CCCLX.—*The Formation of Liesegang Rings as a Periodic Coagulation Phenomenon.*

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DURING the past 32 years, a vast amount of experimental work has been performed on the production of stratified precipitates in gels, and from this work there emerges the important fact that the phenomenon is of a general nature; indeed, it is probable that, given the right conditions, rhythmic banding of a precipitate can be formed from any pair of interacting salts. Most of the numerous theories which have been advanced to account for the observed phenomena apply only to the particular case studied (see Hedges and Myers, "The Problem of Physicochemical Periodicity," 1926,

E. Arnold and Co.), but reference may be made to the four most important theories which are of general applicability, *viz.*, those of Wilhelm Ostwald ("Lehrbuch der allgemeinen Chemie," Leipzig, 2nd edn., 1891, ii, 778), Bradford (*Biochem. J.*, 1916, **10**, 169; 1917, **11**, 14), Dhar and Chatterji (*Kolloid-Z.*, 1922, **31**, 15; 1925, **37**, 2), and Wo. Ostwald (*ibid.*, 1925, **36**, 380).

The reactions which give rise to these banded precipitates are often designated as "rhythmic" or "periodic," but there is nothing to suggest that the reaction–time curve is periodic, and it is therefore proposed to apply the term "periodic structures" to the cases under discussion, and to restrict the term "periodic reactions" to chemical processes where it can be shown that the reaction velocity varies periodically. One of the aims of the present research has been to obtain evidence on this aspect of the matter by determining whether the bands of precipitate are formed primarily in the diffusing wave-front, or whether the banding is a secondary phenomenon occurring after formation of the substance. We believe that we have definitely established the truth of the latter view.

<div align="center">EXPERIMENTAL.</div>

<div align="center">*The System Silver Dichromate–Gelatin.*</div>

When a large drop of 20% silver nitrate solution is placed on a 10% gelatin gel containing 0·4% of potassium dichromate, it is generally observed that in the initial stages of diffusion concentric rings of precipitate are formed at the edge of the diffusing wave-front, and somewhat later the rings are surrounded by a pale yellow fringe. The fringe increases gradually in breadth, often to the extent of 1 cm. or more.

By conducting the experiment in a test-tube, down the outside of which a thin strip of paper is pasted, and marking the positions of the extreme edge of the yellow fringe and of the last red ring after various time intervals, it can readily be shown that the rings are formed some distance behind the diffusing wave-front. These observations cannot be taken as evidence that the production of rings is a secondary effect, since the nature of the pale yellow fringe is not definitely known. Friend (*J.*, 1922, **121**, 472) regards it as colloidal silver chromate, whereas according to Riegel and Reinhard (*J. Physical Chem.*, 1927, **31**, 713) it consists of silver chloride, formed by the sodium chloride present as an impurity in commercial gelatin. It is stated that no such haze is produced if the gelatin has previously been washed thoroughly. Our observations support the view of Riegel and Reinhard, but we cannot agree with them that the production of red rings of silver dichromate

is dependent on the substructure due to the chloride; for we find that after the chloride in a gelatin sol has been completely precipitated by dilute silver nitrate solution and the stirred liquid allowed to set to a structureless gel with addition of potassium dichromate, good rings are produced by allowing 20% silver nitrate solution to diffuse into the gel. Further, if a drop of 20% silver nitrate solution be placed on the yellow fringe in the ordinary diffusion experiment, an independent ring system develops immediately, which can bear no relation to the pre-existent substructure.

Experiments to be described later have shown that when very dilute solutions of silver nitrate and potassium dichromate are mixed together in gelatin no precipitate is formed, the product apparently remaining in a colloidal state, protected by the gelatin. A considerable excess of silver nitrate causes coagulation of the colloid to a red precipitate. It seems unlikely, therefore, that silver dichromate is precipitated in the direct chemical reaction during the course of the formation of Liesegang rings, but rather that the first product of the reaction is colloidal silver dichromate, which is afterwards coagulated in rings by excess of the diffusing silver nitrate.

