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Investigations concerning some factors influencing rhythmic crystallization from aqueous solution

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INVESTIGATIONS CONCERNING
SOME FACTORS INFLUENCING RHYTHMIC
CRYSTALLIZATION FROM AQUEOUS SOLUTION

M. M. MASTERS 1934
INVESTIGATIONS CONCERNING

SOME FACTORS INFLUENCING RHYTHMIC

CRYSTALLIZATION FROM AQUEOUS SOLUTION

Majel Margaret MacMasters

Presented in partial fulfillment of the
requirements for the degree of Doctor of
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Amherst, April, 1934.
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I. INTRODUCTION.

In 1896 Liesegang began publication of his extended researches on rhythmic precipitation in the presence of a gel. Today scarcely any scientist ignores the importance of further study of the Liesegang phenomenon. The studies already carried out have pointed to probable explanations of many varied phenomena. Such studies, furthermore, have indicated means of practical application in numerous fields.

More recent work has shown that the presence of a colloid is not essential for rhythmic precipitation or crystallization. There is still strong feeling, however, that specific impurities must be present, or that optimum conditions of concentration and temperature must be maintained, for rhythmic crystallization to ensue. The data leading to these beliefs are fragmentary and not entirely convincing. The present investigation was undertaken in an attempt to answer some of the questions which investigators in the field of rhythmic crystallization are now asking.
II: REVIEW OF LITERATURE AND THEORETICAL DISCUSSIONS

A. The Liesegang Phenomenon.

1. Definition.

The Liesegang phenomenon may be defined, broadly, as banded structures resulting from precipitation in a colloidal medium. The bands of silver chromate produced by metathesis of silver nitrate and potassium chromate in a gel are characteristic of the phenomenon, and are often used as a type example.

Because of the regularity with which the bands are spaced, such precipitation is often called periodic crystallization, rhythmic crystallization, or rhythmic banding. These terms do not necessarily imply any time periodicity, as does the term periodic reaction, which is reserved for phenomena in which the velocity of a chemical reaction varies periodically with time.

2. History.

The first detailed study of rhythmic precipitation was reported by R.E. Liesegang (1,2) in 1896. Rhythmic precipitation had, however, already been reported by other investigators. Bradford (3) claims priority for Lupton (4) whose work was published in 1892; while Hepburn (5) quotes from The Influence of Colloids upon Crystalline Form and Cohesion, published
by Ord in London, 1879, (6), to show that this author had, in 1869, obtained and recognized stratified precipitates of calcium oxalate.

As early as 1855, however, Runge (7) discussed the reaction of aqueous solutions of metallic salts in sheets of porous paper, emphasizing the life-like form of the structures produced. This cannot be classed under the Liesegang heading, strictly speaking, as no colloid was present, but it is now evident that the porous paper was, in effect, a colloid substitute.

Because of the detailed investigations carried on by Liesegang, who has published more than forty papers on the subject, periodic banding in the presence of a colloid is known as the Liesegang phenomenon, though the actual priority of other claimants in the field is not denied.

3. Production of the Liesegang Phenomenon.

Liesegang (1,2) first noted periodic precipitates while staining histological specimens by Golgi's method. Golgi's silver method is used for demonstrating the shape and relationship of neurons. The method consists essentially of immersing fresh pieces of nervous tissue first in a solution containing potassium dichromate (and usually osmic salt), and then in silver nitrate. A black deposit
of a reduced silver salt is formed in and around the processes and cell-bodies of many of the neurons.

(178, p. 344.)

In general, the method of preparation consists in using a solution of one of the reacting substances made up with enough gelatin to form a gel. After gel formation, either a drop of strong solution or a crystal of the other reacting substance is placed at a point on the gel, and from this point permeates the gel in all possible directions. Often the experiment is carried out in a test tube. In such a case bands or discs of precipitate are formed at successive depths in the tube. When a flat plate is used, successive circles of precipitate form about the drop or crystal of the second reactant (9, pp. 12-3).

Gels other than gelatin may be used (10, 11, 12, 13, 14, 15, 16, 17, 18). Among those which have been used might be mentioned silica gel (11, 14, 15, 18), agar gel (12, 14, 16, 17, 18), starch and various hydroxides (14). Lloyd and Moravek (19) report banding of certain precipitates in all of three gels, viz., starch, agar and gelatin gels. Riegel (20) reports banding from contact of two silica gels containing the reacting substances.

Cases are known in which only one substance and the colloid are present. Davies (21) reports
rhythmic bands of dyes on filter paper, cotton cloth and unglazed porcelain, obtained by regulated evaporation. Copisarow (22) obtains rhythmic precipitates by the diffusion of picric acid, tannic acid, lactic acid, phenol, phosphoric acid, or alpha-tri-nitrotoluene into gelatin gel.

Dhar and Mittra (23) obtain periodic precipitates in the slow coagulation of ferric hydroxide, chromic hydroxide and stannic hydroxide by univalent electrolytes such as potassium chloride and sodium bromate.

In general, when a reaction resulting in precipitation or coagulation takes place within a gel (or within a colloid substitute), Liesegang structures may result.


a. Influence of Concentration.

Köhler (24) states that the bands are blurred when the reactants are too concentrated, and that, on the other hand, when the reactants are too weak, the bands are not perfectly developed.

It is alleged by Stansfield (25) that when a concentrated diffusing agent is used with a dilute reactant in the gel, ring formation is favored.

Bradford (26) gives experimental data to show that halving the concentration of the diffusing
hypertonic reagent makes but slight difference in the distances between mid-points of bands within the gel, while a similar change in the concentration of the gel solute produces a much greater increase in these distances.

It is stated by Hedges (9, p.16):

"In general, in a given system the ring formation depends on the concentration of both reagents and of the gel, and as a rule the distance between the bands decreases with increasing concentration of reagents and gel."

Anomalous cases noted by Mukherjee and Chatterji (13) and by Hedges and Henley (27) show that an increase in the concentration of the diffusing electrolyte may lead to an increase in the distance between bands of precipitate.

b. Influence of Light on the Liesegang Phenomenon.

It is stated by Davies (28):

"Light is one of the most important variables in making rhythmic bands of gold in silicic acid. At the concentrations used no bands were formed in the dark at either 0° or room temperatures. Periodic variations of strong light and darkness produce bands in those regions in which there is still adsorbed molecular gold, excess of acid and suitable amounts of the by-products of the reaction. ——— Rhythmic bands of silver chromate form in gelatin in the dark at 0° and at room temperatures."

