows. Three samples of gelatine solutions were prepared, the first sample was made in complete darkness while the second and the third in an ordinary room. The first and the second were set in the dark place and the third, in an ordinary room. Three days later, silver nitrate solution was poured on these gels. After standing the former two in the dark and the latter in the light for a week, rhythmic precipitates of silver chromate were recognised in

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(19) Isemura, this Bulletin, **8** (1933), 108.
(20) Küster, *Kolloid-Z.*, **13** (1913), 192.
(21) Davies, *J. Am. Chem. Soc.*, **44** (1922), 2698.
(22) S. Blair, *Phil. Mag.*, **49** (1925), 90.

all three test tubes and no irregularity was noticed. From this fact it has been ascertained that the formation of bands is not affected by the darkness.

According to Blair the bands become irregular when the gel has been irradiated with visible light. But Cluzet and Kofmann⁽²³⁾ stated that the formation of rhythmic precipitates was unaffected by visible light. The author found that the radiation of visible ray has an important effect on the formation of bands though the bands do not become irregular even by the strong irradiation of direct sun light. The experiment was done as follows: 2.5% gelatine gel containing potassium dichromate (0.1%) as an inner electrolyte was allowed to set in test tubes and they were kept in a dark place. After the gel set firmly, it was covered with 15% silver nitrate solution. Then each of the test tubes was exposed to direct sun light for different interval of time. The light was filtered through the layer of water to avoid the effect of heat ray. In this case, the number of the formed bands increases in proportion to the time of exposure. But when a certain time interval was exceeded, the bands formed too close to each other and the whole appeared as a dark brown column. Analogous results were obtained by the influence of diffused light.

We can conclude from these results, that the visible light caused to increase the number of bands and to decrease the distance between bands. It seems that these changes which are caused by the exposure to light, are due to the transformation of gel structure and to the interaction of gelatine and potassium dichromate. After long exposure, gel becomes somewhat difficultly soluble and does no more reset. From this fact, it is probable that the gel changes somewhat in its structure or at least the micelle of gelatine suffers some changes.

The author conceives, from these facts, that at first the gelatine reacts with potassium dichromate on exposure to light and changes to insoluble modification. This modification has a less protective action from crystallisation of silver chromate than before. So the bands become closer and the number of them increases.

Blair, studied the effect of visible light by the exposure to the radiation from a half watt lamp, instead of sun light, at very short distance (6 in. range), and recognised that the bands become irregular. In writer's opinion, by the radiation from a short distance as in Blair's experiment, the energy of light delivered to the gel system does not distribute equally as in the case of parallel ray as sun light. Hence the irregular bands were formed.

According to Blair, ultra-violet ray from quartz mercury lamp makes the formation of bands impossible even in a few hours, while Cluzet and Kofmann found that the formation of Liesegang rings was retarded by ultra-violet light. The retardation of formation of rings is also recognised by the author's experiment. And rings became finer and closer each other than in the non-illuminated case.

Recently Köhn and Mainzhausen⁽²⁴⁾ have published an interesting results on the influence of light. According to their result, the influence

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(23) Cluzet and Kofmann, *Compt. rend. soc. biol.*, **104** (1931), 1001.
(24) Köhn and Mainzhausen, *Kolloid-Z.*, **79** (1937), 316.

of light is recognised when a photo-sensitive substance such as silver chloride is formed in the gel. Subsequently, the author has repeated the experiment on the influence of light that was reported in formerly published work using the gelatine purified by the method of Loeb.(25) Most impurities in gelatine were desorbed, and it was verified by Lüppo-Cramer's method.(26) The gelatine thus purified was almost perfectly free from chlorine or other halogen ions. The obtained results were the same with the former one. The number of bands formed was increased according to the time of exposure to light before superposing the diffusing electrolyte, and the intervals between them became short. It seems that the variation of the distance between bands and the number of them have no concern with the content of chlorine or halogen ions. It gives a very important suggestion on this problem whether rhythmic precipitate of chromate of any metal which does not form a photo-sensitive salt, are affected or not by the irradiation of light. The effect of light on barium chromate bands was studied using the purified gelatine. In this case, the effect of light is also considerable. The experiment was done as follows: a 3% gelatine gel containing 0.5% potassium dichromate as the inner electrolyte was allowed to set in three test tubes in a dark place. The first tube was exposed to direct sun light for about two hours, the second kept in an ordinary room for a day, and the third kept in the dark throughout. A 1 N barium chloride solution was poured on the gels and all three tubes were kept in the darkness. In the test tube exposed to direct sun light the bands became close and blurred and in the test tube kept in diffused light the bands also became close but each band was distinguishable.

Analogous results were also obtained by the influence of ultra-violet ray which is shown in Fig. 8. A gelatine solution which was prepared as above described, was poured into three test tubes of fused silica. One was exposed directly to a quartz mercury lamp, the other exposed to ultra-violet ray filtered from visible rays by a special filter, and the last kept in the dark throughout. The lamp used for this experiment was "Acme"mercury quartz lamp which was made by Shimazu factory. Input of the current applied to the apparatus was 110 volts and 10.2 amperes and the distance between the test tubes and the lamp was about 20 cm. In the photograph, the left is one which was exposed directly to the mercury quartz lamp and the middle to ultra-violet ray and the right unexposed one.

According to the author's opinion, the tanning effect of light plays an important rôle in these cases. This is clear from another fact that light has no influence on the rhythmic banding of the system which does not cause the photochemical reaction between medium and inner electrolyte. For example, lead iodate bands in gelatine are not influenced by light when it was experimented in the condition entirely similar to that of the above described silver chromate system. Also, copper chromate bands in a silicic acid gel are not affected at all by irradiation, for silicic acid and potassium chromate do not react photochemically with each other. On the other hand, there are some rhythmic precipitates on

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(25) Loeb, *J. Gen. Phisiol.*, **1** (1918), 237.
(26) Lüppo-Cramer, *Kolloid-Z.*, **5** (1909), 249.

the formation of which light has an essential significance. This is the case, for example, with a rhythmic precipitate of gold. Davies(29) has found first that light has an essential effect on the rhythmic banding of gold. The author considered that red-blue-green zones are probably formed by the variation of external irradiation. This assumption was confirmed by the following experiment: To 20 c.c. of a mixture of equal volumes of a 1.158 density sodium silicate solution and 3 N sulphuric acid, it was added 0.8 c.c. of 1% auric chloride. The gel set in a day or two. This gel was kept in a thermostat and covered with a saturated solution of oxalic acid and irradiated with a 60 watt lamp from 50 cm. distance. As oxalic acid diffused into the gel, auric chloride was reduced. The reduced gold was scattered uniformly, but in transmitted light, many bands could be distinguished in the red violet coloration of colloidal gold. These bands may be formed either by the variation of the light intensity or by the true periodic precipitation. Experiment was done under the irradiation of constant light intensity, which was obtained by using accumulators of large capacity as an electric source. By the continuous irradiation of lamp which was supplied by a current from the accumulators, colloidal gold was separated out and scattered uniformly, and no band was observed in it. So it must be referred to the fact that the bands formed by irradiation with the lamp, are produced by the variation of the intensity of light. A rhythmic precipitate of gold differed from so-called Liesegang ring which is formed by the periodic precipitation of entirely chemical cause, and is only a reflex of external rhythms.

The Effect of Temperature. It is reasonable that the solubility of a precipitate and the diffusion velocity of reactants are affected by temperature. The formation of a rhythmic precipitate on which the solubility and the diffusion velocity have a serious influence, may also be affected by the temperature. In many cases, the lower the temperature is the larger the number of bands formd, and the smaller the intervals between the bands, if the conditions are kept constant excepting temperature. For example, rhythmic precipitates such as silver iodate, silver arsenite and lead iodate in gelatine gels are the cases. The results are shown in the following tables (Table 16–18). Nevertheless, in certain

Table 16.
Band of Silver Iodate.

Temperature (°C.)	Total number of bands	Number of bands*
5	18	12
13	18	10
18	20	6

Inner electrolyte:
silver nitrate 0.13%.
Outer electrolyte:
potassium iodate 5%.
Gelatine 2.8%.

Table 17. Bands of
Silver Arsenite.

Temperature (°C.)	Number of bands**
5	16
13	14
18	13

Inner electrolyte:
sodium arsenite 0.67%.
Outer electrolyte:
silver nitrate 5%.
Gelatine 4.0%.

Table 18.
Bands of Lead Iodate.

Temperature (°C.)	Number of bands*
5	20
15	15
20	13

Inner electrolyte:
potassium iodate 0.4%.
Outer electrolyte:
lead acetate 0.5 mol.
Gelatine 2.0%.

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(27) Davies, *J. Am. Chem. Soc.* **44** (1922), 2700; *ibid.*, **45** (1923), 2261.

rhythmic precipitates the inverse results were obtained, i.e. the higher the temperature is, the smaller the intervals between bands become. Examples of this case are the rhythmic precipitates of silver carbonate and magnesium hydroxide in gelatine. In the case of silver carbonate, the experiment was carried as follows: sodium carbonate was dissolved in a concentration of 0.17% in 2.5% gelatine and a 5% solution of silver nitrate was placed on it as an outer electrolyte. The experiments were made at 5, 13, and 18°C. In these experiments, the number of bands formed were the same, as shown in Table 19, but in the samples at lower temperatures, the intervals between bands became wider. Popp found that the distance between bands of magnesium hydroxide in gelatine increased as the temperature was lowered.(18) The effects of temperature on the bands differ in case to case, which may be principally caused by the degree of change of diffusibilty of ion and solubility of the formed precipitate. On the whole, the diffusibilities of ions increase with temperature and it seems that the degree of change of diffusibility are not so great and almost of the same extent with various ions, while the difference of degrees of solubility change has a serious significance. The changes of solubilities of the above mentioned substances with temperature are tabulated in the following.

Table 19.

Bands of Silver Carbonate.

Temperature (°C.)	Number of bands
5	7
13	7
18	7

Inner electrolyte: sodium carbonate 0.17%.
Outer electrolyte: silver nitrate 5%.
Gelatine 2.5%.

Table 20.

Silver Carbonate.

Temperature (°C.)	Solubility (mol./l.)
15	1.18×10^{-4} (28)
25	1.16×10^{-4} (29)

Table 21.

Magnesium Hydroxide.(30)

Temperature (°C.)	Solubility (%)
15.5	2.8×10^{-2}
100	4.0×10^{-3}

The solubility of silver carbonate is almost unchanged by the variation of temperature, while that of magnesium hydroxide decreases as temperature is elevated. In general, however, the solubilities of solids increase with the rise of temperature. So, the increase of solubility causes a rhythmic precipitate of large intervals. When the solubility does not change with the change of temperature, the effect of the change of diffusibility is recognised.

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(28) Kremers, *Pogg. Ann.*, **85** (1852), 42.
(29) Spencer and M. le Pla, *Z. anorg. Chem.*, **65** (1909), 11.
(30) Fyfe, "Gmelin Handbuch der anorganischen Chemie", II 1, 429.

The author pointed in the foregoing paragraphs, that there are rhythmic bands which are caused by the rhythmical irradiation of light. Similarly, there are bandings which are caused by the rhythmical change of temperature. So-called diurnal bands are made by the rhythms of temperature as well as by those of light. Rhythmic banding of mercuric iodide in a silicic acid gel, which had been presented by Holmes,(31) is an example of such a type. By the author's experiment, it was found that this banding is caused by the rhythmical change of temperature. According to Holmes' description, in a U-tube with a silicic acid gel (obtained by mixing equal volumes of a 1.06 density water glass solution and 1 N acetic acid) filling the bend, 0.5 N mercuric chloride in one arm and 0.1 N potassium iodide in the other, sharp red bands of mercuric iodide followed the curve like ranks of soldiers pivoting in regular formation. The present author noticed, at first that the bands formed are greatly influenced by the weather, and so it was supposed that the bands may be formed by the light. But it was observed that the rhythmic bands have formed even if the U-tube was cut off from any light. Next, the reaction was tried in a thermostat in a dark place, no band was formed and crystals of mercuric iodide were uniformly distributed in the gel. When the U-tube in which the bands were growing, was transferred into a thermostat in a dark place, then the banding has stopped. An example thus obtained is shown in Fig. 9. Diurnal bands are sometimes caused by intermittent light, but many diurnal bands of substances excepting photo-sensitive ones are caused by the change of temperature.

The Influence of the Presence of Impurities or Third Substances. Impurities in gels have often profound influences on the periodic precipitation and the bands formed. It was already pointed that the formed bands are greatly affected by the species of gelatine. This fact is partly referred to the quantities of the species of impurities in the gels. Chlorides and phosphates are contained in the ordinary gelatine as impurities. In the case of silver chromate bands, these impurities form the so-called secondary rhythmic bands by the reaction with silver nitrate. In a gelatine gel which was dialysed and the hydrogen ion concentration regulated adequately, rhythmic precipitates free from secondary bands could be obtained. The secondary band will be treated again in later pages. The existence of a very small quantity of potassium ferrocyanide in gelatine hindered the formation of silver chromate bands and red brown precipitate has deposited uniformly in the gel. The impurities in the gel react with the diffusing electrolyte and form insoluble precipitate which does not form the rhythmic bands. These precipitates hindered the formation of band. For this reason lead iodate, silver arsenite, barium chromate, silver iodate, barium carbonate and lead sulphate are not obtained as rhythmic precipitates in commercial non-dialysed gelatine. The following curious result was obtained in the formation or rhythmic precipitate of lead iodate. A 3% non-dialysed gelatine sol containing previously as much of potassium iodate as to be 1% in concentration was gelatinised and then lead acetate was allowed

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(31) H. N. Holmes, *J. Am. Chem. Soc.*, **40** (1918), 1187.

to diffuse into the gel. Continuous white precipitate was formed for the first several days. But a few days later, the first band was formed a little distant from the continuous precipitate. After an interval of one or two days, the second band appeared. When this second band began to appear, the first increased its width and got near enough to touch the continuous precipitate. Then a little later the second band grew and grew, when the first band completely joined the continuous precipitate. When the growth of the second band became prominent, the third began to appear. When the third developed, the second also joined the continuous precipitate. This course was repeated on in order, and finally all the bands were joined into one continuous precipitate. Upon observing this continuous precipitate by holding to a reflective light, it apparently contained the discontinuous parts, which ranged at regular intervals and varied in whiteness.

Therefore, originally, lead iodate must be regarded as to precipitate rhythmically in gelatine. But this result seems to be ascribable to the presence of impurities of such a kind as to produce a white precipitate, probably of phosphate and chloride, by their action on lead ion in the gelatine. It is certified that lead iodate forms a very distinct rhythmic precipitate in a purified gelatine .On the other hand, silver chromate has an entirely different colour from that of silver chloride and silver phosphate which are formed in gelatine by the reaction between impurities and the diffusing electrolyte, silver nitrate. So the bands of silver chromate are formed irrespective of the existence of such impurities.