An experiment was devised to separate the chemical reaction and the coagulation into two stages and to determine which stage is responsible for the periodicity. The method consisted in adding to the gelatin–potassium dichromate mixture an equivalent quantity of silver nitrate and, after the mixture had set to a gel, causing 20% silver nitrate solution to diffuse into it. To conduct this experiment, it does not suffice to add directly to the gelatin equivalent quantities of the two reactants, for the chlorides, etc., in the gelatin dispose of some of the silver nitrate preferentially, leaving some potassium dichromate free. It was necessary, therefore, to determine the substances in the gelatin which could react preferentially with silver nitrate. This was done by igniting a weighed amount of gelatin and titrating the aqueous extract of the ash with silver nitrate in presence of potassium dichromate as an indicator. Since the composition of one gelatin leaf differs from that of another from the same source, a large amount of 10% gelatin sol was prepared and 25 c.c. were withdrawn for the analysis, which was thus performed on the same sol as that used for the experiments. The sol (25 c.c.) was evaporated to dryness in a platinum dish and finally heated over the blowpipe until the ash attained a constant weight, which was 1·64% of the weight of dry gelatin. This amount of ash (0·0410 g. in 25 c.c.) was equivalent to 2·95 c.c. of 0·5% silver nitrate solution.

From these data, a sol of silver dichromate in 5% gelatin was

made by mixing (a) 20 c.c. of 10% gelatin + 20 c.c. of 0·2871% potassium dichromate solution with (b) 20 c.c. of 10% gelatin + 14·74 c.c. of 0·5% silver nitrate solution.   After the mixture had set to a gel in a number of test-tubes, 20% silver nitrate solution was poured over the top : the resulting periodic structure due to coagulation is reproduced in Fig. 1.   The bands are as well defined as those produced by chemical reaction, and, moreover, they are subject to the same peculiarities; for example, the bands in one tube formed a spiral.   The silver dichromate was not coagulated by diffusing a saturated solution of potassium dichromate into the gel.

In a second series, a 30% excess of silver nitrate was added to silver dichromate in gelatin.   Bands were produced by diffusing 20% silver nitrate solution into the mixture, but they were not so well marked as in the former case, a considerable amount of precipitation occurring in the spaces between the bands.   In this system, bands were formed by the interdiffusion of a saturated solution of potassium dichromate, affording confirmation that there was excess of silver nitrate in the gel.

The experiments indicate that the banding is not concerned with the chemical reaction, but is a secondary phenomenon occurring after the reaction.   The two stages have been separated, the chemical reaction having been carried out first without periodic phenomena, and a stratified precipitate being produced in the second stage of coagulation by excess of silver nitrate.

Measurement of the Critical Concentration of Silver Nitrate.