Dhar and Chatterji (29), working on the formation of rings of metallic halides in silicic acid gel, find that 'rings of silver chloride and silver iodide are affected by diffused daylight, whilst
those of lead chloride and lead iodide are unaffected by light. They further find that "tubes containing mercuric iodide rings when exposed to diffused daylight show more rings in light than in dark."

Hedges (9, p.17) refers to Odén and Köhler (30), stating that these authors have observed that light of short wave-length is most effective. He also cites Blair (31), who, he says, has made a similar report.

Diurnal bands of colloidal platinum have been obtained by Davies and Sivertz (32). They allow oxalic acid to diffuse into a gel containing 10cc. 3N acetic acid, 10cc. water-glass (d. 1.16) and 0.8cc. one percent platinic acid, in tubes exposed to ordinary daylight. When continuous illumination is used, however, reduction occurs without the formation of bands.

Hedges (9, p.18) says:

"According to Cluzet and Kofman (33), the formation of Liesegang rings from silver nitrate, potassium dichromate, and gelatin is unaffected by visible light, X-rays, or radium rays, but is retarded by ultraviolet light."

Miss Roy (14) investigated a number of cases of rhythmic banding to determine the influence of light. The substances used include thallous iodide in starch, agar, zinc arsenate and manganese arsenate gels; cuprous iodide in agar gel; silver iodide in starch and in silicic acid gel; silver chromate in
ceric hydroxide gel; barium and thallous chromates in silicic acid gel. She concludes that the periodicity is, in general, more marked when diffusion takes place in the light than in the dark. It is argued that the light influences the phenomenon by accelerating the process of coagulation.

Heck and Mellon (18), working with organic precipitants, find no changes in structure due to the effect of light.

Hedges (9, pp.17-9) cites other authors and concludes:

'It is clear from this brief survey that some of the reported effects of light are contradictory, but that there is, nevertheless, a strong support for the following two general conclusions: (1) Light modifies periodic precipitation, at least when the precipitated substance is light-sensitive (e.g., silver salts), probably by aiding processes of crystallisation or coagulation; (2) Periodic illumination may cause an otherwise continuous structure to become periodic.'

c. Influence of Temperature on the Liesegang Phenomenon.

Liesegang (34), as early as 1914, in discussing the influence of a change in the external conditions upon the origin of laminated dispersed systems, notes the effect of external rhythms upon the production of periodic structures. He later (35) suggests that some of the effects previously attributed to light, by others, may, in reality, be due to temperature differences caused by the illumination.
The experiments of Miss Popp (36) show that with decreasing temperature the rings, as well as the spaces between them, become wider. Miss Popp also diagrams a tube, one side of which was kept at 0° while the other side was maintained at a temperature of 20°. The banding shows tilting, due to differences of spacing of bands and intermediate areas on the two sides. The inclination of rings towards the illuminated side of the vessel, observed by Copisarow (37), and attributed by him to the effect of light upon the rate of diffusion, is suggested by Hedges (9, pp.19-20) to be another instance of tilting of rings by temperature differences. Hedges points out the desirability of carrying out experiments under thermostatic conditions whenever possible.

d. Influence of the Reaction Medium on the Liesegang Phenomenon.

As early as 1912, Marriage (38) reports that the nature of the gelatinous medium is an important factor in the formation of banded structures. Since that time many writers, among whom Moeller (39,40), Zacharias (41), Dhar and Chatterji (42) and Dogadkin (43) are outstanding, have emphasized the idea that the gel plays an important role in the production of Liesegang rings.
Bradford (26) states:

"Only precipitates with great specific surface form bands. The specific surface of the precipitate is influenced by the reaction medium, by the presence of ions and particularly of trivalent ions.

"The occurrence, or non-occurrence, of bands of the same substance in different gels is due to the influence of the reaction medium on the dispersity of the precipitate.

"These principles have been tested by application to the well-known cases of silver chromate and dichromate which form bands in gelatin gels and not in agar. The non-occurrence of bands in the latter medium is due to insufficient specific surface of the precipitate. By increasing the dispersity, beautiful bands of both substances have been obtained in agar gels."

It has been demonstrated by Burton and Bell (44) that the rings formed in a gelatin-potassium dichromate gel, allowed to set upon a rubber sheet and then stretched, are not circular, as in the usual case, but are in the form of concentric ellipses, with the major axes in the direction of the stretching force.

The age of the gel may also play an important part in the phenomenon. As early as 1907, the influence of age of the gel was recognized by Liesegang (45). Miss Foster, in 1918, (46, 47) reports that the spacing of (groups of) bands obtained by her depends upon the age of the gel into which diffusion takes place.

Koenig (48) finds that a gelatin-potassium chromate gel, with copper sulfate solution as the diffusing
substance, gives more and more irregular bands, the longer the gel has stood before the copper sulfate solution is poured on.

Schleussner (49) recommends that gelatin gels be kept twenty-four hours before the diffusing substance is added for formation of periodic bands.

Not only are the identity, age and condition of the medium important; the presence of impurities, either naturally occurring in the gel, or added, may cause great differences in the resulting banded structures, and may even be a deciding factor for the presence or absence of such bands. Liesegang (45, 50) reports that small quantities of acid and of gelatose must be present in the gelatin if well-developed rings of silver dichromate are to be formed.

Copisarow (22) notes that high grade gelatins, containing only very small quantities of the products of hydrolysis, tend to form honeycomb structures rather than stratified precipitates.

Hatschek (51, 52) finds "small variations in the brand of gelatin, its acid and gelatose content, in the concentration of the reacting solutions and in the procedure adopted to be sufficient to affect the sensitive processes which result in Liesegang structures."
Koenig (48), using a fresh silicic acid gel 1/80 molar with respect to potassium chromate, and using 1/2 molar copper sulfate as the infusing substance, finds:

"The bands of the precipitate may be modified by the presence in the gel of such substances as alcohols, urea and sugar, which modify the rates of diffusion of the reacting substances and the solubility of the precipitated substances.

"The rhythmic bands may be broken up more or less by the presence in the gel of various inert powders unevenly distributed and by the presence of small particles of soap, all of which tend to interfere with the uniform diffusion of the reacting substances."

Friend and Vallance (53) state:

"When the silver nitrate solution is added to a slab of gelatin impregnated with dichromate, colloidal silver chromate can be seen ahead of the rapidly forming rings."