There are often cases in which the presence of a third substance is favourable for the formation of rhythmic bands. The precipitate of silver chromate becomes very fine in the presence of some potassium citrate, and sharp and thick well-developed bands of orange red colour are observed.(11) This effect, of citrate, is caused by the increase of metastable limit of the solubility of silver chromate in the existence of a salt of polyvalent acid. The author tried to make silver chromate bands in gelatine in the presence of aconitate of the same concentration, being a salt of tervalent organic acid as citrate. Bands have been formed better in the presence of aconitate than in its absence. The particles of silver chromate are fine and bands are sharp and thinner than in the case of the presence of citrate. It is well known that silver chromate does not form bands in agar-agar. Bradford succeeded, however, in obtaining silver chromate bands in an agar-agar gel when the gel contained relatively large quantity of potassium citrate with potassium dichromate. Bradford recommended the following procedure; 2 N silver nitrate solution is allowed to diffuse into a 1% agar-agar gel containing N/100 of potassium dichromate and N/55 of potassium citrate.(8) In the same condition, the author substitute aconitate for citrate and tried to obtain the bands but the trial failed. Accordingly, even if we use an analogous substance, we can not expect the similar results. So it seems that every third substance has its specific effect.

The addition of potassium citrate to the gel is effective for the banding in many examples. When a rhythmic precipitate is indistinct by the deposition of coarse crystals in the interspaces between bands, then the addition of a small quantity of citrate often brings the bands very distinct. Bands of cobalt phosphate, lead phosphate, silver iodate and lead iodide in silicic acid gels are examples of such cases. It is a well-known fact that when potassium iodide diffuses into a silicic acid gel which contains lead acetate, fern-like fronds grow down into the gel, mixed with many large hexagonal plates. As it was mentioned above, lead iodide makes occasionally a rhythmic precipitate even in silicic acid gel when its crystals are relatively small. We can obtain well-developed bands of lead iodide if there is a third substance which makes the crystals of lead iodide small. Citrate and tartrate are fit for this purpose. Experiments were conducted as follows: At first 0.7–2.0 c.c. of 1 N lead acetate, then 0.05–1.00 c.c. of a 3% solution of potassium citrate were added to a silicic acid gel, which was prepared by mixing 10 c.c. of a 1.06 density solution of water glass and an equal volume of 1 N acetic acid. The gels were prepared in about 100 different conditions. A 2 N solution of potassium iodide was poured on these gels. When both lead acetate and potassium citrate were small in quantity, the separated crystals were relatively coarse and scattered, so that the formation of the bands could not be recognised. When they were large in quantity, a white compound, probably lead citrate, was produced in the sol and precipitated at the bottom of the test-tube. There are, therefore, some limits in adding quantities of lead acetate and potassium citrate. Formation of the rhythmic precipitate was recognised within the limits of 0.4–0.6 c.c. in potassium citrate and of 0.85–1.1 c.c. in lead acetate. The most favourable result was obtained in 0.55 c.c. of potassium citrate and 0.9 c.c. of lead acetate, when 2 N potassium iodide was used as a diffusing electrolyte. Tartrate ion is weaker than citrate ion in the ability of making the crystals of lead iodide finer. Accordingly, in producing the bands of lead iodide by the aid of tartrate ion, a relatively large amount of the ion should be mixed. But in the presence of a large amount of tartrate ion, it produces white precipitate by acting on the ion in the sol. There is naturally some limit in its use. A 2 N solution of potassium iodide was diffused into gel, which was prepared by adding 1.2 c.c. of a lead acetate solution (1 N) and 0.8 c.c. of 3% tartaric acid to a sol prepared by mixing 10.c.c. of sodium silicate solution ($d = 1.06$) and an equal volume of acetic acid (1 N). In this case the most favourable result could be obtained. In comparison with the case of citrate ion, the crystals were coarse, which stood close and formed thin bands. In Fig. 10, the left shows a typical precipitate, fern-like fronds, of lead iodide in silicic acid gel, the middle a rhythmic precipitate occasionally obtained and the right a rhythmic precipitate in gel containing citrate.

In a preceding communication, the author already reported that the presence of a small quantity of some alcohols, fatty acids or amino acids has a considerable effect on the formation of silver chromate bands.(32) The formation of bands was often strongly inhibited by the presence of a small quantity of fatty acids. The number of bands generally increases in the presence of alcohol but decreases in the presence of amino acids such as glycine and alanine. Koenig(33) pointed out that the

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(32) Isemura, this Bulletin, **9** (1934), 236.
(33) Koenig, *J. Phys. Chem.*, **24** (1920), 466.

diffusion and the solubility of the reaction product are so affected and consequently the rhythmic precipitate in a silicic acid gel is also profoundly influenced when alcohols, urea or sugars were added to the gel. When a small quantity of some salts such as potassium iodide or potassium bromide was added to a gel containing soluble phosphate and calcium nitrate was diffused into the gel, a rhythmic precipitate of calcium phosphate in the silicic acid gel will be obtained. In this case, the first four or five bands, consisting of relatively large crystals, were apart but the following bands were blurred, for the crystals were too coarse. The coarseness of the crystals are caused by the fact that the solubility of calcium phosphate is increased in some salts solutions. At the upper part of the gel the ion which forms a rhythmic precipitate is in excess, so the precipitation occurs easily. But, at the lower part of the gel, the small difference of the solubility will largely affect the separation of precipitate. In general, the crystals separate more slowly from more soluble media and the size of the crystals are large. It seems that this is the cause of indistinctness and irregularity of the bands.

In the case of the experiments on the rhythmic precipitation in a silicic acid gel, the gel is usually prepared by mixing a solution of water glass with some acid, and it is used without dialysis. Such a gel always contains a sodium salt of the acid which is formed on the double decomposition of sodium silicate by the acid. These salts as a third substance may have a profound influence on the banding. According to Holmes, the gel which was prepared by mixing a solution of sodium silicate with sulphuric acid, is adequate to the bading of gold but the gel prepared by mixing a solution of water glass with hydrochloric acid or acetic acid is inadequate to the same purpose. The present author, however, obtained good gold bands in the gel prepared by hydrochloric or acetic acid. The appearance of bands is somewhat different from the gel prepared with sulphuric acid.

Holmes said that bands of mercuric iodide are blurred in the presence of chlorine ion, so the use of hydrochloric acid is inadequate to prepare the gel for the formation of those bands. In this case, the gel which was prepared by mixing water glass with acetic acid is adequate. In the case of a rhythmic precipitate of silver chromate in a silicic acid gel, the best developed bands were formed in the gel prepared by mixing water glass with nitric acid. These facts may be considered as the influence of a third substance which is indifferent to the reaction.

Bismuth chromate banding is obtained, when bismuth chloride was forced to diffuse into a silicic acid gel which was prepared by mixing water glass solution with hydrochloric acid. Fig. 11 shows such bands. If the gel was prepared by mixing water glass with acetic acid, bands are difficult to obtain. When bismuth nitrate is allowed to diffuse into the gel prepared by mixing water glass with hydrochloric acid, no band can be obtained. In this case coarse globular precipitate, probably of bismuthy chloride is deposited. In the gel prepared from water glass and acetic acid, on the contrary, a well-developed banding is obtained, while its appearance is quite different from that of the banding by the diffusion of bismuth chloride. This is another example of the fact that a third substance has an important significance on the formation of rhythmic bands.

The Effect of Ageing. It is interesting that the banding is affected with the age of jellies before superimposing the diffusing electrolyte. Schleussner(34) recommended to keep a gelatine gel for twenty four hours before pouring the diffusing solution. The most remarkable observation which has ever been done, is that of Scott Blair.(22) He has made measurements which show that the distance of the last bands from the upper end of jelly increases regularly with the age of gel. This result has been reproduced by the present author.

The author has found another interesting fact. The effect of ageing on the formation of bands did not appear if the experiment was carried as follows. The gelatine solution was prepared and poured into several test-tubes and allowed to set. Then, after different time intervals, each of the test-tubes excepting one, was warmed, melted the gel and allowed again to reset. In this manner, the gels of different age were prepared. Then silver nitrate solution was poured on them. In this case, the formed bands in the respective tubes appeared quite equal and identical to that of unmelted gel, i.e. the most aged gel. From these results the author concludes that the ageing effect of gel on the formation of Liesegang rings is not caused by the change of structure of gel as Scott Blair considered, but by the change of modification of gelatine into less protective one by an interaction of potassium dichromate and this change proceeds with the age. It is considered, moreover, that the decrease of potassium dichromate after ageing was not recognised as Scott Blair observed, for this change of modification is probably caused by spending very small amount of potassium dichromate.

The effect of ageing was also studied on the system of copper chromate in silicic acid gel within the range of three months. The remarkable results as in the case of silver chromate was not seen. According to Koenig,(33) a fresh silicic acid gel gives best bands while the gel kept before diffusion gives irregular results. In the author's experiments on copper chromate, however, even the three months aged gel also gave good regular bands and showed no essential difference from that in a freshly prepared gel.

Subsequently, the author's view was confirmed by some other experiments. The effect of ageing was tested with a rhythmic precipitate in a gel which does not react with the inner electrolyte. Lead iodate bands in a gelatine gel and calcium phosphate bands in a silicic acid gel were investigated. The sol containing the adequate concentration of the inner electrolyte was poured into several test tubes. Then the test tubes were kept in a thermostat. After the gel set, the diffusing electrolyte was superposed on the gel in one of the test tubes. After a while, the diffusing electrolyte was poured on the gel of the second test tube and later on the gel of the third, and so on. After the outer electrolyte had diffused to the bottom of the test tubes, the formed rhythmic precipitates were compared with each other. No recognisable differences were observed. Thus, when the inner electrolyte does not react with the gel, the effect of ageing of gel is not recognisable, so that the effect of ageing is not referred to the change of structure of gels by age.

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(34) Schleussner, *Kolloid-Z.*, **31** (1922), 347.

The Influence of the Hydrogen Ion Concentration. In general, the solubility of a salt is considerably influenced by the hydrogen ion concentration of the solution. In many cases, its solubility increases with the hydrogen ion concentration of the medium. It is considered that the Liesegang's phenomenon will be strikingly affected by the hydrogen ion concentration of the gel, because the solubility of the salt is an important factor in the formation of rhythmic precipitates and for the formed bands. However, in many experiments which were hitherto conducted by many investigators, little attention was paid to the hydrogen ion concentration. In view of this point, the author studied thoroughly the influence of hydrogen ion concentration of the medium.

First, silver chromate bands in gelatine was tested. It is well known that the rhythmic precipitate of silver chromate is well developed in an ordinary commercial gelatine. When a small quantity of alkali is added to the gel, the intervals between bands become short and the number of formed bands increases. Inversely, when a small quantity of acid is added in the gel, the intervals between the bands become large, the bands consist of relatively coarse precipitate and have often imperfect appearance and the number of formed bands decreases. On the other hand, the well-developed bands of silver chromate are difficult to obtain in a gelatine which was purified by dialysis. Also it is difficult to obtain in a gelatine of the highest quality. These facts are ascribed by Liesegang⁽³⁵⁾ to the presence of gelatose, the hydrolytic product of gelatine in an ordinary commercial gelatine. But in the author's opinion, the concentration of hydrogen ion in gelatine jelly is a more significant factor than the presence of gelatose. Ordinary commercial gelatines have the *p*H ranging from 5.5 to 6.4, but pure dialysed gelatines have the *p*H ranging about its isoelectric point that is about 4.7. Accordingly, the author considered that the hydrogen ion concentration of the gel is rather more important than the presence of gelatose. In the jelly which was prepared with "gelatine alba pulvis" from Merck, well-developed bands of silver chromate were formed. But in the jelly which was prepared with the ash-free gelatine (the same gelatine purified by Loeb's method), no bands or only two or three imperfect bands were obtained. However, if a small quantity of caustic soda is added to thus purified gelatine, silver chromate bands were again obtaind in such a gel. When too much alkali was added, the bands became close to each other and blurred. A result of a series of experiments with purified gelatine is shown in Table 22. Table 23 is a result of a series of experiments with purified gelatine, the manufacturer of which is unknown. These cases give coincident results. The bands are formed best at the *p*H range of 5.5–6.0. When the influence of the species of gel on the banding was described in the preceding paragraphs, it was pointed out that the banding is markedly affected by the species of gelatine. The author measured the values of *p*H of those gelatines in its 3% solutions. The results are shown in Table 24. The formation of band, however, can not be referred only to the *p*H of gelatine. Because the band are not the same, even in the same *p*H with different gelatines. The *p*H of the photographic gelatines was also

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(35) Liesegang, *Z. physik. Chem.*, **88** (1914), 1.

measured and shown in Table 25. With these gelatines, rhythmic precipitates were easily obtainable in the range of pH which is somewhat larger than the preceding examples.

Table 22.

Bands of Silver Chromate.

Sodium hydroxide (0.25 N) added (c.c.)	Number of bands
0.00	4
0.10	16
0.20	27
0.30	39

Inner electrolyte: potassium dichromate 0.15%. Outer electrolyte: silver nitrate 5%. 3.2% gelatine 7 c.c.

Table 23.

Bands of Silver Chromate.

Sodium hydroxide (0.25 N) added (c c.)	Number of bands
0.00	0
0.10	10
0.15	12
0.20	26
0.25	32

Inner electrolyte: potassium dichromate 0.15%. Outer electrolyte: silver nitrate 5%. 3.0% gelatine 7 c.c.

Table 24.

Species	pH
Home production A	6.40
Home production B	6.30
Coignet A	5.75
Coignet D	5.55
Coignet No. 1.	5.60

Table 25.

Species	pH
Gelatine A for pos. film	5.90
Gelatine B for pos. film	6.30
Gelatine C for pos. film	5.90
Gelatine A for neg. film	5.95
Gelatine B for neg. film	5.65
Gelatine C for neg. film	6.50
Gelatine D for neg. film	5.70

Barium chromate bands in gelatine are greatly influenced by the hydrogen ion concentration. When a cobalt acetate solution was diffused into a gel containing a small quantity of trisodium phosphate as an inner electrolyte, rhythmic precipitate of cobalt phosphate in gelatine are formed while no band is formed in a gel containing secondary sodium phosphate. This fact is also ascribed to the effect of hydrogen ion concentration.

In a gel of organic colloid, such as gelatine, pH value of the gel is in a narrow range, if some acid or alkali is not added to the gel. But in the case of a silicic acid gel, pH value of the gel will vary widely by the quantities of acid and water glass, which were used to prepare the gel. Accordingly, it seems that the effect of the hydrogen ion concentration on the rhythmic banding in a silicic acid gel is still more remarkable than in the case of gelatine gel. Holmes showed that rhythmic precipitates of copper chromate and basic mercuric chloride are formed in somewhat basic gels of silicic acid. The basic gel contains, in general, some undecomposed sodium silicate in a small extent. When a solution of a salt of heavy metal diffuses into such a gel, it reacts with undecomposed sodium silicate and forms precipitate of silicate of the heavy metal. There deposits such a precipitate of silicate side by side with the precipitate that forms the rhythmic bands. For example, silver chromate bands in a silicic acid gel are the case. It has long been considered that silver chromate does not make rhythmic bands in the silicic acid gel. This must be ascribed also to the effect of hydrogen ion concentration. In the gel of relatively low hydrogen ion concentration, silver silicate is formed side by side with silver chromate and often hinders the rhythmic handing. When the hydrogen ion concentration is high, the silicic acid does not set to a gel. So the range of hydrogen ion concentration favourable for the formation of typical rhythmic bands is very narrow which has been already pointed out by the present author.(10)

Table 26 shows the results obtained in the gels which have been made by mixing equal volumes of sodium silicate solution (density = 1.06) and nitric acid of different concentrations. With more concentrated nitric acid than 0.70 N, the silicic acid does not gelatinise.