The experiments described in this section were designed, not only to gain an idea of the critical concentration of silver nitrate necessary to coagulate silver dichromate under the conditions prevailing in the former experiments, but also to test the suggestion made by Hedges and Myers (op. cit., p. 27), that the formation of periodic structures may have its explanation in the periodic opacity phenomenon of Holker (Proc. Roy. Soc., 1923, A, 102, 710).   According to this author, the opacity of a precipitated colloid is in many cases a periodic function of the concentration of the precipitating electrolyte, and the suggestion was made (Hedges and Myers, op. cit.) that, since in the formation of a periodic structure the advancing diffusion wave is subject to a progressive dilution, a series of opacity bands is to be expected, corresponding with the peaks of Holker's curves.   If such be the case, one would expect that, when a series of test-tubes containing colloidal silver dichromate in gelatin is treated with progressively increasing concentrations of silver nitrate (each tube receiving a higher concentration than its predecessor), then precipitation would occur in some tubes and not in others,
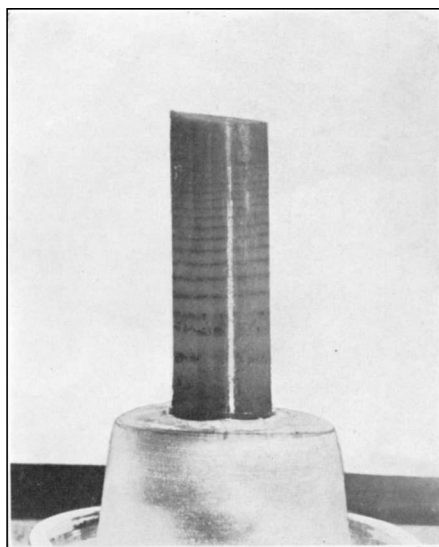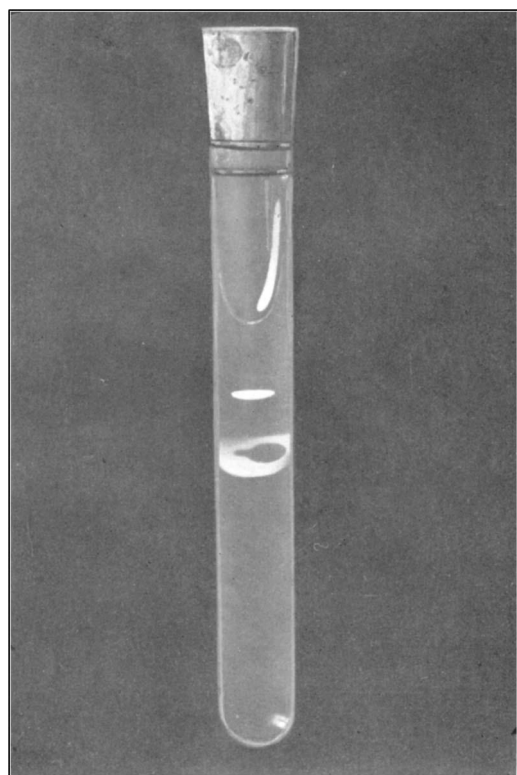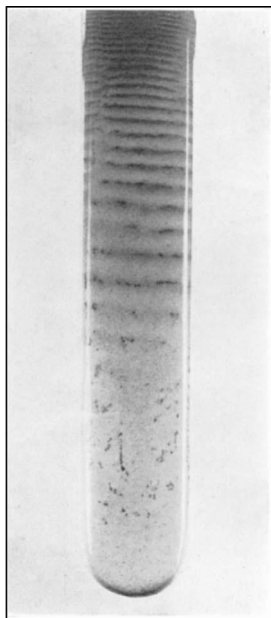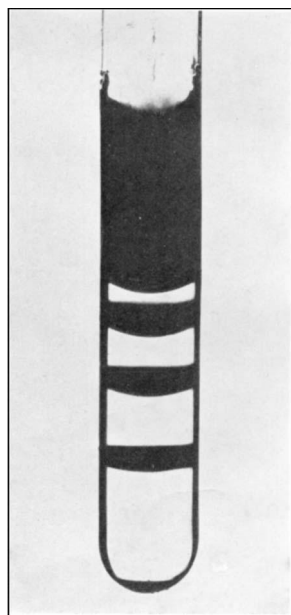
Fig. 1.

Fig. 2.

Fig. 4.

Fig. 3.

the arrangement being periodic throughout the series, but the experiments do not lend any support to this view.

To each of a series of tubes containing 5 c.c. of silver nitrate solution were added 5 c.c. of a sol prepared by mixing equal volumes of 0·125% silver nitrate in 5% gelatin and 0·1435% potassium dichromate in 5% gelatin. Silver nitrate solutions were examined over the concentration range 0·1% to 3·0%. All the solutions up to and including 0·29% silver nitrate remained a clear yellow after addition of the silver dichromate–gelatin mixture, but a red precipitate was produced in the 0·30% solution. A further series was conducted with twelve tubes in which the concentration was varied from 0·288% to 0·299% at intervals of 0·001%. At first sight it seemed that there was actually a periodic change, produced by progressively increasing concentration. It appears, however, that the production of precipitate in any one tube is fortuitous, depending, for instance, on the nuclei provided by the tube and on the rate of mixing. The whole series was repeated three times in tubes which had previously been soaked thoroughly in a mixture of nitric and chromic acids. In these experiments there was a complete lack of correspondence in the behaviour of individual tubes : those concentrations which were the first to give a red precipitate in one experiment were the last to retain their yellow colour in the next. No reliance can be placed, therefore, on values of critical concentration measured in terms of less than 0·01%. The critical concentration required to coagulate colloidal silver dichromate under the conditions described may be taken as 0·29%.

We believe that these observations offer a satisfactory explanation of the unpublished experiment performed by Holker and reported by Hedges and Myers (*op. cit.*, p. 27).

The System Lead Iodide–Agar.

Periodic structures can readily be obtained by diffusing 30% lead nitrate solution into an agar gel containing potassium iodide (see Hatschek, " Laboratory Manual of Colloid Chemistry," 1925, p. 144). This system has been treated in the same manner as the preceding one, and it has again been shown that the chemical reaction can be carried out first, the bands being obtained subsequently by coagulation.