This pale-yellow fringe, which later surrounds the rings, is not thought by Riegel and Reinhard (54) to be colloidal silver chromate. They consider it to be silver chloride, formed by the sodium chloride which occurs as an impurity in commercial gelatin, and they further state that if the gelatin is thoroughly washed, no such hazy fringe is observed.

Schleussner (49, 55) shows that rings of silver salt, easily recognized with the aid of a lens, are formed between the bands of silver dichromate in gelatin in which chloride and phosphate impurities are present.

Avdalian (56) reports that the presence of sodium chloride reduces the distance between rings of silver
It is reported by Stempell (57) that a substance emanates from minced onions which produces a distortion of Liesegang rings. A similar distortion is reported by Siebert (58), produced by substances which are themselves volatile products, such as garlic, asafoetida and formaldehyde.

Ghosh and Prakash (59) report rhythm in drying gels of ferric phosphate and ferric arsenate. Davies (60) shows pictures of silicic acid gels which show rhythmic splitting.

Lloyd and Moravek (19) take the position that the effect of the gel must in each case be explained, but that the role of the gel is a purely secondary matter.

It appears that the consensus of opinion is that the gel plays an important part in the production of Liesegang rings; it also appears that impurities, present in the gel, or added, may greatly influence the occurrence and structure of periodic precipitates.

When so many different factors have been found to influence the formation of Liesegang rings, it is of interest to note the conclusions of Copisarow (61), who, after a study of Liesegang rings and other periodic structures, concludes:

"Periodicity is dominated by transition, movement or change of phase, rather than by any specific condition or number of components."
B. Periodic Precipitation in the Absence of a Gel.

1. Introduction.

In the last section we showed that the gel was considered to be an important factor in the production of Liesegang rings. We might be led, by the authors cited there, to conclude that a gel must be present if a banded precipitate is to result. This, however, is not true. Under proper conditions, it is possible to obtain structures which would be called Liesegang rings if they were produced in a gel, but which have actually been produced in the absence of a gel. These are the structures we now propose to discuss.

2. Production.

a. By Metathesis of Compounds in Solution.

The structures described by Runge (7) were obtained in sheets of porous paper. The porous sheets were "soaked with aqueous solutions of metallic salts which reacted with each at the boundaries." (62, p.21.) Undoubtedly, however, the capillary spaces in the paper may have played somewhat the role of a gel.

As early as 1903, Morse and Pierce (63) point out that the presence of gelatin is not necessary for the formation of banded precipitates.

Dreaper (64) obtains rhythmic banding in a capillary tube:

"One solution is drawn up into the capillary tube to its total length, and the top end sealed. The open end is then inserted into a second and larger one containing the other solution. This outer tube
has a bulb blown at its closed end, which acts as an additional receiver for the necessary supply of the second solution.

Dreaper obtains banding of lead chloride, lead ferrocyanide, lead sulfate, silver ferrocyanide, barium sulfate and barium carbonate produced in the manner just described. He (64, 65) reports the formation of crystals of lead chloride in the capillary by immersion of the tube containing 3% lead acetate solution in a 5% solution of hydrochloric acid. The form of the lead chloride crystals is abnormal; they are elongated at one side and present to the present writer the general appearance of one-sided horse-shoe nails. Photographs of these crystals accompany both articles cited above.

McGuigan and Brough (66) obtain rings of silver dichromate by placing a moistened silver nitrate crystal on a thin film of potassium dichromate which has been allowed to dry on a glass plate. They express the belief that banding is the normal method of precipitation, but that bands are usually destroyed by existing conditions, such as currents in the solute, etc. They have observed production of rings by freezing water.

Brodersen (67) describes bands of silver chloride caused by diffusion of a 2% solution of sodium chloride into a 10% solution of silver nitrate, the latter in a capillary space. His technique is so ingenious as
to merit description. A strip of glass 2mm. wide and an ordinary cover-glass stuck together with vaseline in such a way that a capillary space is formed between the glass strip and the cover-glass. The depth of this space is measured by means of a micrometer screw and microscope. The 10% silver nitrate solution is introduced into the capillary space, and the whole apparatus placed in a rectangular space cut out near the center of a piece of nickel plate 2mm. thick. A groove in this plate allows the flow of 2% sodium chloride solution into the capillary space which now contains the silver nitrate. With this arrangement it is possible to follow the formation of the lines under the microscope.

Similar experiments have been reported by Notboom (68), who places a dilute solution of potassium iodide on a slide and covers it with a cover glass. A drop of concentrated lead nitrate solution is now placed at the edge of the cover glass, and, on flowing into the first solution, produces a banded precipitate of lead iodide. The space between the cover-glass and slide may well be of capillary dimensions.

Investigations carried on in this laboratory by Miss Abbott (69) show similar bandings of lead iodide precipitated in thin films or capillary spaces.

Morse (70) has investigated many cases of rhythmic precipitates in aqueous solution. His method is to drill a hole in the center of a microscope slide,
place a drop of one of the reacting solutions on the slide, and cover with a cover-glass. The whole is then inverted and a drop of a concentrated solution of the other reactant, or a small crystal of the solid salt in a drop of dilute solution, is placed over the hole and allowed to diffuse in. In some cases he has used plugs of macerated filter paper in the holes to make diffusion more nearly free from any possible disturbances. A modification of Morse's method was used by Miss Abbott.

Morse finds that the rings so obtained show spacing ratios directly comparable to those shown by ring systems in gelatin. Morse has been one of the leaders in the development of the theory of rhythmic precipitation, and we shall have occasion to refer to his work in more detail later.

Other examples of periodic structures in the absence of a colloidal medium are discussed by Hedges and Meyers (62, p.32) and Hedges (9, pp.21-2).

b. Production of Periodic Precipitates by Reactions between Gases.

Koenig (48) reports the presence of rhythmic bands of ammonium chloride formed in a long, narrow tube connecting two one-liter flasks, containing ammonia and hydrogen chloride respectively.

Similar structures are obtained by Karrer (71); he places two vials, containing ammonium hydroxide and
hydrochloric acid respectively, on a flat surface, and covers them with an inverted bottle, so that a closed space is present about and above the vials. Rings always appear in the upper portion of the vial containing hydrochloric acid; in some cases these structures, while appearing to be rings when viewed horizontally, are actually discs, like cellular partitions in the vial.