Table 26. Silver Chromate Bands in Silicic Acid Gel.

Concentration of HNO_3 (N)	Nature of rhythmic bands
0.67	Typical rhythmic precipitates consisting of relatively coarse crystals of red black plates were obtained. The intervals between bands were large.
0.63	Typical rhythmic precipitates were obtained. Crystals were small needles.
0.58	At the top of the gel Liesegang bands accompanied by dendrites were recognised. In the middle, only dendrites were seen, and at the bottom again rhythmic bands appeared but they were those formed by diurnal cause.
0.55	The result was analogous to the case of 0.58 N. But the number of formed Liesegang bands was less.
0.50	No Liesegang band was formed. Dendrites and diurnal bands were seen.

Outer electrolyte: $AgNO_3$ 5%. Gel: 6.0 c.c. of Na_2SiO_3 solution ($d = 1.06$)+6.0 c.c. of HNO_3+0.4 c c. of 5% $K_2Cr_2O_7$ as inner electrolyte.

It is desirable that the gel prepared with plenty of acid, is dialysed thoroughly, though it accompanies some difficulties in addition of the inner electrolyte. In many experiments which were carried out by the present author, the gel which was prepared by mixing equal volumes of a sodium silicate solution ($d = 1.06$) with 0.7 N nitric acid, 0.7 N sulphuric acid or 0.75 N acetic acid, was favourable for various bandings. The author(36) reported, previously, the banding of nickel dimethylglyoxime in a silicic acid gel. It was studied in the gels of the value of *p*H ranging

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(36) Isemura, *J. Chem. Soc. Japan*, **57** (1936), 546.

from 3.90 to 8.00. The rhythmic precipitate was formed in the *p*H range between 4.80 and 6.40. Relatively long needles were formed in the region of the *p*H value below 4.80, while very minute crystals were formed continuously and no bands were obtained in the region above 6.40. The crystals were large, the thickness of every band was also large and the number of formed bands was small in the lower *p*H region between 4.80 and 6.40. On the contrary, in the higher *p*H, crystals formed were minute, bands were sharp and thin, the number of band was large and the intervals were narrow.

How was the banding influenced, in a silicic acid gel, when the bands were formed as tablets instead of bands consisting of relatively large crystals? On this problem, bands of calcium phosphate were investigated.⁽⁷⁾ The results obtained on this rhythmic precipitate are tabulated in Table 27. As shown by this table, it was found that the rhythmic precipitate of calcium phosphate could be formed in the range of *p*H between 5.30 and 7.04. The precipitation of calcium phosphate was difficult below 5.30, while the precipitation occurred continuously and no band was formed above 7.04. In the range between 5.30 and 7.04 the smaller the value of *p*H is, the larger the intervals between bands and the smaller the number of formed bands becomes. The distance between the surface of gel and the last formed band becomes large with the value of *p*H of the gel. That is to say, the higher the acidity of the gel is, the more difficult the banding is.

Table 27. Calcium Phosphate Bands in SilicleAcid Gel.

Concentration of acetic acid (N)	*p*H of gel	Number of bands
0.60	8.98	A continuous precipitate
0.70	7.72	A continuous precipitate
0.75	7.04	9
0.80	6.01	7
0.90	5.50	4
1.00	5.30	3
2.00	4.67	0

Outer electrolyte: $CaCl_2$ 30%. Inner electrolyte: Na_2HPO_4 0.4%.
Na_2SiO_3 ($d = 1.06$).

Equal volumes of Na_2SiO_3 and acetic acid were mixed to make a gel. As much of the gel was taken as to fill to a height of 6 cm. of a test tube of 1.2 cm. internal diameter and 11 cm. in length.

Besides these, the formation of many other rhythmic precipitates, especially such as copper iodate etc., in silicic acid gel were strongly affected by the hydrogen ion concentration. The effect of the concentration of acid which was used to prepare a gel, to the banding was studied, and the results will be given in Part V in this paper.

The hydrogen ion concentration of the diffusing electrolyte as well as that of the gel, has also a profound influence on the rhythmic precipitation. On the formation of rhythmic bands of bismuth chromate, the bismuth nitrate solution in nitric acid of various concentration was used as the outer electrolyte. With bismuth nitrate in diltue nitric acid, bands were formed from the top of gel; the number of them was large and the interspaces between them were very small. On the contrary, with bismuth nitrate in concentrated nitric acid, the band was not formed at the top of the gel but appeared at a certain depth from the surface. The number of formed bands were small and interspaces between them were large. The distance from the top of the gel to the first formed band was increased with the concentration of nitric acid. The distance to the last formed band from the surface of the gel was also increased with the concentration of nitric acid. These results are all referred to the increase of solubility of formed bismuth chromate with increasing acidity.

III. Regularity of the Intervals Between Bands.

It is an established fact that in the Liesegang phenomenon the intervals between bands become larger as the distance increases from the contact surface with the outer electrolyte solution. Schleussner(37) said that the interval of the nth band and that of the $(n+1)$th band stood in a constant ratio. The author(38) experimentally proved that the intervals of bands beared a relation of a quadratic equation to the numbers of the formed bands. When the interval of nth band is shown by $\varDelta X_n$, we can obtain as equation.

$$\varDelta X_n = a + bn + cn^2 \qquad (1)$$

in which a, b and c are constants.

Bauer,(39) supposing that an equation of the same form as the partial differential equation of heat conduction could be applied in the diffusion of ion into a gel, set up the equation:

$$\frac{\partial u}{\partial t} = a^2 \frac{\partial^2 u}{\partial X^2}$$

where u means the concentration of the ion to diffuse from an external liquid into the gel; t the time; x the interval; and a^2 the diffusion constant. From this equation he theoretically drew a conclusion from the standpoint of super-saturation theory that the ratio of the interval of nth band to that of $(n+1)$th band could be shown by

$$\frac{\varDelta X_{n+1}}{\varDelta X_n} = 1 + p$$

in which p is

$$\frac{\varDelta X}{x^*} \sim \frac{\varDelta t}{2t^*} = p \sim \text{const.}$$

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(37) Schleussner, *Kolloid-Z.*, **34** (1924), 338.
(38) *J. Chem. Soc. Japan*, **55** (1934), 809.
(39) *Kolloid-Z.*, **64** (1933), 181.

where t^* is the time required to form precipitates and x^* is the distance to the locality where the precipitate is formed.

If the interval between the stopper* and the first band is shown by ΔX_0, we can obtain and can set up in order

$$\frac{\Delta X_1}{\Delta X_0} = 1+p$$

$$\frac{\Delta X_2}{\Delta X_1} = 1+p$$

$$\frac{\Delta X_3}{\Delta X_2} = 1+p$$

$$\cdots\cdots\cdots\cdots$$

$$\frac{\Delta X_n}{\Delta X_{n-1}} = 1+p\ .$$

Multiplication in each side of the equations gives the following relation

$$\frac{\Delta X_n}{\Delta X_0} = (1+p)^n\ .$$

If the right side of this equation is expanded by the binominal theorem, we obtain

$$\frac{\Delta X_n}{\Delta X_0} = \left\{1+np+\frac{n(n-1)}{2\,!}\,p^2+\frac{n(n-1)(n-2)}{3\,!}\,p^3+\cdots\cdot\right\}.$$

As p is a number of small value, we may neglect the higher terms of p and we get

$$\Delta X_n = \Delta X_0\left\{1+np+\frac{n(n-1)}{2}\,p^2\right\}$$

or

$$\Delta X_n = \Delta X_0+\Delta X_0\left(1-\frac{p}{2}\right)pn+\frac{\Delta X_0}{2}\,p^2n^2\ . \qquad (2)$$

As ΔX_0 and p are constants, we may denote,

$$\Delta X_0 = a\ , \qquad \Delta X_0\left(1-\frac{p}{2}\right)p = b\ , \qquad \frac{\Delta X_0}{2}\,p^2 = c\ .$$

Now this equation is identical with the above-mentioned empirical formula

$$\Delta X_n = a+bn+cn^2\ .$$

In Table 28, as an example, the results are shown on the rhythmic precipitate of copper chromate in a silicic acid gel. Second column shows the observed values and the fourth column the values which were obtained by the empirical equation (1), and the fifth column the values

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* The word stopper means the german "Propfen" after Popp. (*Kolloid-Z.*, **36** (1925), 208).

which were obtained by the equation (2) in which a, b and c were calculated from the experimentally determined p and ΔX_0.

Table 28. Copper Chromate in a Silicic Acid Gel.

No.	$\Delta X_{\text{obs.}}$	$1+p=k$	$\Delta X_{\text{calc.}}$ by empir. formula	$\Delta X_{\text{calc.}}$ by theor. formula
1	0.09	1.11	0.09	0.09
2	0.10	1.20	0.10	0.10
3	0.12	1.08	0.11	0.12
4	0.13	1.08	0.13	0.13
5	0.14	1.14	0.14	0.14
6	0.16	1.14	0.16	0.16
7	0.18	1.11	0.18	0.17
8	0.20	1.10	0.20	0.19
9	0.22	1.09	0.23	0.21
10	0.24	1.13	0.26	0.23
11	0.27		0.28	0.25
		Average 1.117		

In the empirical formula (1), calculation was made in taking $a = 0.080$, $b = 0.075$, and $c = 0.001$. In the theoretical formula (2), it was made by using the constants a, b and c which were calculated from $\Delta X_0 = 0.083$ and $p = 0.117$. It was ascertained that both formulas gave almost identical values.

Subsequently, the formula was applied on other rhythmic precipitates namely, those of calcium phosphate in silicic acid gel, silver arsenite in gelatine, and lead iodate in gelatine. The distances between bands calculated from the theoretical formula were fairly concordant with the experimental data. But the calulated values of the higher number is always somewhat smaller than observed values.

Table 29 gives the results obtained with calcium phosphate in a silicic acid gel. The values of the fourth column were obtained from the assumption of $a = 0.173$, $b = 0.00241$, and $c = 0.00029$, and those of the fifth column calculated from $\Delta X_0 = 0.176$ and $p = 0.154$.

Table 29. Calcium Phosphate in a Silicic Acid Gel.

No.	$\Delta X_{\text{obs.}}$	$1+p=k$	$\Delta X_{\text{calc.}}$ by empir. formula	$\Delta X_{\text{calc.}}$ by theor. formula
1	0.20	1.15	0.20	0.20
2	0.23	1.17	0.23	0.23
3	0.27	1.15	0.27	0.27
4	0.31	1.13	0.31	0.31
5	0.35	1.11	0.37	0.35
6	0.39	1.15	0.42	0.40
7	0.45	1.20	0.48	0.45
8	0.54	1.13	0.55	0.51
9	0.61	1.20	0.62	0.57
10	0.73		0.71	0.63
		Average 1.154		

Table 30 gives the results obtained with silver arsenite in gelatine, which were calculated on the assumption; $a = 0.083$, $b = 0.0049$, $c = 0.000145$, $\Delta X_0 = 0.083$, $p, = 0.0611$.

Table 30. Silver Arsenite in Gelatine.

No.	$\Delta X_{\text{obs.}}$	$1+p=k$	$\Delta X_{\text{calc.}}$ by empir. formula	$\Delta X_{\text{calc.}}$ by theor. formula
1	0.087	1.046	0.087	0.087
2	0.091	1.088	0.092	0.092
3	0.099	1.020	0.098	0.098
4	0.101	1.087	0.104	0.104
5	0.110	1.091	0.110	0.110
6	0.120	1.017	0.117	0.117
7	0.122	1.058	0.123	0.123
8	0.129	1 070	0.130	0.130
9	0.138	1.068	0.138	0.138
10	0.147	1.028	0.146	0.146
11	0.151	1.100	0.153	0.153
12	0.165		0.162	0.162
		Average 1.0611		

Table 31 gives the results obtained with lead iodate in gelatine, which were calculated on the assumption: $a = 0.132$, $b = 0.01006$, $c = 0.00075$, $\Delta X_0 = 0.131$, $p = 0.096$.

Table 31. Lead Iodate in Gelatine.

No.	$\Delta X_{\text{obs.}}$	$1+p=k$	$\Delta X_{\text{calc.}}$ by empir. formula	$\Delta X_{\text{calc.}}$ by theor. formula
1	0.143	1.189	0.143	0.144
2	0.156	1.078	0.155	0.157
3	0.168	1.070	0.169	0.172
4	0.180	1.116	0.184	0.189
5	0.201	1.085	0.201	0.206
6	0.218	1.064	0.219	0.225
7	0.232	1.095	0.239	0.244
8	0.254	1.107	0.260	0.265
9	0.281	1.157	0.283	0.286
10	0.325		0.308	0.311
		Average 1.096		

As seen from these four tables, the values of ΔX obtained by the empirical formula and those calculated from the theoretical formula are in good concordance.

IV. Classification and Secondary Bands.

Classification of Rhythmic Precipitates. Among the banded precipitates which are known commonly as rhythmic precipitates, some are produced by different causes from that of the so-called Liesegang phenomenon. So, the rhythmic precipitates can and must be arranged at least into the following three classes.

(1) Rhythmic precipitate as a Liesegang phenomenon.
(2) Rhythmic precipitate as the reflex of external rhythms.
(3) Compound rhythmic precipitate.

Silver chromate bands in gelatine are a typical Liesegang phenomenon. Many rhythmic precipitates such as lead iodate, magnesium hydroxide, silver carbonate in gelatine, copper chromate, calcium phosphate in silicic acid gel, etc. belong to this type. By the aspects of the bands formed, this class can be further divided into two sub-classes. These two sub-classes have been indicated as the two classes of rhythmic precipitate by Chatterji and his collaborators,(40) the classification of which is based on the shape and not on the nature. The classification based on structure will be described later.

A rhythmic precipitate formed as the reflex of external rhythms may be obtained in many precipitating reactions. It is caused by the change of diffusion velocity or by the furtherance and the hindrance of precipitation by external rhythms. External rhythms occur naturally with the change of day and night, which brings the periodical change of light and temperature. For example, the rhythmic banding of gold is caused by the rhythm of light intensity while that of mercuric iodide in a silicic acid gel is produced by the rhythm of temperature. The characteristic of this type of rhythmic precipitate is that one band is formed by one rhythm and that the intervals between hands become smaller with the advance of band formation. It is because diffusion velocity becomes gradually slow that the intervals become smaller. At the bottom of the gel, the inner electrolyte is exhausted and the intervals between bands become large again. Accordingly, rhythmic precipitates made by external rhythms often have minimum intervals between bands in the lower part of the gel.