Equal volumes of 1% agar solutions containing 0·6% of potassium iodide and 0·6% of lead nitrate (equivalent weights) were mixed while hot and allowed to set in test-tubes. On cooling, the lead iodide did not separate, although its solubility in water was exceeded many times. However, when kept for some days, such gels gave a yellow deposit in patches on the side of the test-tube.

30% Lead nitrate solution was poured into the space above the gel in two tubes; after 2 days, five successive discs had appeared in the tube.   These discs did not reach to the walls of the tube, but were suspended in the gel; the first two were sharply defined, and the remainder more diffuse; the mean distance between the bands was about 1 cm., becoming greater with increasing depth in the tube.

Diffusion of 20% potassium iodide solution into another tube gave a ring system comparable in every respect with that produced by chemical reaction.   Within an hour, numerous fine bands were visible.   It seems that in this instance either of the reactants serves as a coagulating agent, but potassium iodide is much more effective than lead nitrate.

In order to eliminate any possible complications due to the concomitant production of potassium nitrate in making up the gel mixture, the experiments were repeated and extended in agar gels containing lead iodide in absence of other electrolytes.   These were prepared by dissolving recrystallised lead iodide in 1% agar solution at 100°, and allowing it to cool.   A few trials indicated that the cooled gel would hold as much as 0·2% of lead iodide, although the solubility in water at the ordinary temperature is only 0·04%.

A number of test-tubes containing 1% agar gel with 0·2% lead iodide were treated with various diffusing agents.   Periodic structures, exactly similar to those described for gels prepared by the former method, were produced when 30% lead nitrate or 20% potassium iodide was the diffusing solution.   An example of the bands produced when potassium iodide diffused into the gel is given in Fig. 2.

Other solutions were allowed to diffuse into the above mixture and bands were observed in some cases; 20% silver nitrate, 20% sodium carbonate, and a saturated solution of mercuric chloride gave rings, but 30% aluminium sulphate, 20% cupric chloride, dilute nitric acid, and ammonia (d 0·880) gave none.

The System Magnesium Hydroxide–Gelatin.

The periodic structure produced when ammonia diffuses into a gelatin gel containing magnesium chloride has been described by Popp (*Kolloid-Z.*, 1925, **36**, 208), and the system is unique in that it produces only a small number of sharply defined, relatively massive bands.

For coagulation experiments, a 6·5% gelatin gel was used, containing 5% of crystallised magnesium chloride with an equivalent amount of ammonia.   The magnesium hydroxide remained in colloidal solution under these conditions.   The mixture was allowed to set to a gel in test-tubes, and ammonia solution (d 0·880) was

poured over each. After 4 days, the periodic structure portrayed in Fig. 3 was produced. These rings are comparable with those produced by direct diffusion of strong ammonia into gelatin containing magnesium chloride alone. The photograph was taken by transmitted light, and the white rings of magnesium hydroxide therefore appear dark and the clear spaces white.

Chemical Analysis.of the Periodic Structure.—The system magnesium hydroxide–gelatin lends itself admirably to investigation by means of chemical analysis, as a result of the macroscopic nature of the effect. Some analyses (for which no great accuracy is claimed) were therefore undertaken with this system, the object of the examination being solely to determine whether a very uneven distribution of material between the bands and spaces occurs, or whether these approximate to each other in composition. It has often been supposed that the actual amount of product in equal volumes of the bands and the clear spaces is in many cases nearly equal (compare Hatschek, *British Association, Second Colloid Report,* 1918), but the results of the present analysis show that the composition of the bands differs widely from that of the clear space.

According to Ostwald (*Kolloid-Z.*, 1925, **36**, 380), Popp carried out some analyses of the system under discussion, and found the concentration of chlorine ions in the bands directly after formation to be almost double that in the original gel, but experimental details were not given. We reproduce our results, since they not only differ quantitatively from those of Popp, but are in the opposite sense. The divergence is probably to be explained by the fact that, whereas the determinations reported by Ostwald were made on new-born rings, those now given refer to the completed structure a week or more old. The structures were prepared by diffusing ammonia (*d* 0·880) into 7·5% gelatin gel containing 5% of crystallised magnesium chloride. Such a concentration of gel was necessary to secure rigidity in cutting and handling, although Popp recommends a 3% gel for giving the best bands.