A modification of Karrer's experiment is described by McGuigan and Brough (66), who place the hydrochloric acid in the sealed end of a long narrow tube, plug the open end of the tube with cotton and place upon the cotton a few drops of ammonium hydroxide. The ammonium chloride bands show clearly in the upper part of the tube.

3. Influence of Various Conditions on Production of Periodic Precipitates in the Absence of a Gel.

a. Influence of Concentration.

It has been the general practice, in the production of banded precipitates, to place the more concentrated reagent on the outside, allowing it to diffuse into the more dilute solution (69, 70). Miss Abbott (69), however, says:

"----- the above experiments have shown that the concentration of the outer solution may be only 4 per cent of that of the inner one."

This refers to the precipitation of lead iodide by metathesis of lead nitrate and potassium iodide,
the former diffusing into the latter.

Quoting further from the same author:

"Concentration of the diffusing agent affects spacing very definitely when the thickness of the film and the concentration of the inner solution are kept the same throughout a series of experiments. Measurements have been made of spacing of bands in nine concentrations of the diffusing agent, and variations of from 42 to 1 band per millimeter have been observed with concentrations of lead iodide between 3 normal and 0.025 normal."

It is certain that there is a definite relationship between spacing of bands and concentrations of the reacting solutions. It is probable, however, that banding can be obtained by the use of reagents of widely varying concentrations.

b. Influence of Temperature on the Production of Periodic Precipitates.

So far as can be gathered from the literature rhythmic banding from aqueous solution has usually, if not always, been carried on at room temperature. No cases are described in which the reaction and subsequent precipitation have been allowed to proceed at either very high or very low temperatures. It is, therefore, impossible to say what influence temperature might have upon the formation of periodic precipitates produced by the metathesis of salts in solution.

Hedges (72), after repeating the work of Koenig (48), reports that the bands of ammonium chloride obtained
by reaction between gaseous ammonia and hydrogen chloride are true periodic structures, and are not dependent upon temperature differences for their formation.

No other case of rhythmic precipitation from reacting gases has been investigated with thermal control, so far as the present writer can discover. It is impossible to predict what influence temperatures much higher or much lower than normal room temperatures might have upon the phenomenon.

C. Periodic Banding of Single Substances.

1. Introduction.

Up to now we have considered the rhythmic precipitates formed by metathesis of two reactants in aqueous solution or in a colloid. There are known, however, several instances in which periodic banding of pure substances, crystallizing from solution or from the melt, takes place. In some cases the bands may be formed of colloidal particles, rather than of true crystals.

2. History.

The first record of the periodic banding of single substances is the work of Sir David Brewster, 1853 (73). He describes periodic crystallization both from the melt and from solution. The list of compounds studied includes organic as well as inorganic substances. The list includes (using Sir David’s
nomenclature) salicine, asparagine, disulfate of mercury, palmic acid, nitrate of uranium, palmine, chromic acid, berberine, sulfate of cadmium, cacao butter, white wax, tallow, oil of mace, borax in phosphoric acid, and other compounds.

Since that time numerous investigators have reported similar instances of periodic banding. Several of these will be cited in the following sections.

3. Production of Periodic Crystallization of Single Substances,
   a. From Solution.
   
Brewster's work (73) is the first record of periodic banding of single substances crystallizing from solution. He took no careful measurements and, apparently, did not follow this first publication with any further observations.

The best known example of the phenomenon under discussion is the crystallization of potassium dichromate from aqueous solution. This rhythmic banding was described first by Miers (74). The method is as follows: A drop of a concentrated solution of potassium dichromate is placed on a microscope slide, warmed gently over a flame, and quickly transferred to the microscope stage. Miers (74) notes that rapid dendritic growth takes place for a time; this is followed by a period of slower growth of plates and flattened rods. The explanation offered will be
discussed later. The rhythmic banding of potassium dichromate is easily reproduced and is a favorite example used by workers in the field.

Another method of production of rhythmic crystallization of potassium dichromate from aqueous solution is described by Miss Abbott (69). A slide is dipped into a boiling solution of the dichromate, allowed to drain and crystallize over the solution, in the steam; it is then wiped clean on one side and examined. Good results are also obtained by allowing a thin film of the hot solution to crystallize between two microscope slides, which are then pulled apart for examination. The rhythmic crystallization resulting from the use of these methods is much finer in detail, and generally more constant in spacing than that obtained by Miers (74) and subsequent workers who have used his method. Miss Abbott (69) also reports rhythmic crystallization of sodium dichromate and of ammonium dichromate, produced under the conditions described above.

In 1919, Vorländer and Ernst (75) report rhythmic banding of 5-nitrophenyl-2-glycine-l-carboxylic acid from aqueous solution. The crystallization takes place in open vessels.

Hofsäss (76) finds rhythmic banding of sodium carbonate under peculiarly limited conditions. He allows the evaporation, on a microscope slide, of a few drops of 0.1 N sodium hydroxide which has been
used to absorb the carbon dioxide produced in the combustion of graphite. Rhythmic banding results. But when the experiment is repeated after combustion of other forms of carbon (as coal or wood), only the usual dendritic forms of sodium carbonate result. There is very regular spacing of the rings obtained as described above; they are reported to be 0.002 mm. apart.

Kägi (77) discusses the rhythmic banding of menthyl-alpha-benzylacetoacetate. Results are best when a benzene solution of the racemic ester (m.p. 48-51°) is used, but this compound also shows rhythmic banding when crystallized from a mixture of alcohol and glacial acetic acid. The levo ester (m.p. 68°) does not show rhythmic banding.

Kutzelnigg (78) reports rhythmic banding of stearic acid from strong alcohol and from saturated ether solution.

Rhythmic banding of both chrome alum and barium nitrate, crystallizing from thin films of their respective solutions, is reported by Hedges and Meyers (79). These authors also picture concentric imperfect spherical shells of closely packed benzoic acid crystals, alternating with spherical shells of very loosely packed crystals. They state:

"This phenomenon can be reproduced by warming 5 g. of benzoic acid with 12-20 c.c. of an equal-volume mixture of sulphuric acid and ethyl alcohol and setting aside to cool." The present writer has not been able to duplicate these experiments.
Hrynakowski (80) has studied rhythmic crystals of potassium alum, obtained by placing a crystal of the alum at the boundary between a supersaturated and a saturated solution of the alum. The rhythm is shown by the structure of successive layers of the crystal, and the present writer questions whether it can, in a strict sense, be called rhythmic banding, unless we also include under this title the growths shown by many crystals of various types. It is not uncommon to find step-wise growth, for example, in which the steps are remarkably uniform.