In a rhythmic precipitate of gold, there exists several secondary bands which are caused by the change of intensity of irradiation. A band always consists of red-violet-blue-green-yellow zones. This fact is connected with the change of light intensity of morning, noon and evening.

Compound rhythmic precipitate is the one composed of true Liesegang phenomenon and the rhythmic precipitate of diurnal causes. For example, lead iodide in a silicic acid gel containing a small quantity of citrate formed often this type of rhythmic precipitate. In this case diurnal black bands caused by the partial decomposition of lead iodide by light and diurnal bands caused by the change of temperature were

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(40) Chatterji and Dhar, *J. phys. Chem.*, **28** (1924), 41; *Kolloid-Z.*, **40** (1926), 97; Mukherjee and Chatterji, *Kolloid-Z.*, **50** (1930), 147.

formed in addition to a rhythmic precipitate as a Liesegang phenomenon. These three banding appeared simultaneously. This is a good example of compound rhythmic precipitate.

Rhythmic precipitates may be classified according to the structure as follows:

(1) Banded precipitate (or Liesegang rings)
    Sub-class I
    Sub-class II
(2) Helicoidal precipitate. (or spiral precipitate)
(3) Banded precipitate with bands of saturn structure.
(4) Radial precipitate.(41)
(5) Complicated modification.

Ordinary rhythmic precipitates form bands in test tube, while they form rings on glass plate. This class may be divided into two subclasses: I, the tablet-like bands separated by marked gaps or empty spaces and II, the rhythmic precipitate of the type which has deposition maxima. In the former the precipitate is often paste-like, but in the latter, it is often well-defined crystals. As examples of type I, we can indicate calcium phosphate in silicic acid gel and magnesium hydroxide in gelatine, and as an example of II type, lead iodide in silicic acid gel.

A helicoidal precipitate is obtained in a test tube, while a spiral precipitate is obtained on a glass plate. If the diffusing electrolyte is superposed on a gel before it sets firmly enough, a helicoidal precipitate is often formed. So, it is closely connected with the deformation of the gel, which is mechanically caused by the addition of the diffusing electrolyte. Bands of saturn stucture are, of course, obtained only in a test tube, while a radial precipitate is obtained on a glass plate. It seems, the formation of bands of saturn structure depends on the ease of precipitation along the glass wall and active diffusion in the center of the test tube. Other forms of band are special cases. These can be included in the complicated modifications.

Secondary Bands. When a rhythmic precipitate of silver chromate is formed in gelatine, many thin faint layers are usually observed in the interspaces between brick red bands of silver chromate. These layers are known as secondary bands, and ascribed, by Köhler,(42) to the rhythmic precipitation of ammonium nitrate or potassium nitrate which is formed by the interaction of ammonium dichromate or potassium dichromate and silver nitrate. On the other hand, Schleussner(43) insists that these secondary bands are caused by silver chloride or phosphate which is formed by the interaction of the diffusing silver nitrate and chloride or phosphate contained in gelatine as an impurity. The author support Schleussner's consideration from the standpoint of the following experiments.

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(41) Veil, *Compt. rend.*, **196** (1933), 1491.
(42) Köhler, *Kolloid-Z.*, **19** (1916), 65.
(43) Schleussner, *Kolloid-Z.*, **31** (1922), 347.

When silver nitrate solution is allowed to diffuse into gelatine without any inner electrolyte, then there are obtained a number of thin bands. In this case the bands must consist of silver salt, for such a soluble salt as potassium nitrate or ammonium nitrate is generally difficult to obtain in a rhythmic precipitate. It is interesting that with increasing *p*H the intervals between silver chromate bands decrease but the intervals between secondary bands increase. This change of the intervals of secondary bands with *p*H is inverse to the cases of general rhythmic precipitates. In gelatine without chromate, however, the intervals between secondary bands decrease with increasing *p*H. So, it seems that in gelatine of large *p*H, more silver ion is consumed by the precipitation of silver chromate bands, and in such a gel, the secondary bands have larger intervals because silver ion decreases and the result obtained is exactly the same as by the decrease of concentration of the diffusing electrolyte.

The author experimented on the formation of silver chromate bands with gelatines which were dialysed in different degrees. In the less dialysed gelatine, the number of the secondary bands formed is large and the intervals between them are small, but in well-dialysed gelatine, the number of secondary bands is small and the intervals between them become large.

V. Special Part.

Conditions for the Formation of Some New Examples. In the course of the present study, the author found many new examples of rhythmic precipitates. Some detailed description of these examples will be given in the followings. Conditions for banding have also been investigated of some rhythmic precipitates which were hitherto reported by other authors giving no detailed description. Among the following experiments, those with bismuth chromate, bismuthyl chloride, bithmuthyl nitrate, calcium phosphate, and lead iodide in silicic acid gel were conducted in the test tubes of internal diameter of 1.5 cm., while the other experiments were all conducted in the test tubes of internal diameter of 1.2 cm.

Barium Chromate in Gelatine Gel. When a solution of barium chloride was poured on a pure ash-free gelatine jelly containing potassium dichromate as the inner electrolyte, bands were obtained of pale yellow relatively coarse particles of barium chromate. It is remarkable that these bands formed only in purified gelatine, but not in ordinary non-dialysed gelatine. This may be explained by the fact that the impurities contained in gelatine react with barium chloride and form insoluble salt distributing uniformly in the gel and prevent the band formation of barium chromate.

In the test tube the gelatine jelly is dehydrated, probably, by the tanning action of barium chloride and the meniscus of the jelly is depressed in the centre. Accordingly every band has remarkably concave form in its central part. At the top of the gel the bands are thin, but in the lower part of the gel they are thick consisting of relatively large crystals. The conditions for the banding are summarised in the following table. In this table, the 1st column expresses the number of experiment, the 2nd, the volume of 3.2% gelatine solution, the 3rd, the water added to the gelatine to make the definite volume of gel, the 4th, the inner electrolyte, and the 5th, the added alkali.

Table 32.

No.	Gel				Outer electro-lyte	Results
	Gelatine solution (3.2%) (c.c.)	Water added (c.c.)	$K_2Cr_2O_7$ solution (5.0%) (inner electrolyte) (c.c.)	NaOH solution (1.0%) (c.c.)		
1	5.00	0.00	2.00		$BaCl_2$ 1 N	Diffused bands.
2	5.00	1.00	1.00		,,	
3	5.00	1.50	0.50		,,	Typical rhythmic bands.
4	5.00	1.90	0.10		,,	Some faint bands.
5	5.00	1.95	0.05		,,	No band formation.
6	7.20	0.30	0.80	0.00	,,	Well-developed bands.
7	7.20	0.20	0.80	0.10	,,	
8	7.20	0.10	0.80	0.20	,,	
9	7.20	0.00	0.80	0.30	,,	

No. 1 and No. 2 gave bands, which were thin and compact at the top of the gel while they became diffuse and they consisted of coarse crystals in the lower part. No. 3 was the most favourable condition and gave typical bands. In No. 4, the concentration of the inner electrolyte was too dilute to form a distinct rhythmic precipitate. Consequently, faint bands have formed only at the top of the gel. No. 5 gave no bands, but a scattered precipitate. From No. 6 to No. 9, there appears the influence of the acidity of the gel. In an acidic gel such as No. 6, the bands consisted of coarse crystals and were somewhat indistinct. The less acidic the gel became, the more easily the precipitation occurred; and the more distinct the bands became, within the extent of the above experiments. As already stated, this banding is strongly affected by the irradiation of visible or ultraviolet light before superposing the diffusing electrolyte.

Lead Carbonate in Gelatine Gel. Lead acetate or lead nitrate solution is diffused into a gel, which has been prepared from gelatine purified by Loeb's method and contains sodium carbonate or ammonium carbonate as the inner electrolyte. Then well-developed rhythmic bands consisting of a somewhat coarse globular precipitate are obtained. In the case of relatively low concentration of the inner electrolyte the bands consisting of crescent shaped fragments are obtained. In gels containing somewhat more concentrated inner electrolytes, bands of saturn structure are often formed. In the presence of a sufficient quantity of inner electrolyte in the gel good typical bands are obtained. Conditions for the experiments are given in Table 33. The meaning of the data in the table is quite the same with the former table.

In the experiment No. 1 many crescent shaped fragments of bands were formed, which was so incomplete that they were scarcely perceived as a rhythmic precipitate. From No. 2 to No.4, there were many bands of saturn structure in the lower part of gel. No. 5 gave typical bands. As seen from the table (No. 2–No. 7), the number of formed bands increases with the concentration of the inner electrolyte. No. 8 gave bands consisting of coarse crystals. In this case thin white bands were formed at first, which then converted into bands consisting of coarse crystals. In No. 9 the first four bands were distinct and all convex, but those in the lower part of the gel were blurred. No. 10 and No. 11 gave also typical bands which indicate that the interchange of inner and outer electrolytes gave small influence on the banding. The right photograph in Fig. 12 is an example of this rhythmic precipitate.

Table 33.

No	Gel			Outer electrolyte	Number of bands	Results
	Gelatine solution (3.0%) (c.c.)	Water added (c.c.)	Inner electrolyte (c.c.)			
1	5.0	0.6	Na_2CO_3 (5%) 0.4	$Pb(CH_3COO)_2$ 1 N		Fragmental bands.
2	5.0	0.5	,, 0.5	,,	12	Bands of saturn structure.
3	5.0	0.4	,, 0.6	,,	15	
4	5.0	0.3	,, 0.7	,,	15	
5	5.0	0.2	,, 0.8	,,	22	Typical rhythmic bands.
6	5.0	0.1	,, 0.9	,,	29	
7	5.0	0.0	,, 1.0	,,	31	
8	5.0	0.6	$(NH_4)_2CO_3$ (5%) 0.4	,,		
9	5.0	0.2	,, 0.8	,,		
10	5.0	0.5	$Pb(CH_3COO)_2$ (1 N) 0.5	$(NH_4)_2CO_3$ 5%		Typical bands.
11	5.0	0.5	,, 0.5	Na_2CO_3 5%		

Lead Carbonate in Silicic Acid Gel. When lead acetate or lead nitrate solution diffuses into a silicic acid gel containing sodium carbonate as inner electrolyte, lead carbonate bands are obtained. As it was already mentioned in the preceding paragraphs, the rhythmic bands of lead carbonate in gelatine consisted of globular particles. In silicic acid gel, however the bands consisted of relatively long needles, sometimes accompanied by a small amount of globular particles. The length of the needles obtained often attained several millimeters in a gel of somewhat high acidity. The conditions of the experiments are summarised in Table 34.

Table 34.

No.	Gel				Outer electrolyte	Number of bands	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	CH_3CO_2H solution (c.c.)	Inner electrolyte (c.c.)	Water added (c.c.)			
1	3.0	0.75 N 3.0	Na_2CO_3 (5.0%) 0.2	0.8	$Pb(NO_3)_2$ 1 N	12	Typical rhythmic bands
2	3.0	,, 3.0	,, 0.4	0.6	,,	14	
3	3.0	,, 3.0	,, 0.6	0.4	,,	26	
4	3.0	,, 3.0	,, 0.8	0.2	,,	36	
5	3.0	,, 3.0	,, 1.0	0.0	,,	45	
6	3.0	,, 3.0	,, 0.6	0.4	$Pb(CH_3CO_2)_2$ 1 N	18	
7	3.0	,, 3.0	,, 0.8	0.2	,,	40	
8	3.0	,, 3.0	,, 1.0	0.0	,,	50	
9	3.0	0.60 N 3.0	,, 0.5	0.5	$Pb(NO_3)_2$ 1 N		Close bands
10	3.0	,, 3.0	,, 0.5	0.5	$Pb(CH_3CO_2)_2$ 1 N		
11	3.0	0.65 N 3.0	,, 0.5	0.5	$Pb(NO_3)_2$ 1 N		
12	3.0	,, 3.0	,, 0.5	0.5	$Pb(CH_3CO_2)_2$ 1 N		
13	3.0	07.0 N 3.0	,, 0.5	0.5	$Pb(NO_3)_2$ 1 N		Typical bands
14	3.0	,, 3.0	,, 0.5	0.5	$Pb(CH_3CO_2)_2$ 1 N		
15	3.0	1.0 N 3.0	,, 0.3	0.7	$Pb(NO_3)_2$ 1 N	1	Only one band was obtained
16	3.0	,, 3.0	,, 0.5	0.5	,,	3	
17	3.0	,, 3.0	,, 0.7	0.3	,,	3	
18	3.0	,, 3.0	,, 0.9	0.1	,,	5	
19	3.0	,, 3.0	,, 1.0	0.0	,,	6	Bands consisted of long crystals
20	3.0	0.75 N 3.0	$Pb(NO_3)_2$ (1 N) 0.3		Na_2CO_3 5.0%	4	Some diffused bands
21	3.0	,, 3.0	$Pb(CH_3CO_2)_2$ (1 N) 0.3		,,	3	

In No. 1. typical rhythmic bands were obtained, which consisted of needles and were separated by large clear interspaces. No. 2 also gave a typical rhythmic precipitate, the crystals of which were distributed more densely. In No. 1–No. 8, the number of bands formed increased with the concentration of inner electrolyte. In No. 3–No. 8, every band that consisted of globular precipitate was sharp at the lower surface on which the needles grew. At the bottom of the gel two or three bands have deposited which were consisted only of globular precipitate. In No. 9, there formed a white continuous precipitate down to the middle part of the gel, while many indistinct bands formed from the middle to the bottom of the gel. They were complicated probably by the formation of lead silicate. In No. 10, at the middle of the gel close bands and at the bottom of the gel distinct ones were formed. The bands did not consist of needles. No. 11 was analogous to No. 9, the bands being more distinct. No. 12 was analogous to No. 10, the bands being also more distinct. Both No. 13 and No. 14 gave typical rhythmic bands. At the middle of the gel, the bands blurred by the growth of crystals, but at the bottom the bands became distinct again, because the intervals between them increased. In No. 15 only a band was obtained consisting of small globules at 1.2 cm. from the top of the gel. No. 16–No. 18 gave bands similar to those of No. 15, but they consisted of somewhat shorter needles. No. 19, gave bands formed by the cluster of long crystals. No. 20 and No. 21 did not give good bands. In No. 15–No. 19, the effect of the concentration of the inner electrolyte was observed as usual.

It is seen from the foregoing results that a rhythmic precipitate of long crystals is well developed in a gel which is prepared by mixing an equal volumes of a 1.06 density water glass solution with a 0.7 N or more concentrated solution of acetic acid. In a gel which is prepared by mixing equal volumes of a water glass solution ($d = 1.06$) and 0.65 N or less concentrated acetic acid, banding is not good. The appearance of crystals is quite different by the acidity of the gel. This is caused probably by the formation of lead silicate and lead carbonate. In Fig. 12, the middle photograph shows a typical rhythmic precipitate of lead carbonate in silicic acid gel and the left an example of the bands consisting of long needles.