The following device for removing the gels from the tubes was found eminently satisfactory. After excess of the diffusing liquid had been poured away, a groove was cut by means of a glass knife so as to encircle completely the tube near the lower, closed end. The end of the tube could be removed as a cap by applying a red-hot splinter of glass to the groove. The tube was then dipped for 1 second into water at about 80°, which had the effect of loosening the gelatin adhering to the glass, and the entire structure could readily be blown out of the tube. All other methods of extricating the gels failed because of the strong adherence of gelatin to glass. Agar gels can conveniently be removed by cracking open the tubes.

The structures were cut up into bands and clear spaces by means of a safety-razor blade.

The white bands were found to be fairly hard and relatively heavy (the density was about 1·7 times that of the clear space), and were readily detached in the form of pastilles from the intervening gel spaces. Three bands and the two enclosed clear spaces were chosen for the analysis. In order to gain an indication of the distribution of material in equal volumes of band and space as well as in equal weights, the length of gel taken was measured in addition to the weight. The error of measurement of the length was great, however, and much more trust may be placed upon the results expressed per unit weight of gel.

Determination of magnesium. The method was to heat the gel gently in a platinum crucible until water had ceased to be driven off, and later over the blowpipe until a constant weight of magnesium oxide was obtained. In the meantime, the ammonium chloride volatilised. The weight of gelatin ash was subtracted from the total weight. Slight alterations due to differences in swelling, etc., may be disregarded. The results are summarised in the following table :

Determination of MgO (structure 7 days old).

	Length of gel (mm.).	Wt. of gel (g.).	Wt. of MgO.	G. of MgO per mm.	G. of MgO per g. of gel.	Relative amounts of MgO, per unit vol.	per unit wt.
Band	5	1·47	0·046	0·009	0·031	20	12
Clear space	20	3·51	0·009	0·00045	0·0026	1	1

Determination of chloride. The gel was made up to 100 c.c. by addition of dilute nitric acid. Direct titration with silver nitrate and potassium thiocyanate yielded poor results, as the end-point was changed by the presence of the gelatin. A method similar to that used for the determination of chlorides in blood was therefore adopted. The gelatin was precipitated by means of tungstic acid, and after filtration, silver nitrate and nitric acid were added in excess, and portions of the solution were titrated with standardised potassium thiocyanate. A good end-point was obtained with the solution from the clear space, but that from the bands gave a poor end-point. The following table contains the results :

Determination of chloride (structure 9 days old).

	Length of gel (mm.).	Wt. of gel (g.).	Total chloride.	G. of chloride per mm.	G. of chloride per g. gel.	Relative amounts of chloride per unit vol.	per unit wt.
Band	7	1·543	0·0060	0·00086	0·0039	1·0	1·0
Clear space	26	4·240	0·054	0·00207	0·0127	2·4	3·26

The analyses show that the amount of precipitate contained in the bands is 12 times as great as that present in an equal weight of clear space, whereas the chloride content of the bands is less than one-third of that of the clear space. The equivalent ratio, $\frac{1}{2}$Mg : Cl, is 14·0 : 1 in the bands, and 1 : 2·8 in the clear space.

It may be observed that the total chloride in the gel is not equivalent to the total magnesium. The missing chloride was found in the diffusing solution standing above the gel, indicating that the soluble product, ammonium chloride, diffuses out of the gel and into the ammonia solution. Experiments were therefore conducted in which this outward diffusion was prevented by dissolving in the diffusing ammonia solution sufficient ammonium chloride to give a concentration just equal to that produced in the gel by reaction. Excellent bands developed in these tubes, so that the outward diffusion of ammonium chloride is not essential to the production of the periodic structure.

Other experiments were carried out, in which equivalent solutions of magnesium chloride and ammonia were mixed in 7·5% gelatin, and water was placed over the gel, in order to see whether, with the outward diffusion of the ammonium chloride, the magnesium hydroxide would be precipitated in bands ; but no precipitate was formed.

The " diffusion-wave " theory of Wo. Ostwald (loc. cit.) is founded largely on observations on the magnesium hydroxide system. The theory is admitted to be applicable only to rhythmic structures produced by chemical reaction, and the existence of three diffusion waves (those of the two reacting substances and of the soluble product) is postulated. Since the work described in the present paper has shown that essentially similar structures can be produced after the chemical reaction is completed, it would seem that the theory is not very comprehensive. An instance where the diffusion-wave theory appears to fail completely is in the production of rhythmic structures by potassium iodide or lead nitrate diffusing into lead iodide in agar. Here, the greatest possible number of diffusion waves which can be set up is two, and yet the resulting structure does not differ from that produced as the result of chemical interaction of lead nitrate and potassium iodide.