Linzk and Korinth (81) report that sulfur crystallizing from carbon disulfide thickened with Canada balsam or with rubber, forms droplets entirely surrounded by free spaces. This may be classed as a rudimentary form of rhythmic banding.

A spiral structure of potassium dichromate, prepared as directed by Miers (74), is reported by Hedges (82). Attention will be given to other spiral forms in a subsequent section.

b. Production of Rhythmic Crystallization from the Melt.

The first note of rhythmic banding from the melt is that of Brewster (73), to which reference has been made already. This was published in 1853. The next outstanding investigation along this line is that of
Alexeyev (83), in 1906; he reports good rhythm from a melt of the tetraethyl ester of ethanetetracarboxylic acid, and very indistinct rhythm from melts of benzo-
phenone and of coumarin.

Many other organic compounds are known to show rhythm when solidified from the melt. Vorländer and Ernst (75) report rhythmic solidification of the ethyl ester of p-ethoxy-benzylidene-aminophenylpropionic acid. Schall and Kirst (84) note that, on solidification in a thin layer, the oxime of 1-menthone shows rhythmic crystallization. Garner and Randall (85) state:

"Myristic, lauric, undecolic, and decolic acids, when in the form of thin films, crystallize in a rhythmic manner, due to the formation of a solid skin which wrinkles, giving a waved surface." These authors give excellent photomicrographs.

Schubert (86) describes rhythmic banding from films of p-toluonitrile, salol and methyl salicylate. He also says that if sulfuric acid be heated in an oil bath to 180° and as much sulfanilic acid put in as will dissolve at this temperature, rhythmic banding appears in from six hours to two days after the flask with the mixture is put in ice water. This would appear to be a case of rhythmic banding of sulfanilic acid from sulfuric acid solution, although Schubert describes it, with the other cases noted, under the general title: Rhythmic Crystallization from Fused Masses.
Bernauer (87) has studied rhythmic crystallization phenomena in melts of benzophenone, benzoic acid, benzoin, hippuric acid, santonin, salicylic acid, sulfonal, malonamide, antipyrine, benzonaphthol, asparagine salts, diaminonaphthalene, and m-diethylaminophenol.

Hedges (82) says:

"I carried out some experiments on the crystallisation of thin films of molten organic substances and found that crystallisation in concentric rings readily takes place with benzil, benzoin, benzophenone, menthol, m-dinitrobenzene, and acetaldehyde.

Rhythmic crystallization from the melts of piperonal, terpin hydrate, vanillin, phenyl benzoate, phenanthrene, cinnamic acid, thymol and 3:5-dichloro-4-methylphenyl is reported by Dippy (88). He states that the last named compound gives the best rhythm of those mentioned.

Many inorganic substances are not as easily melted as are large numbers of organic compounds. Sulfur, however, is commonly known to exhibit rhythmic crystallization from its melt, and, no doubt, other inorganic substances may, also. The rhythmic banding of sulfur is described by Fischer-Treuenfeld (89), and by Köhler (90). Hughes (91) reports measurements on cases of periodic banding from sulfur melts; we shall refer to these in more detail later.

a. Concentration.

The periodic crystallization of potassium dichromate reported by Miers (74) takes place from a saturated solution.

Hedges and Myers (79) also recommend the use of a solution saturated at room temperature (referring in this case to rhythmic crystallization of chrome alum and of barium nitrate). They claim that five grams of benzoic acid in from twelve to twenty cc. of an equal-volume mixture of ethyl alcohol and sulfuric acid will give rhythmic crystallization; in this case saturation is doubtless achieved, even with the lower concentrations.

Miss Abbott (69) reports rhythmic crystallization from dilute solutions of potassium dichromate placed in a desiccator.

Melts, of course, are not subject to concentration changes.

b. Temperature.

Both Miers (74) and Hedges and Myers (79) warm the solution upon a slide (in a dish in the case of benzoic acid) and then allow it to crystallize while cooling.

Miss Abbott (69) dips the slide into a hot solution, in many cases, and allows it to crystallize in the
warm atmosphere above the solution. She also, however, places a drop of solution at room temperature upon a slide and allows it to crystallize in a vacuum desiccator, still at room temperature. By both methods, rhythmic crystallization results.

In the case of melts, it is obvious that the material must crystallize while passing from a comparatively high temperature to a lower one.

c. **Influence of the Thickness of Film on Rhythmic Crystallization.**

There has been no report of specific study as to the effect of the thickness of film upon the occurrence of rhythmic crystallization from solution.

When a drop or two of a solution is placed upon a clean microscope slide, the solution will spread to form a comparatively thin film. Only on dirty slides will drops maintain a globular shape. It is, therefore, safe to assume that whenever crystallization is reported to have taken place from a solution placed upon a slide, it took place from a thin film.

On the other hand, Hedges and Myers (79) carry out the crystallization of benzoic acid, referred to above, in what appears, from the photographs, to be a round-bottomed flask; in this case they obtain three-dimensional rings, i.e., concentric spheres.

Miss Abbott (69) finds a correlation between the periodicity and thickness of film, the coarser
periodicity being exhibited in the thicker films.

Rhythmic crystallization from the melt is usually reported from moderately thin films.

Alexeyev (83) reports rhythmic crystallization from a melt of the tetraethyl ester of ethanetetra-carboxylic acid spread out on any surface and allowed to cool.

The rhythmic crystallization of sulfur reported by Fischer-Treuenfeld (89) takes place in very thin layers of molten sulfur.

Schall and Kirst (84) note the rhythmic crystallization of the oxime of 1-menthone, on solidification in a thin layer.

The rhythmic crystallization of undecoic and other organic acids, reported by Garner and Randall (85) takes place when the acids are in the form of thin films.

Dippy (88) has investigated the effect of the thickness of film upon rhythmic crystallization from the melt. He finds that moderately thin films exhibit good rhythm, but that the crystallization from abnormally thin films is continuous. He further adds:

"It has also been observed that where rhythmic crystallisation occurs, the thinner the film, the more rapid are the pulsations of crystal growth, that is, the narrower and more frequent are the bands; whilst on the same slide thicker portions of film crystallise with slower pulsations and consequent production of wider bands."
Repeated attempts were made at bringing about rhythmic crystallisation in melts contained in glass tubes of 5 mm. diameter ——- met with no success. In all cases crystallisation was continuous. Variations of degree and rate of supercooling appeared not to influence the mode of crystallisation. This result agrees with the behaviour of some unusually thick films of melt which crystallise spontaneously in continuous form.