Even if the inner electrolyte is interchanged with the outer electrolyte, the rhythmic bands still formed. But when sodium carbonate or ammonium carbonate is allowed to diffuse into the gel, the bands are not so distinct as the case where the lead salts diffuses into the gel.

Bismuth Chromate in Silicic Acid Gel. When a solution of bismuth nitrate or bismuth chloride diffuses into a silicic acid gel containing potassium chromate as inner electrolyte, yellow bands of bismuth chromate are obtained. The appearance of this rhythmic precipitate is greatly affected by the kind of acid which was used to prepare the gel, by the species of the diffusing electrolyte, and by the acidity of the diffusing solution and of the gel itself. The conditions for obtaining this rhythmic precipitate are shown in Table 35.

In this table, $Bi(NO_3)_3$ I indicates a 0.5 mol solution of bismuth nitrate in 3 N nitric acid, and $Bi(NO_3)_3$ II, a 0.5 mol solution in the least concentration of nitric acid that does not cause hydrolysis. The rhythmic precipitate has better developed by the diffusion of bismuth nitrate than that of bismuth chloride. The solution of bismuth chloride which was used in the present experiments is a 1 mol solution in hydrochloric acid. The rhythmic bands formed by the diffusion of bismuth nitrate were yellow and had many pores in the bands. The precipitate grew at the interface between the glass and the gel, and the bands in the lower part of the gel were cloaked with this yellow film of the precipitate.

When the rhythmic precipitate was made by the diffusion of a bismuth nitrate solution in relatively concentrated nitric acid, the band was first formed at a point somewhat distant from the top of the gel. In No. 1, the first band formed at a point 1.3 cm. distant from the top of the gel; in No. 2, 1.7 cm.; in No. 3, 2.2 cm.; and in No. 4, 2.4 cm. In No. 5–No. 8, only several faint bands formed at the top of the gel, then a globular precipitate uniformly formed and no bands and no precipitate formed from the middle to the bottom. In No. 9–No. 12, we

Table 35.

No.	Gel			Outer electrolyte	Number of bands	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	Acid (c.c.)	Inner electrolyte (c.c.)			
1	6.5	CH_3CO_2H 6.5 (0.5 N)	K_2CrO_4 1.0 (1 mol)	$Bi(NO_3)_3$ I	5	Typical rhythmic precipitates were formed.
2	6.5	,, 6.5	,, 0.8	,,	3	
3	6.5	,, 6.5	,, 0.5	,,	3	
4	6.5	,, 6.5	,, 0.2	,,	3	
5	6.5	,, 6.5	,, 1.0	$BiCl_3$		Faint rhythmic bands were formed.
6	6.5	,, 6.5	,, 0.8	,,		
7	6.5	,, 6.5	,, 0.5	,,		
8	6.5	,, 6.5	,, 0.2	,,		
9	6.5	,, 6.5	,, 1.3	$Bi(NO_3)_3$ II	15	Typical rhythmic bands were formed.
10	6.5	,, 6.5	,, 1.0	,,	18	
11	6.5	,, 6.5	,, 0.8	,,	22	
12	6.5	,, 6.5	,, 0.5	,,	18	
13	6.5	HCl 6.5 (0.85 N)	,, 1.0	$BiCl_3$		No bands were obtained.
14	6.5	,, 6.5	,, 1.0	$Bi(NO_3)_3$ I		
15	6.5	,, 6.5	,, 1.0	$Bi(NO_3)_3$ II		
16	6.5	HCl 6.5 (0.5 N)	,, 0.5	$Bi(NO_3)_3$ I		
17	6.5	HCl 6.5 (0.5 N)	,, 0.5	$Bi(NO_3)_3$ II		
18	6.5	,, 6.5	,, 1.3	$BiCl_3$	2	Well developed rhythmic bands were obtained.
19	6.5	CH_3CO_2H 6.5 (0.5 N)	,, 0.5	$Bi(NO_3)_3$ I	6	
20	6.5	,, 6.5	,, 0.5	$Bi(NO_3)_3$ II 2 N HNO_3	6	
21	6.5	,, 6.5	,, 0.5	$Bi(NO_3)_3$ 1 N HNO_3	19	

obtained the best bands. Fig. 13 shows an example of this type of rhythmic precipitate. In No. 13, there formed many large spherulites, but no bands. In No. 14–No. 17, the results were analogous to that of No. 13. In No. 18, a stopper of the precipitate and two large bands, separated by large interspaces formed and these all consisted respectively of secondary rhythmic bands.

Thus the bands which were obtained by the diffusion of bismuth chloride in a gel prepared with hydrochloric acid were quite different to those formed by the diffusion of bismuth nitrate in a gel which was prepared with acetic acid. Fig. 11 shows an example of this type of rhythmic precipitate. This is partly referred to the fact that bismuth chloride hydrolyses more easily than bismuth nitrate. The bands formed by bismuth chloride is always accompanied by bismuthyl chloride. They seemed to be a compound rhythmic precipitate of bismuth chromate and bismuthyl chloride.

In the examples of No. 5–No. 8 and No. 13–No. 17, many globular particles are seen. These are not bismuth chromate but probably bismuthyl chloride. The formation of bismuthyl chloride and bismuthyl nitrate bands in silicic acid gel wil be treated later again. The rhythmic bands of bismuth chromate are never formed by the diffusion of bismuth nitrate into the gel prepared with hydrochloric acid. It has already been stated that when bismuth nitrate diffused into a gel prepared with acetic acid like in the experiments No. 1–No. 4, bands having many pores were obtained. Moreover, the bands often showed the saturn type or more complicated structures. When this rhythmic precipitate are stood for a long time (five to six months), the crystallisation of bismuth chromate occurred, and orange clusters of crystals have deposited by the further advance of the diffusion. With the growth of these crystals the bands began to chip, and crescent shaped bands formed. At last, the bands disappeared entirely and several somewhat large spherical clusters of crystals remained.

Bismuthyl Chloride and Bismuthyl Nitrate in Silicic Acid Gel. The author studied the formation of rhythmic precipitates of bismuthyl chloride and bismuthyl nitrate in silicic acid gel, for bismuth chloride and bismuth nitrate are both readily hydrolysable. When bismuth chloride or bismuth nitrate diffuses into a silicic acid gel which contains no inner electrolyte, a white rhythmic precipitate is formed. The best bands were formed when bismuth chloride is allowed to diffuse in the gel prepared with hydrochloric acid. The conditions for the experiments are summarised in Table 36.

Table 36.

No.	Gel			Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	Acid (c.c.)	Outer electrolyte	
1	7.0	CH_3CO_2H (0.5 N) 7.0	$BiCl_3$	No bands were formed.
2	7.0	,, 7.0	$Bi(NO_3)_3$ I	
3	7.0	HCl (0.5 N) 7.0	$BiCl_3$	Rhythmic bands were formed.
4	7.0	HCl (0.42 N) 7.0	,,	
5	7.0	CH_3CO_2H (0.5 N) 7.0	$Bi(NO_3)_3$ II	

The concentrations of the diffusing electrolyte were the same as in the case of bismuth chromate. In No. 1, a white globular precipitate formed uniformly all through the test tube. In No. 2, there is no band and a small amount of precipitate formed sparsely. In No. 3–No. 5 rhythmic bands were formed. In No. 4 four compact bands and one consisting of globular particles were formed, each band being consisted of far smaller crystals than in the case of No. 3. In No. 5 eight bands were formed, each of which consisted of a small amount of scattered crystals.

From the foregoing results we can conclude that no band is formed in a gel which is prepared by mixing a water glass solution and acetic acid when bismuth chloride is chosen as diffusing electrolyte. Bismuth nitrate is less hydrolysable than bismuth chloride, so when $Bi(NO_3)_3$ I diffuses in a gel there is no band formation. But when $Bi(NO_3)_3$ II diffuses, rhythmic bands form, because $Bi(NO_3)_3$ I is difficultly hydrolysable in an excess of nitric acid.

Cobalt Phosphate in Silicic Acid Gel. When cobalt acetate diffused into a gel containing a small quantity of soluble phosphate as inner electrolyte, a red rhythmic precipitate of cobalt phosphate were formed. Every band was thick while the particles forming the bands were considerably coarse. The bands were not so distinct because the particles forming them were coarse and scattered. When a very small quantity of citrate was added to the gel, well developed bands such as shown in Fig. 14 was obtained. The left photograph is an example of cobalt phosphate bands in a silicic acid gel. The experimental conditions are summarised in Table 37 and the results are given in the following lines.

Table 37.

No.	Gel					Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	Water	CH_3CO_2H solution (1 N) (c.c.)	Inner electrolyte (c.c.)			
1	3.0	0.6	2.4	Na_3PO_4 (0.5 mol)	0.2	$Co(CH_3CO_2)_2$ 10%	Bands consisting of coarse crystals were formed.
2	3.0	0.7	2.3	,,	0.2	,,	
3	3.0	0.8	2.2	,,	0.2	,,	Somewhat indistinct bands were formed.
4	3.0	0.9	2.1	,,	0.2	,,	
5	3.0	1.0	2.0	,,	0.2	,,	
6	3.0	1.1	1.9	,,	0.2	,,	
7	3.0	1.2	1.8	,,	0.2	,,	
8	3.0	1.3	1.7	,,	0.2	,,	Distinct bands were formed.
9	3.0	1.4	1.6	,,	0.2	,,	
10	3.0	0.8	2.2	Na_2HPO_4 (0.5 mol)	0.7	,,	A few bands and a long stopper were formed.
11	3.0	0.8	2.2	,,	0.5	,,	
12	3.0	0.9	2.1	,,	0.5	,,	Irregular bands were formed.
13	3.0	0.6	2.2	,, +Citrate (3%)	0.5 0.2	,,	Very distinct bands were formed.
14	3.0	1.2	1.8	Na_2HPO_4 (0.5 mol)	0.5	,,	Close bands were formed.
15	3.0	0.9	2.1	Phosphate mixture	1.0	,,	A few bands were formed.
16	3.0	1.1	2.1	,,	0.8	,,	
17	3.0	1.3	2.1	,,	0.6	,,	Some indistinct bands were formed.
18	3.0	1.5	2.1	,,	0.4	,,	
19	3.0	1.8	2.1	,,	0.1	,,	No band was formed.
20	3.0	0.9	2.1	$Co(NO_3)_2$ (5%)	0.5	Na_2HPO_4 0.5 mol	A stopper and two bands were formed.

The bands of cobalt phosphate were often irregular. The bands and the large stopper of precipitate were influenced by diurnal cause. In No. 1, five bands consisting of relatively coarse crystals were formed. In No. 2, seven bands were formed, being somewhat irregularly distributed. No. 3–No. 7 gave what seemed to be compound bands of cobalt phosphate and probably of cobalt silicate. In these cases seven or eight rather indistinct bands were formed. In No. 8 and No. 9, the precipitate deposited continuously from the top to the middle part of the gel and eight bands were formed at the bottom. No. 10 gave a stopper 18 mm. long and five bands of relatively coarse crystals. No. 11 gave a stopper of 19 mm. long and three distinct bands consisting of coarse crystals, every band being about 3 mm. thick. In No. 12, five irregular bands were formed. In No. 13, a stopper 18 mm. long and three very distinct bands were formed as shown in Fig. 14. In No. 14, bands were close to each other and a precipitate grew even in the interspaces between bands.

The phosphate mixture, which was used in the experiments of No. 15–No. 19, was a mixture of six volumes of 0.5 mol secondary sodium phosphate and four volumes of 0.5 mol primary potassium phosphate. In this mixture, hydrogen ion concentration was almost the same with that of a neutral solution. The effect of the concentration of inner electrolyte were investigated in these experiments. In No. 15 a stopper and three distinct bands were formed, and in No. 16 a stopper and three bands were obtained. In No. 17 and No. 18 a stopper and four bands were formed, and the crystals were so coarse and so widely scattered, that the bands were very indistinct. No. 19 gave no bands. In No. 20, a stopper of 14 mm. length and two thick bands, 4 mm. and 8 mm. thick respectively, were obtained. The interchange of the inner and the outer electrolyte was possible in this case.

Cobalt Phosphate in Gelatine Gel. The formation of rhythmic bands of cobalt phosphate in silicic acid gel has already been described in a preceding paragraph. The formation of a similar rhythmic precipitate in gelatine was subsequently examined. Five percent solution of cobalt nitrate was poured on a gelatine gel (3%), which was made from purified ash-free gelatine and contained the secondary sodium phosphate as its inner electrolyte. The gel was made by mixing 5.5 c.c. of gelatine solution with 0.5 c.c. of 0.5 mol solution of secondary sodium phosphate. In this case we obtained two imperfect bands consisted of scattered crystals. This result was due to the relatively large acidity of the gel, and to the fact that cobalt phosphate has a considerable solubility in such an acidic gel.

If tertiary sodium phosphate was added to the gel instead of secondary one, a well-developed rhythmic precipitate of cobalt phosphate can be obtained. It seems, from this result, that acidity of the gel was favourable to the formation of rhythmic bands. The right photograph in Fig. 14 shows the rhythmic precipitate of cobalt phosphate in gelatine.

Cobalt Sulphide in Silicic Acid Gel. When a barium sulphide solution diffuses into a gel containing cobalt acetate or nitrate as inner electrolyte, very close black bands are obtained. Riegel⁽⁴⁴⁾ had experimented on this subject, who placed a silicic acid containing sodium sulphide on a solid silicic acid gel containing cobalt nitrate, and obtained the rhythmic bands of cobalt sulphide. In this case, however, the sodium sulphide finally destroys the silicic acid gel. So sodium sulphide is inadequate as an outer electrolyte to obtain this rhythmic precipitate. The present author, therefore, used barium sulphide as the diffusing electrolyte instead of sodium sulphide, and obtained very close but sharp bands. Thus more than 20 bands were often counted in the range of 10 mm. which situated at the depth of 30 to 40 mm. from the top of the gel. The conditions and the results are shown in Table 38.

Table 38.

No.	Gel			Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	CH_3CO_2H solution (c.c.)	Inner electrolyte (c.c.)		
1	3.0	0.75 N 3.0	$Co(NO_3)_2$ (5%) 0.20	Saturated solution of BaS	Close black, distinct bands were formed.
2	3.0	,, 3.0	,, 0.10	,,	
3	3.0	,, 3.0	,, 0.05	,,	
4	3.0	,, 3.0	$Co(NO_3)_2$ (1%) 0.20	,,	
5	3.0	,, 3.0	,, 0.15	,,	
6	3.0	,, 3.0	,, 0.10	,,	No band was formed.
7	3.0	1.0 N 3.0	$Co(NO_3)_2$ (5%) 0.10	,,	Many bands of saturn structure were formed.
8	3.0	0.75 N 3.0	Sat. solution of BaS 0.12	$Co(NO_3)_2$ 5%	Somewhat incomplete banding occurred.
9	3.0	,, 3.0	$Co(NO_3)_2$ (5%) 0.20	Saturated solution of BaS	Close typical bands were formed.
10	3.0	,, 3.0	,, 0.20	3/4 sat. solution of BaS	
11	3.0	,, 3.0	,, 0.20	1/2 sat. solution of BaS	
12	3.0	,, 3.0	,, 0.20	1/4 sat. solution of BaS	

The intervals between the bands became larger with the decrease of the inner electrolyte. In No. 1, the bands were so close that we could scarsely see them even by transmitted light. In the order of No. 2, No. 3, and No. 4, the bands were separated by progressively larger interspaces. The number of bands formed became very small in No. 5, and no bands formed in No. 6. In such a gel of high acidity as in No. 7, the bands were separated from each other and often many bands of saturn structure were formed. The influence of the concentration of outer electrolyte was remarkable. The number of bands between 30 mm. and

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(44) Riegel, *J. Phys. Chem.*, **35** (1931), 1675.