The Periodic Coagulation of Sols of Arsenious Sulphide and Ferric Hydroxide.

As a corollary to the experiments on the production of periodic structures after the chemical reaction has been carried out, it should be possible to obtain such structures by simple diffusion of

a coagulating electrolyte into a sol contained in a gelatin or agar gel.   Experiments have been conducted on these lines with sols of arsenious sulphide and of ferric hydroxide in agar gels.

An arsenious sulphide sol was prepared by passing hydrogen sulphide into a solution containing 0·5 g. of sodium arsenite in 500 c.c. of water, and removing the excess of hydrogen sulphide by means of a stream of hydrogen.   Three gels containing different amounts of arsenious sulphide were prepared.   Gel 1 was made by mixing the arsenious sulphide sol with an equal volume of 2% agar sol; Gel 2 was prepared by diluting the arsenious sulphide to one-half of the original concentration with water, and mixing equal volumes of the diluted sol and 2% agar; and in Gel 3 the arsenious sulphide sol was first diluted to one-fourth of its concentration and then mixed with an equal volume of 2% agar.   The diffusing electrolyte was ferric chloride or aluminium sulphate at concentrations of 30, 10, 5, and 1%.

In these systems the process of diffusion was slow, and results of observations made after 20 days are given below.   With ferric chloride as the diffusing agent, no bands were produced in Gel 3 for any of the concentrations, Gel 2 produced poor bands, and Gel 1 good bands.   The best results were obtained with 5 and 1% of ferric chloride.   The formation of the bands, therefore, is favoured by a high concentration of colloid and a low concentration of electrolyte.   As shown below, a still higher concentration of arsenious sulphide sol is unfavourable to band formation, suggesting that there is an optimum concentration.

In transmitted light the periodic structure appeared as a number of dark bands across the test-tube, which were just discernible in reflected light by their deeper yellow colour.   The spaces between the bands contained a considerable amount of arsenious sulphide.

The most characteristic feature of these structures is the fact that the distance between successive bands *decreases*, whereas in most periodic structures the successive bands become more widely spaced throughout the diffusion.   This fact agrees with the observation that the mean distance between the bands is greater the more concentrated the diffusing solution, and is contrary to the usual observation.   With 30% and 1% ferric chloride, the mean distances between the bands were respectively 9 mm. and 3 mm. One such instance of a periodic structure has been recorded (Davies, *J. Amer. Chem. Soc.*, 1917, **39**, 1312), which occurs in the precipitation of mercury when mercurous nitrate diffuses into sodium formate contained in gelatin.

The results were similar in the experiments with aluminium sulphate as the coagulating agent.   Bands were observed only in

Gel 1, and the best results were obtained in the tubes containing the lower concentrations of diffusing agent.   The distance between successive bands decreased, and the spacing was wider the more concentrated the solution;   10% aluminium sulphate produced 7 bands occupying 33 mm. along the tube, and 1% aluminium sulphate produced 6 bands occupying 20 mm.

To ensure that these bands were really caused by coagulation of the arsenious sulphide sol, control experiments were conducted in which the solutions were allowed to diffuse into (a) 1% agar gel alone, (b) 1% agar containing sodium sulphide equal in amount to that produced together with arsenious sulphide in the sols discussed above.   No bands were produced in any of these tubes.

A further precaution was taken, in that the experiments were repeated with colloidal arsenious sulphide prepared in almost complete absence of electrolytes.   0·5 G. of arsenious oxide was added to boiling water with two drops of 2N-sodium hydroxide to aid the dispersion.   Dissolution occurred readily and hydrogen sulphide was passed through, the excess being removed by means of hydrogen.   Two concentrations of sol were prepared; in the first, equal volumes of arsenious sulphide sol and 2% agar were mixed, and in the second the arsenious sulphide sol was diluted to one-half of its original concentration with water before being mixed with an equal volume of the agar sol.   The diffusing agents were ferric chloride, aluminium sulphate, and magnesium chloride at concentrations of 10, 5, 1, and 0·5%.   After 12 days, good bands had formed only in the more dilute sol, especially with ferric chloride at concentrations of 0·5 and 1%.   The more concentrated sol gave zonal turbidities rather than definite bands, the best examples occurring with 10% magnesium chloride and 0·5% ferric chloride and aluminium sulphate.   The decreasing distance between successive bands was again noticed in these systems.