"It seems, therefore, that film thickness is a factor influencing rhythmic crystallisation. Measurements already made point to there being definite limits of thickness of film within which rhythmic crystallisation can occur."

D. Details of Rhythmic Structures.

An investigation of the morphological character of Liesegang rings is reported by Küster (92). He uses various reagents in gelatin or agar gels. He illustrates radial and tangential rhythm; a slipped polycentric ring system laced with a zigzag line; ring groups; cog-wheel shaped structures; a combination of tangential and deepened rhythm; rings inserted equidistant between others (much as though each ring had split in half, at one side, and one of the sections had been slipped downwards half the interval of original spacing); and a zigzag chain and gap structure; all these were produced by precipitation of lead iodide in agar gels. He also pictures rhythmic banding of copper sulfate crystals in 10% gelatin; spherical crystals of trisodium phosphate in 4% agar; and rhythmic crystallization of potassium dichromate in agar and in gelatin gel.
Photographs of minor modifications of precipitation from potassium dichromate-gelatin gel, treated with silver nitrate, are given by Janek (93).

Schikorr (94) notes spiral formation by cracks during the drying of precipitates, and Liesegang (95) regards this as a true case of rhythmic structure.

Ghosh and Prakash (59) report formation of spirals in drying gels of ferric phosphate and ferric arsenate. An excellent photomicrograph accompanies their article.

Copisarow (22) reports a tendency towards spiral formation on the diffusion of tannic acid into gelatin gel. Other modifications of Liesegang rings are discussed by Hedges (9, pp. 29-32).

Heck and Mellon (18) report spirals and twins in banded structures resulting from precipitation with organic precipitants.

Banded precipitates, obtained in the absence of a gel, as by Morse (70) and Miss Abbott (69), do not, so far as the present author can discover from the available literature, exhibit any remarkable variations. The banding is usually distinct, and but few crystals appear between bands. Bands produced by shock may show irregularities (70), but these are not true rhythmic structures.

Structures obtained by periodic precipitation from solution may be definitely banded, as in cases observed by Miss Abbott (69); or they may be composed
areas of thickly deposited crystals followed by areas of lesser deposition, as observed by Miers (74) and many subsequent workers.

Hedges (9, p.78 and Fig.12) notes spiral crystallization of potassium dichromate from aqueous solution. Menzies and Sloat (96) report spiral markings on carborundum crystals, which Hughes (91) suggests may be a special case of periodic crystallization. This suggestion is supported by Hedges (82). Other instances of spiral crystallization are cited by Hedges (9, p.78). Lloyd and Moravek (19) find spiral structures in nearly one tube in a dozen, due often to a bubble attached to the surface of the medium inducing irregularity of precipitation.

The periodic crystallization of sulfur from the melt occurs in ridges, as described by Fischer-Treuenfeld (89).

Garner and Randall (85) describe the rhythmic crystallization of organic acids, in which the rhythm is due to the formation of a solid skin which wrinkles, giving a waved surface.

Berz (97) notes the concentric shell form of hailstones. Hedges (9, p.73) says:

"Periodic crystallisation of water is often apparent on a frosted window-pane."

Such periodic crystallization of water has also been observed by the present writer.
It is apparent that rhythm may occur in various forms with numerous modifications. Rhythm may occur due to alternating areas of dense and less dense crystallization, due to a heaping of a crystalline mass at regular intervals, or due to wrinkling of a more or less uniformly thick crystal felt. The periodicity may take the form of concentric circles, concentric spheres, or spirals, or any combination or modification of these forms.

E. Discussion of Theory.

1. The Supersaturation Theory of Liesegang Ring Formation.

At least as early as 1899, Ostwald (98) advanced the supersaturation theory of the formation of Liesegang rings. This theory assumes that a highly supersaturated solution is the first product of the metathetical reaction responsible for ring formation. Crystal nuclei then form at the boundary of the reacting substances, and toward these the supersaturated solution diffuses from all sides, leaving the surrounding areas depleted with respect to both reagents. The advancing (diffusing) reagent must then travel some distance before it enters an area in which the ions of the second reagent (contained in the gel) are plentiful enough for supersaturation again to be attained. This would account for the spaces between the bands of precipitate.
Morse and Pierce (63) report a theoretical and quantitative experimental study of the precipitation of silver chromate in a gelatin gel. They find $H$, the constant metastable concentration product, to be defined by the equation $[\text{Ag}^+] \cdot [\text{CrO}_4^{2-}] = H$; this determines the limit of supersaturation for silver chromate when the solid phase is absent. They report the value for $H$ as $1.4 \times 10^{-6}$, and point out that this means that the concentration of silver chromate in the gelatin when precipitation begins is 145 times that required for saturation in the presence of the solid phase. These authors further report that when the end of a capillary tube containing potassium chromate-gelatin gel is dipped into a solution of silver nitrate, the distance between laminae in a given tube, at a given temperature and for given concentrations of the reactants, is governed by the relationship $X/\sqrt{t} = \text{const.}$, where $X$ is the distance from the end of the tube of a lamina formed at $t$ seconds from the time of dipping into the silver nitrate solution.

In a recent article, Bauer (99) presents, mathematically, conclusions very similar to those derived experimentally by Morse and Pierce (63). Bauer also supports the view, already substantiated experimentally by Young and van Sicklen (100), that
the metastable limit must lie extremely close to the saturation curve. Bauer's article presents a development of mathematical equations to fit the conditions of theory derived from the experimental work of other investigators; no experimental data are included, or used in the theoretical development of the equations.