60 mm. depths from the surface of the gel was counted in No. 9–No. 12, and obtained 72, 54, 49, and 45 bands in No. 9, No. 10, No. 11 and No. 12 respectively.

The interchange of the inner and outer electrolytes was tried in No. 8. When barium sulphide was dissolved in the gel as an inner electrolyte, rhythmic bands were also obtained. But the bands were not so well-developed as in the case in which the cobalt salt was contained in the gel. In this case diurnal bands were also recognised in the lower part of the gel.

Copper Iodate in Silicic Acid Gel. When copper sulphate solution diffused into silicic acid gel containing potassium iodate as an inner electrolyte, a rhythmic precipitate of copper iodate which was different from an ordinary one, was obtained. The bands often consisted of a bluish white stopper of precipitate, a few bluish white compact bands and one or two diffuse blue bands. The conditions for this rhythmic precipitation are given in Table 39.

Table 39.

No.	Gel				Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	Water (c.c.)	Acid (c.c.)	Inner electrolyte (c.c.)		
1	4.0	1.9	CH_3CO_2H (1 N) 2.4	KIO_3 (5%) 0.2	$CuSO_4$ 2 N	A stopper and a diffuse band was formed.
2	4.0	1.6	,, 2.4	,, 0.5	,, ,,	A stopper and a few bands were formed.
3	4.0	1.3	,, 2.4	,, 0.8	,, ,,	
4	4.0	0.6	,, 2.4	,, 1.5	,, ,,	
5	4.0	0.1	,, 2.4	,, 2.0	,, ,,	
6	3.0	0.9	,, 2.1	,, 1.0	,, ,,	
7	3.0	1.0	,, 2.0	,, 1.0	,, ,,	
8	3.0	1.1	,, 1.9	,, 1.0	,, ,,	
9	3.0	1.2	,, 1.8	,, 1.0	,, ,,	
10	3.0	1.3	,, 1.7	,, 1.0	,, ,,	
11	3.0	1.4	,, 1.6	,, 1.0	,, ,,	
12	3.0	1.5	,, 1.5	,, 1.0	,, ,,	
13	3.0	1.7	,, 1.3	,, 1.0	,, ,,	Many close bluish white bands were formed.
14	4.0		CH_3CO_2H (0.6 N) 4.0	,, 1.0	$CuSO_4$ 2 N	A stopper and a few bands were formed.
15	4.0		,, 4.0	,, 1.0	,, 1.5 N	
16	4.0		,, 4.0	,, 1.0	,, 1.0 N	
17	4.0		,, 4.0	,, 1.0	,, 0.5 N	
18	4.0		,, 4.0	,, 1.0	,, 0.25 N	
19	4.0		HCl (0.7 N) 4.0	,, 1.3	$CuSO_4$ 2 N	No band was formed.

In No. 1, a stopper of 2.5 cm. in length and a faint band were formed. As the concentration of the inner electrolyte was increased, the length of the stopper decreased and the number of the bands formed increased. In No. 2, a stopper of 2.0 cm. in length, a distinct and compact band and two diffuse bands consisting of scattered spherulites were formed. In No. 3, the length of the stopper was 1.6 cm., and a distinct band and two thick diffuse bands were formed. In No. 4, stopper of 1.4 cm. in length, a sharp band and three spherulite bands were obtained. In No. 5, no stopper was formed and at a depth of 0.8 cm. from the top of the gel a band 0.5 cm. thick, two other sharp bands and two diffuse spherulite bands were formed. The influence of the acidity of the gel was observed in No. 6–No. 13. The stopper was thin or entirely missing in the more acidic gels, while it was thick in the more basic gels. No. 6 gave no stopper but three bands below the depth of 3 mm. from the top of the gel successively and one more far apart from them. Analogous results were obtained in No. 7 and No. 8, though every band was thicker than those of No. 6. Both No. 9 and No. 10 gave a stopper of 1.5 cm. in length and three globular bands. No. 11 gave two sharp and three spherulite bands and a stopper in which two bands were recognised. In No. 12, a thick stopper, in which also two bands were recognised, and two sharp and three diffuse bands were formed. No. 13 gave many bluish white bands but the banding was irregular. No. 14 gave a stopper of 1.6 cm in length and one sharp and two spherulite bands. No. 15 and No. 16 gave analogous results to No. 14 but the stopper was shorter in No. 15 and still shorter in No. 16. In No. 17 a thin stopper and two spherulite bands, and in No. 18 a still thinner stopper and a spherulite band were formed. In a gel which was prepared by mixing a sodium silicate solution ($d = 1.06$) and hydrochloric acid, copper iodate did not form bands. No. 19 showed this result.

In short, the bands become shorter and the number of sharp compact bands increases with the increase of the concentration of inner electrolyte. With the increase of acidity, the stopper becomes thinner. The number of the bands formed becomes larger in the less acidic gels and in such a basic gel as shown in No. 13, many bluish white bands are formed. These bands are a compound rhythmic precipitate of copper iodate accompanying copper hydroxide and copper silicate. The formation of bands becomes difficult with the decrease of the concentration of copper sulphate, as the compact bands turn into a spherulite bands.

Copper Carbonate in Silicic Acid Gel. A rhythmic precipitate of copper carbonate was obtained by the diffusion of copper sulphate solution into a silicic acid gel containing ammonium carbonate. The bands were not so sharp and the upper and lower surfaces of each band seemed diffuse. The intervals between the bands were large and the thickness of every band was also large. An irregular banding was produced in a basic gel. This seemed also to be due to the formation of copper carbonate accompanied by copper hydroxide and copper silicate. In a fairly acidic gel, the carbonate in the gel was decomposed and escaped from it. Concentrated acid is also inadequate to the rhythmic precipitation. The conditions of the experiments are given in Table 40.

In gels of the same acidity, the larger the concentration of the inner electrolyte is, the thicker the stopper becomes. This was seen from

Table 40.

No.	Gel			Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	CH_3CO_2H solution (c.c.)	Inner electrolyte (c.c.)		
1	3.0	0.5 N 3.0	$(NH_4)_2CO_3$ 1.0 (0.5 N)	$CuSO_4$ 2 N	Irregular bands were formed.
2	3.0	0.6 N 3.0	,, 0.2	,,	Rhythmic bands were formed.
3	3.0	,, 3.0	,, 0.5	,,	
4	3.0	,, 3.0	,, 1.0	,,	
5	3.0	0.73 N 3.0	,, 1.0	,,	
6	3.0	0.75 N 3.0	Na_2CO_3 0.3 (5%)	,,	No band and only a stopper was formed.

No. 2–No. 4. No. 1 gave an irregular banding of bluish white precipitate. No. 2 gave a thin stopper and four bands. In No. 3, a stopper 15 mm. long, two distinct bands, and a faint band were formed. In No. 4, a stopper 17 mm. long, two distinct bands, and two faint bands were formed. In No. 5, three bands which were separated by very large intervals, were formed. Under the same conditions, excepting the acidity of the gel, the stopper was thinner in the more acidic gels. In an acidic gel, the intervals between the bands become larger and the precipitate become greenish. On the other hand, the increase of the concentration of the inner electrolyte tends to shorten the intervals between the bands and change the colour of the bands from greenish blue to bluish white. The most adequate condition for the preparation of a gel for this purpose is attained by mixing a sodium silicate solution ($d = 1.06$) with an equal volume of 0.60–0.73 N acetic acid.

Silver Carbonate in Gelatine Gel. Silver carbonate forms a rhythmic precipitate in ordinary gelatine, which become more distinct in purified gelatine. The conditions for the banding were studied thoroughly,(45) and the results were partly shown in the preceding paragraphs. The most favourable condition was obtained by superposing a 5% silver nitrate solution to a 2.8% gelatine gel in which as much of sodium carbonate had previously been added as to be 0.2% in concentration. This condition gave the rhythmic precipitate in which the distances between bands were very large and it looked as if white tablets were placed in the test tube. These white bands of silver carbonate were tinged with light yellow with the lapse of days, which became black even by diffused light after a long duration.

As an inner electrolyte ammonium carbonate may also be used. In this case, however, the formed rhythmic precipitate differs a little in appearance from that obtained by sodium carbonate. In addition, it was known that the rhythmic bands were formed with ammonium carbonate

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(45) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 629.

in varying the concentration in a considerably wide range. The bands in this case did not take the perfect tablet-like forms as in the case of sodium carbonate, but looked like incomplete net-works or cracked plates.

Silver nitrate may be used as an inner electrolyte. When sodium carbonate solution was poured on the gel containing silver nitrate, bands were not so much manifested and sharp as in the case where silver nitrate was allowed to diffuse. When ammonium carbonate was used as an outer electrolyte, the rhythmic bands were formed which dissolved subsequently in order, and remained the rhythmic cracks.

Silver Arsenite in Gelatine Gel. Silver arsenite does not produce rhythmic bands in a commercial non-dialysed gelatine, while it makes distinct bands in a well dialysed one as in the case of lead iodate. The conditions for the formation were studied thoroughly.(45) The most favourable condition for producing this rhythmic precipitate was as follows. As much of sodium arsenite had been added to 2.0% dialysed gelatine as to be 0.1% in concentration. After the gel set firmly, 5–10% solution of silver nitrate was allowed to diffuse into the gel. In this case a yellow continuous precipitate was formed in the range of about 20 mm. from the top of the gel and many thin and sharply defined bands were formed in a further forward part. This was a very beautiful rhythmic precipitate and sensitive to light, readily changing its colour into dark yellowish green and finally into black by the diffused light.

Contrariwise, silver nitrate may be used as the inner electrolyte. A 10% solution of sodium arsenite was poured on 3% gelatine gel containing silver nitrate at the concentrations of 0.1–1.0%. In this condition, the rhythmic precipitate was always formed. Scarsely any difference was found between the rhythmic precipitate produced by this method and that by diffusion of silver nitrate.

Silver Iodate in Gelatine Gel. It had been reported in a previous communication that the silver iodate make rhythmic precipitate in a well-dialysed gelatine, while it does not, in non-dialysed commercial gelatine.(45) The most favourable condition for producing a rhythmic precipitate of this substance is as follows. A 5% potassium iodate solution was allowed to diffuse into 2.8% gelatine gel, in which as much of silver nitrate had been dissolved as to be 0.1% in concentration. The rhythmic precipitate produced in this case was very peculiar in shape, showing a greatly different form from any rhythmic precipitate which the author had ever seen. That is, one band was a thin disc composed of very fine crystals and an annexed band was above it, which consisted of a small number of extremely fine precipitate. A layer of the same precipitate as one above the thin disc was annexed below. In the lower part, as going downward from it, the precipitated particles became coarse and there was formed a layer of massive particles. These series of layers formed one periodic structure and adjoined the next series across a clear space. The precipitate produced between this thin band and the subsequent one did not originate from the impurities in the gelatine, being different from the so-called secondary bands present between the rhythmic precipitate of silver chromate. It was apparent from the facts that even though potassium iodate was allowed to diffuse into the dialysed gelatine, which was used for the experiment, no precipitate was produced in the absence of inner electrolyte and the band of coarse particles between two successive bands was always only one. Fig. 6 shows an example of this rhythmic precipitate.

In experiment as to whether silver iodate could produce the rhythmic precipitate, the author employed at first, reversely to the above mentioned method, silver nitrate as the diffusing agent and potassium iodate as the inner electrolyte. In this case, the rhythmic bands of utterly different kind from the above mentioned was obtained. The particles of thus obtained rhythmic precipitate was coarse and did not gather close into a tablet-like band. The bands were coarse and uneven, so that they were inevitably indistinct. In addition, scarsely any clear spaces between successive bands was observed. Fig. 5 shows this type of the bands.

Silver Capronate in Gelatine Gel. Silver capronate forms a well defined rhythmic precipitate in gelatine jelly. Well dialysed gelatine, freed from chlorides and phosphates, was dispersed into 4% sol, the acid was added and then allowed to set. The concentration of the acid was 0.05–0.1 mol. per litre. After the gel set firmly, 20% silver nitrate solution was poured on it. White thin bands with relatively large distances were obtained.

Silver Phosphate in Silicic Acid Gel. When a silver nitrate solution was allowed to diffuse into a silicic acid gel which contained sodium phosphate, rhythmic precipitate of silver phosphate was obtainable if the acidity of the gel was adequate to the reaction. In a gel of low acidity, silver silicate would probably have formed accompanying the silver phosphate and yellowish brown close bands were formed. The conditions for the experiments are shown in Table 41.

Table 41.

No.	Gel				Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	Water (c.c.)	CH_3CO_2H (1 N) (c.c.)	Inner electrolyte (c.c.)		
1	3.0	0.8	2.2	Na_2HPO_4 0.3 (8.4%)	$AgNO_3$ 10%	Typical rhythmic precipitate was formed.
2	3.0	0.8	2.2	,, 0.3	$AgNO_3$ 5%	Rhythmic bands were formed.
3	3.0	0.9	2.1	,, 0.3	,, ,,	
4	3.0	1.0	2.0	,, 0.3	,, ,,	
5	3.0	1.1	1.9	,, 0.3	,, ,,	Bands were formed and below bands crystals were scattered about.
6	3.0	1.2	1.8	,, 0.3	,, ,,	
7	3.0	1.3	1.7	,, 0.3	,, ,,	
8	3.0	1.4	1.6	,, 0.3	,, ,,	
9	3.0	1.5	1.5	,, 0.3	,, ,,	Faint bands were formed.

In No. 1, well-developed yellow bands of silver phosphate were formed. In No. 2 and No. 3, seven or eight bands consisting of relatively coarse crystals were formed at the top of the gel and below the last formed band crystals were scattered. In No. 4, the best rhythmic bands were obtained. In a gel which was less acidic, silver silicate would probably have formed accompanying silver phosphate. The bands were closer, and in the lower part of the gel, crystals were coarse and no band was recognisable. No. 5 and No. 6 are the cases. In No. 7 and No. 8, finer close yellowish brown bands were formed, consisting probably of silver phosphate and silicate. No. 9 was inadequate to the banding, for, in this case only faint bands were formed at the top of the gel, and below these there was spread the precipitate uniformly. In short, the conditions from No. 1 to No. 4 were favourable to form a rhythmic precipitate of silver phosphate in a silicic acid gel.