Some experiments of the same type were carried out on undialysed sols of ferric hydroxide, prepared by the ammonium carbonate method (Hatschek, " Laboratory Manual of Colloid Chemistry," 1925, p. 46).   Three concentrations of sol were used, the original concentration being diluted 10, 20, and 40 times respectively.   The gels were prepared by mixing equal volumes of the sols with 2% agar and allowing them to set.   The coagulating electrolytes used were 30% and 10% sodium sulphate, 20% and 5% sodium arsenite, and 20% and 5% ammonium carbonate.   After 13 days, periodic structures had appeared only in the tubes containing the sol of middle concentration, banded turbidities being produced when the coagulating electrolyte was 20% or 5% sodium arsenite or 5% ammonium carbonate.   In the tube containing 5% sodium arsenite,

the distances between successive bands were 15, 12, 10, 9, and 7 mm., a decrease again being apparent. With 20% sodium arsenite the bands made their first appearance about half-way down the tube, showing that in this case also a dilute coagulating agent is favourable.

Anomalous Structures.

Many investigators of the Liesegang phenomenon have commented on the mal-formations sometimes produced. In many cases these are due to lack of homogeneity of the gel or of some other component of the system. It was found in the present work, for example, that deformed rings of magnesium hydroxide were produced when a crystal of ammonium chloride was dropped into the gel containing magnesium chloride. Some experiments in which 30% lead nitrate diffused into 2% potassium iodide contained in an agar gel produced rings in twins. In another experiment, equal volumes of 2% agar and 5% magnesium chloride were mixed in a test-tube and allowed to set; when ammonia (d 0·880) diffused in, a spiral structure of magnesium hydroxide was formed. It was observed that spiral precipitation was not caused directly by helicoid diffusion, but that layers of precipitate reaching half-way across the test-tube were formed alternately on opposite sides, and at different levels; later, these joined to form a spiral. When the bands became more than about 1 cm. apart, they no longer joined up. This effect may be caused by temperature difference due to the exposure of one side of the tube to a draught.

An extreme case of this anomaly was observed in the reverse experiment, in which 50% magnesium chloride solution diffused into a mixture of equal volumes of 2% agar and ammonia containing 5·4 c.c. (d 0·880) in 100 c.c.; the first band consisted of a thin disc suspended in the agar, a short way below the surface, which did not reach to the sides of the tube; it was closely followed by an annulus, the space in the middle corresponding with the disc above, as though the disc had thrown its shadow on to the second band. The ring was succeeded by another disc which in its turn was followed by a corresponding ring. The discs and rings were too close together to be photographed, but a similar experiment in which gelatin was used instead of agar is shown in Fig. 4. The disc consisted of a thick, firm pastille, and was separated some distance from its corresponding ring. The gelatin melted during a warm week-end, before any further discs and rings had formed. This type of structure may be caused by the unequal rate of setting of the gel in the middle and near the walls of the tube.

Summary.

The production of periodic structures of silver dichromate and of magnesium hydroxide in gelatin, and also of lead iodide in agar, has been studied. In each case, by mixing equivalent quantities of the reactants in the gel, and then superimposing a strong solution of the diffusing electrolyte, it has been possible to separate the chemical reaction from the formation of precipitate. Since the rings produced in these experiments are comparable with those produced by chemical reaction, it follows that the formation of periodic structures is a coagulation phenomenon taking place after the chemical reaction. Periodic structures are to be distinguished, therefore, from periodic reactions.

The critical concentration of silver nitrate required to coagulate colloidal silver dichromate has been measured, and the results are discussed in connexion with Holker's periodic precipitation experiments.

A chemical analysis of a periodic structure of magnesium hydroxide in gelatin has been conducted, and the results show that the ratio of magnesium hydroxide contained in the bands to that in the clear spaces is about 12 : 1; the corresponding ratio for ammonium chloride is about 1 : 3.

Periodic coagulation of sols of arsenious sulphide has been effected by diffusing solutions of ferric chloride and aluminium sulphate into the sol contained in 1% agar gel, and similar results have been obtained in the coagulation of colloidal ferric hydroxide by sodium arsenite and by ammonium carbonate. In these cases, there is an optimum concentration of colloid, and band formation is favoured by a dilute diffusing electrolyte.