The supersaturation theory has, at the present time, many supporters, although it has also had its share of criticism. In 1907, Liesegang (101) advanced evidence in refutation of the theory. When a set of silver dichromate rings has been formed by diffusion of a silver nitrate solution into a gelatin gel containing potassium dichromate, according to the supersaturation theory, the rings are composed of crystals of the silver dichromate. If a drop of potassium dichromate solution is now allowed to diffuse into the system, it reacts with the silver nitrate still present. One should expect the silver dichromate crystals already present to act as nuclei for the deposition of the newly formed salt, but Liesegang frequently finds sharply defined lines crossing the lines already formed by the first reaction. For some time this work was thought to have dealt a death-blow to the supersaturation theory, but within a short time Liesegang (102) reported that
the rings were at different levels in the gel; at this time, however, he still believed that the ring formation was not due to supersaturation phenomena. Soon Hatschek (103) presented stronger evidence against the theory. If rings (discs) are made in a test tube in the usual way, and potassium dichromate be added, as in Liesegang's previous experiment on the flat plate systems, a second series of precipitates is again obtained; in this case, there can be no doubt that the pre-existent precipitate could act as nuclei and should act as nuclei, if the ordinary view of supersaturation holds under these circumstances. Since Hatschek (104) had already shown that it was possible to obtain ring systems of lead iodide by diffusion of lead nitrate into a potassium iodide-agar gel already seeded with small crystals of lead iodide, the supersaturation theory had apparently been entirely discredited.

But these objections, while held to be insurmountable by most authors for many years, were finally shown to be inconclusive by the work of Dhar and Chatterji (29). They say:

"It is practically certain that in presence of gelatine or agar or any other protecting colloid substances like silver chromate, lead chromate, lead iodide, etc., which form Liesegang rings are in the peptised condition. In other words silver chromate or lead iodide, etc., remain in a colloid state. From our experience on colloidal matter we know that if some finely divided solid substance is present in a colloidal medium, sometimes the colloidal matter coagulates; but this process is extremely slow in
comparison with the phenomenon of the release of supersaturation from a supersaturated solution. We have not been able to coagulate silver chromate sol protected by a large amount of gelatine by keeping it in contact with solid silver chromate even for several days. On the other hand it has been observed that a sol of antimony sulphide containing a little tartrate gradually coagulates on the moulds formed after a few days due to the presence of the tartrate. From the above considerations it becomes difficult to accept the explanation of Ostwald, but there is some truth in the explanation because it is certain that a nucleus always favours precipitation."

Ghosh (105), however, finds periodic precipitation in the presence of particles of the precipitated substance, and, as late as 1930, raises objections to Ostwald's theory on this basis.

In an early publication, Ostwald (106) distinguishes between the "metastable" state of solution, in which the change to solid form can be brought about only by the presence of the solid itself, and the labile state, in which other causes may affect solidification.

Hedges (9) quotes Bradford (107):

"No one seems to have pointed out that only solutions near the metastable limit are completely upset by the presence of a crystal, and that possibly the concentration of the difficultly soluble salt, at a distance from a given crystal in the gel, might grow at a rate greater than that at which the salt could diffuse towards, and be deposited upon, the crystal."

Hedges (9, p. 41) remarks:

"It is often objected that this theory does not provide for the marked influence of the reaction medium. The criticism is scarcely warranted, since the degree of supersaturation, which is the predominant factor, will vary with the structure of the gel and with the presence of impurities."

Miss Abbott (69, p. 16) points out a probable influence of the gel:
The fact that planted crystals do not act as nuclei in precipitation in capillary spaces may be explained in the opinion of the writer, by a consideration of the relative inactivity of these planted crystals in the medium. In a gel or in a film between hard surfaces the energy changes in the immediate vicinity of the crystal are very slight compared to those in the other parts of the reaction mixture, where heat of crystallization, convection currents, heat of reaction, dilution, and unobstructed diffusion are factors. Visible crystals may block many of the channels through which diffusion toward them would take place, and it is even possible that the gel forms a protective membrane around the crystal thus preventing it from acting as a center of crystallization.

2. The Adsorption Theory of Liesegang Ring Formation.

The originator and chief supporter of the adsorption theory is Bradford (108, 109, 110, 3, 26, 111, 112, 107, 113). The theory, in brief, is that the precipitate is finely divided and adsorbs the solute in the gel from the region between the bands. Bradford (26) claims:

"--- the formation of banded precipitates is due to adsorption of solute from the region between the bands. Only precipitates with great specific surface form bands. The specific surface of the precipitate is influenced by the reaction medium, by the presence of ions and particularly of trivalent ions. By varying its specific surface, a given substance can be obtained in the banded form, or not, as desired. The occurrence, or non-occurrence, of bands of the same substance in different gels is due to the influence of the reaction medium on the dispersity of the precipitate. These principles have been tested by application to the well-known cases of silver chromate and dichromate which form bands in gelatin gels and not in agar. The non-occurrence of bands in the latter
medium is due to insufficient specific surface of the precipitate. By decreasing the dispersity, beautiful bands of both substances have been obtained in agar gels."

Dhar and Chatterji (29) remark:

"----- We have also observed that freshly precipitated $\text{Ag}_2\text{CrO}_4$ hardly adsorbs any potassium chromate even from a dilute solution. In view of these facts it is very difficult to accept the beautiful explanation suggested by Bradford of periodic precipitation. To prove the validity of this theory we must show that substances like $\text{PbCrO}_4$, $\text{PbI}_2$, $\text{Ag}_2\text{CrO}_4$ etc., can adsorb considerably electrolytes like potassium chromate, potassium iodide, etc., which is not corroborated by direct experiments on adsorption."

Daus and Tower (12), however, working with cadmium and zinc sulfides in agar or gelatin gels, find Bradford's theory entirely satisfactory.

As pointed out by Hedges (9, p. 42), the theory has to be modified so that the "process of crystallisation is also considered as adsorption of the solute by the growing crystals. In the opinion of the present writer, the necessity for such drastic modification of the accepted meaning of adsorption makes it obvious that the theory involving the accepted meaning of the term adsorption has been found untenable; apparently the theorist has modified his terms to meet necessary modifications of his theory. As Hedges (9, pp. 42-4) makes clear, Bradford lays stress on adsorption rather than on diffusion as the factor bringing about the movement of the inner electrolyte, when diffusion quite as easily explains the actual phenomenon.
3. The Coagulation Theory of Liesegang Ring Formation.

A theory of Liesegang ring formation has been developed by N.G. Chatterji and Dhar (114) and Dhar and A.C. Chatterji (29, 42, 115, 116). This theory assumes the precipitate to exist first in a colloidal state, and not as the solute of a supersaturated solution. Coagulation of the precipitate is caused either by excess of the diffusing agent or by the soluble product of the reaction.