Silver Arsenate in Silicic Acid Gel. It is expected that silver arsenate forms rhythmic precipitate in silicic acid gel, by the analogy of silver phosphate. Silver arsenate bands in gelatine gel was already reported by Rayleigh.(46) The present author has examined on this substance in silicic acid gel. A sodium arsenate solution (0.3 c.c. of 10% solution) was added to a sol which was prepared by mixing 3.0 c.c. of a water glass solution ($d = 1.06$) with an equal volume of 0.6–0.75 N acetic acid. After the sol set firmly to a gel, 5 or 10% solution of silver nitrate was poured on the gel and let diffuse in it. A chocolate brown precipitate deposited rhythmically. The bands were in contact with each other at the top of the gel, while at the bottom of the gel they were distinct and separated by marked gaps. In an ordinary room, the silver salt was decomposed by light and the rhythmic precipitate was blackened, so this experiment was favourably conducted in a dark room.

Silver Iodate in Silicic Acid Gel. The formation of a rhythmic precipitate of silver iodate in a gelatine jelly was already reported in a preceding paragraph. Now, its formation in a silicic acid gel will be described. By the diffusion of silver nitrate into a silicic acid gel containing potassium iodate as inner electrolyte, somewhat curious white bands consisting of flocculent clusters of relatively coarse crystals were formed. As the diffusion proceeded down, the crystals became coarser and accordingly each of the flocks which formed the bands grew considerably large and the bands became indistinct and uneven. We could see, however that the precipitate had the nature of bands, from the fact that the bands separated by marked interspaces by the addition of a small quantity of citrate to the gel. The conditions for the experiments are summarised in Table 42.

No. 1 and No. 2 gave such bands as described above. About 40 bands were formed within 50 mm. from the surface of gel. In No. 3, no band but yellow precipitate was formed at the top of the gel, which was probably silver iodate accompanying silver silicate, while in the lower part of the gel complicated yellow bands were formed. In No. 4,

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(46) Rayleigh, *Phil. Mag.*, **38** (1919), 738.

Table 42.

No.	Gel			Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	CH_3CO_2H solution (c.c.)	Inner electrolyte (c.c.)		
1	3.0	0.75 N 3.0	KIO_3 (5%) 0.65	$AgNO_3$ (5%)	Rhythmic bands were formed.
2	3.0	0.70 N 3.0	,, 0.65	,,	
3	3.0	0.60 N 3.0	,, 0.65	,,	Irregular banding occurred.
4	3.0	0.50 N 3.0	,, 0.65	,,	No band was formed.
5	3.0	0.75 N 3.0	,, 0.65 +citrate (3%) 0.3	,,	Most distinct bands were formed.
6	3.0	0.75 N 3.0	KIO_3 (5%)+ 0.65 aconitate (1.5%) 0.3	,,	Distinct bands were formed.
7	3.0	0.50 N 3.0	KIO_3 (5%) 0.65	,,	Irregular bands were formed.

however, a yellow precipitate was formed from the top to the bottom of the gel, and no band was recognisable. As it was already stated, the presence of a small quantity of citrate in the gel favours the formation of these rhythmic bands. In No. 5, the best bands were obtained. Each band consisted of many floculent clusters of crystals separated by marked gaps. The effect of aconitate in making the crystals small is less than that of citrate. In No. 6, the bands were less distinct than in No. 5. In No. 7, a result analogous to No. 3 was obtained.

In a gelatine jelly, when the inner electrolyte was interchanged with the outer electrolyte, that is to say, by the diffusion of potassium iodate into a gel containing silver nitrate, a rhythmic precipitate of an entirely different appearance was formed. In a silicic acid gel, however we cannot dissolve silver nitrate, because it reacts with silicic acid and precipitation occurs. So the interchange of the electrolytes is impossible in a silicic acid gel.

Calcium Phosphate in Silicic Acid Gel. Several reports have already published in regard to the formation of rhythmic precipitate of calcium phosphate in other medium than the silicic acid gel. But the banding in the silicic acid gel have never been reported. The present author therefore has tried an experiment in order to know whether the Liesegang phenomenon of calcium phosphate could be caused or not in the silicic acid gel.(16) And it was certified that calcium phosphate produced an extremely prominent rhythmic precipitate even in the silicic acid gel, and that the banding was closely related to the hydrogen ion concentration of the medium. The results were partly described in the preceding part of this paper.

The following is one of the most favourable conditions. That is, for dissolving phosphate in the gel, 1 c.c. of a 8% solution of secondary sodium phosphate was added to 10 c.c. of a 0.75 N acetic acid and then 10 c.c. of a solution of sodium silicate ($d = 1.06$) was added to it and allowed to stand to gelatinise. After the gel set firmly, 2 mol solution of calcium nitrate was superposed on it.

For dissolving calcium salt in the gel, after a sodium silicate solution ($d = 1.06$) was mixed with 10 c.c. of 0.75 N acetic acid and 1.0 c.c. of a 10% calcium chloride solution was added to the mixture, while stirring up. After the gel set firmly, 8% secondary sodium phosphate was poured on it. White sharp bands were formed in both cases spacing regular intervals.

Calcium Oxalate in Silicic Acid Gel. Calcium oxalate forms a rhythmic precipitate in silicic acid gel. The adequate condition for the banding is as follows: To 5 c.c. of sodium silicate solution ($d = 1.06$) add 5 c.c. of a mixture of acetic acid and oxalic acid (0.5 N, ratio of the two acids; 1:1 or 1:3). The silicic acid gel set in one night. Then ca. 5 c.c. of calcium chloride solution (10–25% solution) are poured on the gel. The rhythmic bands are formed which has an appearance like an opal. Clear spaces between bands are so narrow that the bands can better be seen by the transmitted light. Too large or too small quantity of oxalic acid prevents the formation of calcium oxalate bands.

Strontium Oxalate in Silicic Acid Gel. Strontium oxalate forms a rhythmic precipitate in silicic acid gel in the presence of potassium citrate as the third substance. The condition for the banding is as follows: To 5 c.c. of sodium silicate solution ($d = 1.06$) add equal volume of the mixed acid above described and 0.01–0.02 g of potassium citrate. After setting the gel, put 5 c.c. of 25% strontium nitrate solution on it. About a week later, the formation of bands is observed by the transmitted light. Citrate accelerates, in this case, the formation of nucleus of the crystals. No strata were formed when no citrate was added in the gel. The nucleus formation is accelerated by the presence of the citrate and accordingly the formation of strata will become easier. The author found the formation of dense, white bands of strontium oxalate by adding a small quantity of citrate to the mixture before setting.

Nickel Dimethylglyoxime in Silicic Acid Gel. When an alcoholic solution of dimethylglyoxime is added to a solution of nickel salt, a red voluminous precipitate of nickel dimethylglyoxime is produced. Such a complex compound forms also rhythmic bands in a silicic acid gel.(47) Five cubic centimeters of a solution of sodium silicate ($d = 1.06$), was taken into test tube and mixed with 5 c.c. of 1 N acetic acid and then 0.25 c.c. of a saturated solution of dimethylglyoxime in alcohol was added to it and the mixture was left quiet until it set. A 15% solution of nickel sulphate was poured on the gel. Red rhythmic precipitate was formed which consisted of dendrites of fine crystals.

If the used quantity of dimethylglyoxime was smaller than 0.1 c.c. the precipitate was so coarse that no bands were produced. If the

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(47) Isemura, *J. Chem. Soc. Japan*, **57** (1936), 546.

quantity was larger than 0.5 c.c., the bands were so dense that the formation of a rhythmic precipitate was rather indistinct. .If the solution of nickel sulphate was smaller than 7.5% in concentration, the formed bands were smaller in number and the crystals of nickel dimethylglyoxime became coarse, so that the bands blurred. The adequate concentration of nickel sulphate, therefore, should be 10–20%. The formation of bands of this precipitate was strongly affected by the hydrogen ion concentration of the medium. The most adequate *p*H value for the formation of this rhythmic precipitate was about 5.0–5.5.

Lead Chromate in Silicic Acid Gel. It has generally been considered that the lead chromate forms bands in agar-agar gel but not in silicic acid gel. But the author has obtained the rhythmic bands of this substance in silicic acid gel by modifying the conditions appropriately. It is doubtful, however, whether the bands obtained in this case are the Liesegang phenomenon or not. They are probably the diurnal bands. The condition of the banding is as follows: In 5 c.c. of sodium silicate solution ($d = 1.06$) dissolve 0.01–0.005 g. of potassium chromate as inner electrolyte and 0.03–0.05 g. of glucose. To this solution add an equal volume of a half normal solution of acetic acid. After setting, 10% lead nitrate solution is superposed on the gel as outer electrolyte. Ten or more days later, it was obserbed that many thin and crowded bands were formed. If too much potassium chromate was added, the dendrites were also formed simultaneously, and if too little, the bands became very vague.

H. N. Holmes(34) has found, in the periodic precipitate of mercuric iodide in silicic acid gel, that the presence of glucose in the gel makes the bands very much sharper. The author has found, in the same manner, that the addition of glucose makes the periodic structure of the lead chromate much charper. In this case, two periodicities exist just as the case of silver chromate banding in gelatine containing small amount of soluble chlorides and phosphates. Larger periodicity is easily recognised while smaller one is often difficult to observe without a magnifying glass. At the lower part of the tube, however, both can easily be recognised with the naked eyes. It is interesting that in this case the upper part of the jelly is coloured yellow, the subsequent layer, orange, and the lower, brown. The banding appears under this part and becomes yellow again at the lowermost part. It seems that such a colour change is caused by the difference of the size of formed crystals.

Lead Iodide in Silicic Acid Gel. When potassium iodide solution diffuses into silicic acid gel containing lead acetate, fern-like fronds grow down in the gel, mixing with hexagonal plates. It is believed that the lead iodide does not form rhythmic precipitate in the silicic acid gel. But it was found, in rare cases, that the rhythmic precipitate of this substance occurred accidentally. The author studied the condition under which the rhythmic precipitates are formed,(12) and found that when the crystals become relatively small, the rhythmic precipitates are generally formed. The increase of the inner and outer electrolyte is favourable to the formation of small crystals. A third substance must be added which makes the crystals of lead iodide small in order to make sure the formation of rhythmic bands. Citrate and tartrate are fit to this purpose as already mentioned in the preceding paragraph. One normal acetic acid containing 0.9 c.c. of 1 N lead acetate and 0.55 c.c. of 3% potassium citrate to every 10 c.c. was mixed with the equal volume of water glass solution ($d = 1.06$) and poured into a test tube. After the silicic acid had set firmly, it was covered with 2 N potassium iodide solution. By this procedure good rhythmic bands from fine crystals were always formed. Similarly, to make the gel, 1 N acetic acid containing 1.2 c.c. of 1 N lead acetate and 0.8 c.c. of 3% tartaric acid to every 10 c.c. was mixed with the water glass solution. Then the gel was covered with 2 N potassium iodide solution. Beautiful well-defined rhythmic precipitates consisting of relatively large crystals were produced. These results show that the formation of bands is the true Liesegang's phenomenon. But the crystallisation of lead iodide is much influenced by the temperature and the light. The crystallisation of this substance is faster in day time than in night. Moreover, lead iodide is decomposed by bright light, especially in the presence of citrate and the colour of crystals changes to black. For these reasons, two other periodic deposition of diurnal nature, which are caused by the change of temperature and light, are produced as the reflex of the external periodicities. Frequently, these three rhythms, Liesegang's and two diurnal bandings, appear at the same time in one test tube and the complicated bands are obtained.

Lead Iodate in Gelatine Gel. As already mentioned, lead iodate is hardly obtained as rhythmic precipitate in non-dialysed gelatine. Because the rhythmic bands of lead iodate becomes undistinguishable by a continuous, white precipitate probably consisting of chloride and phosphate of lead in ordinary commercial gelatine, which contains always some impurities of chloride and phosphate. Very beautiful and well-defined rhythmic precipitate is formed by using the gelatine purified by electrodialysis or by Loeb's method.(48) One of the most favourable conditions for the banding is as follows: a 0.5 mol solution of lead acetate was allowed to diffuse into a 2% purified gelatine gel containing as much of potassium iodate as to be 4% in concentration. This rhythmic precipitate is one of the most distinct and beautiful example which the author have ever seen. Lead iodate makes often the helicoidal precipitate. The reason for the formation of helicoidal precipitate is not thoroughly clear but probably it is ascribed to the deformation of gel by the pouring of diffusing electrolyte on it. The conditions for the banding and the effect of various influences were studied and the results were partly shown in the preceding paragraphs. Light has no influences on this rhythmic precipitate and the ageing of gel also has no influences.

Lead Iodate in Silicic Acid Gel. It was already reported in the preceding paragraph, that if lead acetate diffuse into a gelatine gel containing potassium iodate, a very beautiful well-defined rhythmic precipitate is formed. But on standing this rhythmic precipitate for a long time, more lead acetate diffuse into the gel, reacts with the already formed

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(48) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 301.

lead iodate, and transforms the bands into those consisting of large crystals. It seems that the band of coarse crystals are composed of a double salt of relatively high solubility. This transformation from fine well-defined bands to incomplete bands of coarse crystals is far faster in silicic acid gel than in gelatine. The bands were scarsely observed in silicic acid gel after the transformation, because the crystals formed were large scattered globules. The quick transformation is probably due to the lack of protective action of the silicic acid gel. Six c.c. of a sol which was prepared by mixing equal volumes of a sodium silicate solution ($d = 1.06$) and 0.70–0.75 N acetic acid solution is added with 0.6 c.c. of 5% potassium iodate solution. After the gel set firmly, a lead acetate solution (1 N) was poured on the gel. About ten bands were formed after 24 hours but these transformed, successively, from the top, into bands consisting of large globules, which blurred within two or three days.

Lead Phosphate in Silicic Acid Gel. It was examined whether lead phosphate was precipitated in rhythmic bands or not in silicic acid gel. A sol which was prepared by mixing 3.0 c.c. of a ($d = 1.06$) solution water glass with an equal volume of 0.75 N acetic acid, is added with 0.5 c.c. of a 0.5 mol solution of sodium phosphate. After the sol set firmly to a gel, 1 N solution of lead acetate or lead nitrate was superposed on the gel. The banding was indistinct. Somewhat long needles were formed and it seems that these needles distribute to make faint bands. When 0.3 c.c. of a 3% potassium citrate solution was added beforehand to the gel, distinct rhythmic bands were formed. When a lead acetate solution (1 N) diffused into the gel, more than twenty bands were recognised. But in the case of the diffusion of lead nitrate, the bands were often imperfect and consisted of fragments.

Lead Phosphate in Gelatine Gel. The lead phosphate precipitates in silicic acid gel as somewhat long needles and the rhythmic nature of this precipitate is, as already mentioned, indistinct. In the presence of a small quantity of citrate, however, the crystals became smaller and they appeared as a rhythmic precipitate. It is known that crystals formed in gelatine are generally smaller than those formed in a silicic acid gel. So, it is expected that lead phosphate forms rhythmic bands in gelatine. The author made an experiment on it. Sodium phosphate (0.5 c.c. of 0.5 mol solution) was dissolved in 6 c.c. of a 3% solution of purified ash-free gelatine. After the gel set firmly, 1 N solution of lead acetate was poured on the gel as the outer electrolyte. Seven white bands were formed and then the crystals deposited uniformly below these bands.

Cerium Iodate in Silicic Acid Gel. The bands of cerium iodate were obtained by the diffusion of cerium nitrate into silicic acid gel containing potassium iodate as inner electrolyte. The condition for the banding was as follows. A sol which was prepared by mixing 3.0 c.c. of a water glass solution ($d = 1.06$) with an equal volume of 0.7 N acetic acid was added with 1.0 c.c. of a saturated solution of potassium iodate. After the sol set firmly to the gel, 5% solution of cerium nitrate was superposed on it. White beautiful bands were obtained. Every band formed close to each other. For the first 2.5 cm. from the top of the gel, a continuous white precipitate was formed and for the next 2.5 cm. 15 bands were recognised, separated by narrow clear gaps.

Silver Ferrocyanide in Silicic Acid Gel. A rhythmic precipitate of silver ferrocyanide was obtained by the diffusion of silver nitrate into silicic acid gel containing potassium ferrocyanide. The bands were very close to each other. More than 15 bands were often formed in one centimeter. This banding was already studied by Mukherjee and Chatterji.(49) They concluded that the intervals between bands become smaller with the advance of diffusion. But in the present experiments all of the bands were separated by almost equal intervals. It is doubtful that these bands were formed as a Liesegang phenomenon. This banding is influenced by the acidity of the gel. Some conditions and the results obtained are given in Table 43 and follows.

Table 43.

No.	Gel				Outer electrolyte (5%)	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	CH_3CO_2H solution (c.c.)		Inner electrolyte (c.c.)		
1	3.0	0.6 N	3.0	$K_4Fe(CN)_6$ (2%) 0.3	$AgNO_3$	A yellow continuous precipitate was formed.
2	3.0	0.7 N	3.0	,, 0.3	,,	A grey continuous precipitate was formed.
3	3.0	0.8 N	3.0	,, 0.3	,,	Close rhythmic bands were formed.
4	3.0	0.9 N	3.0	,, 0.3	,,	
5	3.0	1.0 N	3.0	,, 0.3	,,	
6	3.0	1.0 N	3.0	,, 0.7	,,	

In a gel of low acidity such as No. 1, yellow precipitate was formed uniformly and no band was recognised. In No. 2, also, no band was formed but a white precipitate formed uniformly. In No. 3–No. 5 many close bands were obtained. These bands were type of sub-class II (class II of Chatterji). Generally, the intervals between bands were large in a gel of high acidity. In No. 5, the intervals between bands were larger than those in No. 3 and in No. 4. In No. 6, the bands were very close to each other owing to the relatively high concentration of the inner electrolyte.

Ferric Ferrocyanide in Silicic Acid Gel. Rhythmic bands of ferric ferrocyanide were obtained by the diffusion of ferric chloride into silicic acid gel containing potassium ferrocyanide as an inner electrolyte. These rhythmic bands were indistinct, showing a blue continuous precipitate by reflected light but many bands were seen by transmitted light. The banding was sub-class II type (class II type of Chatterji). The conditions are given in Table 44.

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(49) Mukherjee and Chatterji, *Kolloid-Z.*, **50** (1930), 147.

Table 44.

No.	Gel			Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	CH_3CO_2H solution (c c.)	Inner electrolyte (c.c.)		
1	3.0	0.5 N 3.0	$K_4Fe(CN)_6$ 0.1 (2%)	$FeCl_3$ 5%	Faint bands were formed.
2	3.0	,, 3.0	,, 0.3	,,	
3	3.0	1.0 N 3.0	,, 0.1	,,	No band and only a stopper was formed.
4	3.0	,, 3.0	,, 0.3	,,	
5	3.0	,, 3.0	,, 0.7	,,	
6	3.0	0.6 N 3.0	,, 0.3	,,	Blue rhythmic precipitate was observed by transmitted light.
7	3.0	0.7 N 3.0	,, 0.3	,,	
8	3.0	0.8 N 3.0	,, 0.3	,,	
9	3.0	0.9 N 3.0	,, 0.3	,,	
10	3.0	0.8 N 3.0	,, 0.1	,,	No band was formed.

When the concentration of potassium ferrocyanide was small, either the banding was indistinct or no band was formed as in the cases of No. 1, No. 3, and No. 4. In No. 2, brown bands were formed which were thinner in the lower part and separated by small interspaces. These were probably diurnal bands of ferric basic chloride or ferric hydroxide. At the bottom of the gel some rhythmic bands of prussian blue were formed. No. 3 gave no band and only a brown stopper. In No. 4, many blue bands were observed by transmitted light but no band by reflected light. No. 5 gave brown diurnal bands but blue bands were not observed even by transmitted light for the precipitation was too dense. In No. 6–No. 9 blue rhythmic bands were well observed by transmitted light. No. 10 gave no band. A brown band was always observed at the top of the gel in these banded precipitates. These were probably formed by basic chloride of iron, ferric hydroxide or basic ferric acetate which was produced by the hydrolysis of ferric chloride or its interaction with acetic acid. These brown bands were formed simultaneously with bands of prussian blue, and were affected by external rhythms. So the banding was always very irregular. Moreover, this rhythmic precipitate was affected by the acidity of the gel. In a gel of high acidity, many bands were formed in the lower part of the gel, situating close to each other. This was probably due to the fact that the diffusing ferric chloride was not easily hydrolysable in the more acidic gels and so the consumption of ferric chloride by hydrolysis was small. Accordingly, ferric chloride of the same concentration acts as if it were a cencentrated solution in the more acidic gels.

Uranyl Phosphate in Silicic Acid Gel. A rhythmic precipitate of uranyl phosphate was obtained by the action of uranyl acetate with soluble phosphate in silicic acid gel. A sol which was prepared by mixing 3.0 c.c. of a water glass solution (d =1.06) with an equal volume of 0.75 N acetic acid was added with 0.3 c.c. of a 8.74% solution of sodium phosphate. After the gel set firmly, 2% solution of uranyl acetate was superposed on it. Pale yellow bands consisting of relatively coarse crystals were formed. The appearance was entirely analogous to the bands of uranyl arsenate which will be described later. Coarse crystals have been deposited under the last band. The bands belong to the category of the type of sub-class II.

Uranyl Arsenate in Silicic Acid Gel. The precipitating reaction of uranyl arsenate is analogous to the case of uranyl phosphate. So the formation of rhythmic precipitate of uranyl arsenate in a silicic acid gel was experimented, and a similar result was obtained. A sol which was prepared by mixing 3.0 c.c. of a water glass solution ($d = 1.06$) with an equal volume of 0.75 N acetic acid was added with 0.3 c.c. of a 10% solution of sodium arsenate. After the gel set firmly, 2% solution of uranyl arsenate was superposed on it. Several bands of pale yellow uranyl arsenate were obtained. The crystals forming the bands became coarse with the advance of diffusion. Almost no crystals formed below the last band. These bands were also the sub-class II type.

Summary.

(1) The conditions of the formation of various examples of rhythmic precipitates have been studied. The effects were tested of the change of species and concentrations of gel, inner electrolyte and outer electrolyte, the temperature, the light intensity and the hydrogen ion concentrations of medium and outer electrolyte solution.

(2) The regularity of spacing between bands has been studied. The distance between bands is expressed empirically by the quadratic equation concerning the ordinal number of it. The same equation was deduced from a theoretical standpoint, the physical meaning of the equation being considered.

(3) Classification of the rhythmic precipitates by the cause of formation and by the structure has been proposed. Secondary bands were investigated and discussed.

(4) New examples of rhythmic precipitate have been described, i.e. barium chromate, cobalt phosphate, lead carbonate, lead phosphate, lead iodate, silver arsenate, silver carbonate, silver iodate and silver capronate in gelatine gel, and bismuth chromate, bismuthyl chloride, bismuthyl nitrate, cobalt phosphate, cobalt sulphide, copper carbonate, copper iodate, cerium iodate, calcium phosphate, calcium oxalate, strontium oxalate, ferric ferrocyanide, lead carbonate, lead iodate, lead phosphate, nickel dimethylglyoxime, silver arsenate, silver ferrocyanide, silver phosphate, silver iodate, uranyl phosphate and uranyl arsenate in silicic acid gel. The conditions for the formation of these rhythmic precipitates have been thoroughly investigated.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his kind advices and encouragement throughout the work.

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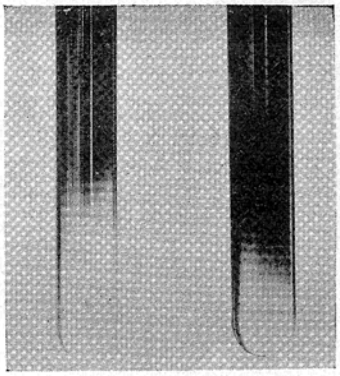


Fig. 1.

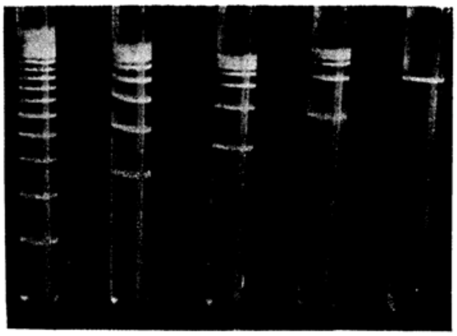


Fig. 2. Na_2CO_3 (conc.) → Na_2CO_3 (dil.)

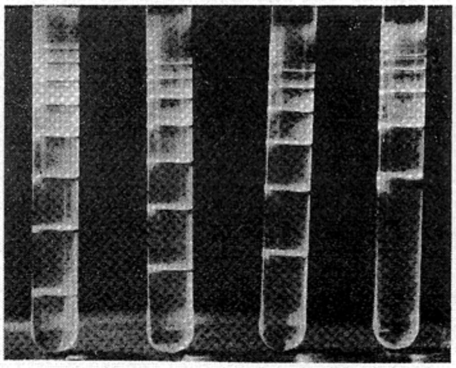


Fig. 3. $AgNO_3$ (conc.) → $AgNO_3$ (dil.)

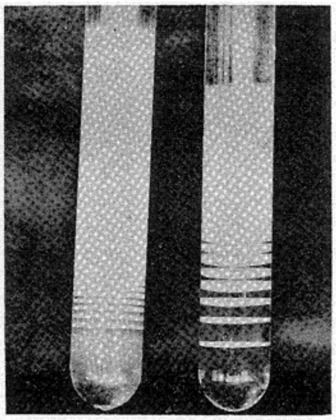


Fig. 4.

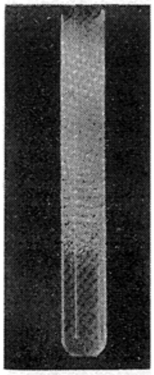


Fig. 5.

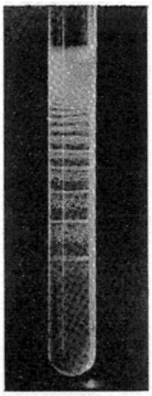


Fig. 6.

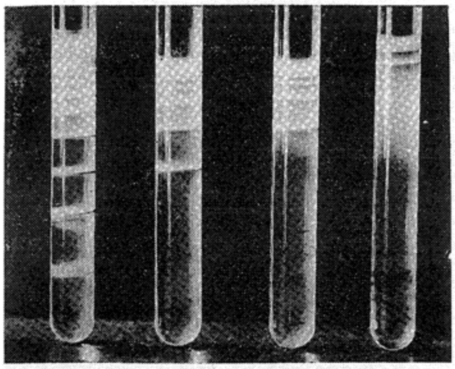


Fig. 7. Gelatine (dil.) → Gelatine (conc.)

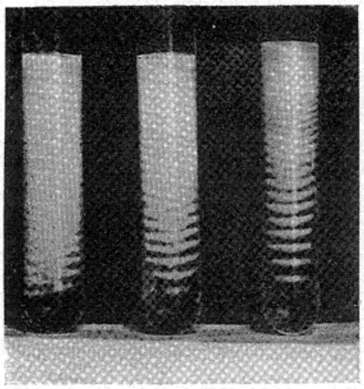


Fig. 8.

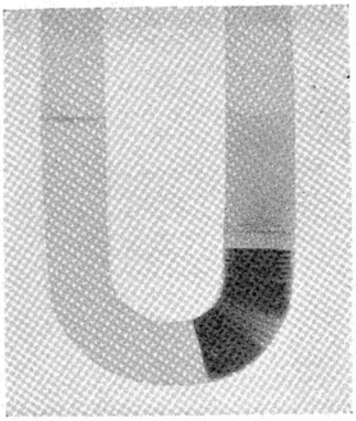
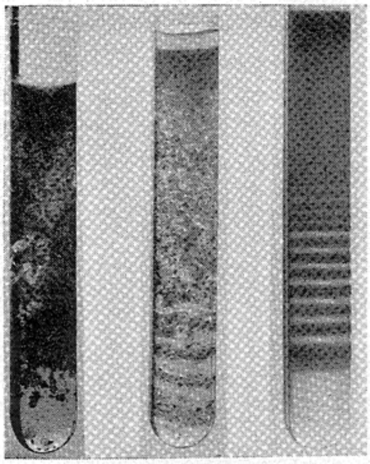


Fig. 9.



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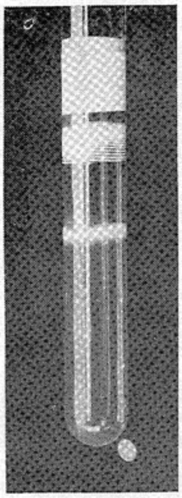

Fig. 11.

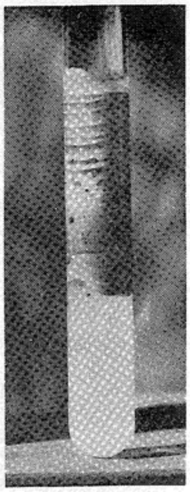

Fig. 13.

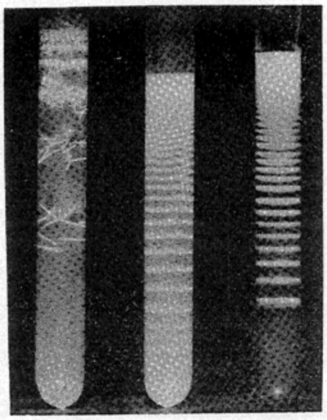

Fig. 12.

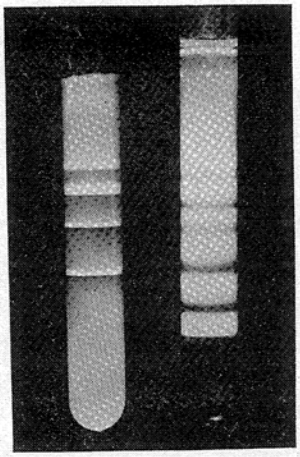

Fig. 14.