Hedges and Henley (27) report on a study of periodic structures of silver dichromate and of magnesium hydroxide in gelatin gel, and of lead iodide in agar gel. They mix equivalent quantities of the reactants in the gel, then superimpose a strong solution of the diffusing electrolyte. In this way, they find it possible to separate the chemical reaction from the formation of the precipitate. They find that the rings produced in these experiments are comparable with those produced by chemical reaction, and conclude that the formation of periodic structures is a coagulation phenomenon taking place after the chemical reaction. Tower and Chapman (117) do not agree with the conclusions of Hedges and Henley.

Wolfgang Ostwald (119) points out the fact that there are many instances of periodic precipitation in the absence of a gel, and holds that the gel, therefore,
can play only a secondary role in the formation of periodic precipitates.

Apparently the coagulation theory has never come into wide favor, and, since it is probably not generally applicable, it is doubtful whether it ever will be received with approval.

4. The Diffusion-wave Theory of Liesegang Ring Formation.

In 1905, Bechhold (120) notes that silver chromate is slightly soluble in ammonium chromate and is precipitated by metathesis of silver nitrate and ammonium chromate or dichromate. He points out that the ammonium nitrate formed in the first precipitation zone, when silver nitrate diffuses into a gel containing ammonium chromate, will tend to prevent the precipitation of more silver chromate in this neighborhood. When a region is reached in which the concentration of the ammonium nitrate is sufficiently low, a fresh precipitation of silver chromate will take place. He adds, however, that other factors may be concerned in the production of rhythmic precipitation; among possible factors he lists the power of ions to promote or hinder the precipitation of suspensions or of colloidal solutions, the effect of diffusing salts upon the setting point of the gelatin, and the ability of colloids
to precipitate each other only when mixed in certain proportions.

Some twenty years later, Wo. Ostwald (121) is found advancing a diffusion-wave theory of Liesegang ring formation; this theory refers only to rhythmic precipitations resulting from chemical reactions in which the components diffuse towards one another.
The two basic assumptions are:

a. In all reaction systems in which typical periodic precipitation occurs there are at least three diffusion waves, those of the outer electrolyte, the inner electrolyte, and the soluble reaction product.

b. Many, and perhaps all, typical rhythmic precipitation reactions are balanced in the sense of the law of mass action, i.e., they are incomplete in contrast with such reactions as the precipitation of barium sulfate.

The diffusion of ammonium hydroxide into a gel containing magnesium chloride is discussed in detail; comparable to this reaction is that between silver nitrate and potassium dichromate, the reaction between lead nitrate and potassium iodide, and many others.

The reaction \( \text{MgCl}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{Mg(OH)}_2 + 2\text{NH}_4\text{Cl} \) will lead to precipitation of magnesium hydroxide when

\[
[\text{Mg(OH)}_2] = K \frac{[\text{MgCl}_2] [\text{NH}_4\text{OH}^2]}{[\text{NH}_4\text{Cl}]^2}
\]

for which the general form may be written:
\[ [\text{Precipitate}] = K [\text{Inner electrolyte}]^x [\text{Outer electrolyte}]^y [\text{Reaction electrolyte}]^z \]

(The brackets in these equations have the usual, conventional, meaning, i.e., they indicate molar concentrations.)

The comment of the present writer is that it is not usual to consider molecular concentrations as the deciding factors for precipitation; ionic concentrations are conventionally considered, and in view of the evidence for complete ionization of many (if not all) inorganic compounds, it is dangerous to set up, for serious consideration, equations such as those just given.

Quoting from Hedges (9, pp. 53-4):

"--------- The magnesium chloride and ammonia diffuse towards each other and react to give insoluble magnesium hydroxide and soluble ammonium chloride. The ammonium chloride is produced at high concentration (whilst that of ammonia is low at the seat of reaction) and has a high velocity of diffusion; it therefore diffuses ahead of the ammonia. Immediately following the precipitate, therefore, there is a region of the gel containing a high concentration of ammonium chloride and a relatively low concentration of magnesium chloride (which has partly diffused towards the ammonia). When the ammonia reaches this region by diffusion the condition is such that, in accordance with the formula given above, magnesium hydroxide is not precipitated. But a little way further on the ammonium chloride has become dilute through diffusion and the magnesium chloride is still relatively concentrated, so the conditions are again such that magnesium hydroxide is precipitated. The reaction at this place produces more ammonium chloride, which diffuses ahead and again prevents reaction taking place in the next zone, and so on. It will be noted that this theory also involves a critical condition for precipitation."
Ostwald was led to this theory as a theoretical explanation of the structures obtained by Miss Popp (36).

Ungerer (122) obtains bands of a blue complex cuprammonium compound and whitish green cupric oxide by diffusion of aqueous ammonia into cupric chloride in agar or gelatin gel. He explains the formation of these structures on the basis of Ostwald's diffusion-wave theory, with the difference that the reaction electrolyte accelerates precipitation or is without influence on the process.

As Hedges (9, pp. 54-5) points out, periodic precipitations are not given only by reactions which are incomplete; but, in general, "one-sided reactions do not lend themselves to periodic precipitation to the same extent."

Lead chromate is considered insoluble ($K_{sp} = 1.77 \times 10^{-14}$ at 18° C. (123, p. 773)), yet Erbring (124) finds the reaction between lead acetate and potassium dichromate to be reversible in the sense of the law of mass action.

In the reaction between dry gaseous ammonia and hydrogen chloride no "soluble" reaction product results to give the third diffusion wave, yet Hedges (72) shows that periodic structures are produced when the dry gases are used.

Hedges (9, pp. 56-7) points out that many examples
of periodic structures are known which are formed when a metallic salt is reduced to the metal, a reaction quite irreversible under the experimental conditions. He adds:

"The diffusion-wave theory has played an important part in directing attention to the rôle of the soluble reaction product, which is apt to be overlooked. In the light of the experiments described, however, this factor cannot be regarded as the fundamental cause of the formation of periodic structures, but rather as one of the most important modifying influences."

A modification of the diffusion-wave theory has been advanced by Lloyd and Moravek (19). On the basis of a large number of varied experiments they suggest the following mechanism: The first precipitate acts as a membrane in which two kinds of ions are precipitated. Close to this membrane there must be a very high concentration of the reaction product, which now diffuses in both directions. A portion of the reaction product diffuses toward the internal reagent until the concentration becomes great enough for the formation of a complex salt. The internal reagent then diffuses toward the reaction product from both directions for the formation of this complex. When the complex is formed, it diffuses in both directions. Meanwhile the ion of the entering salt which forms a part of the insoluble precipitate diffuses through the initial membrane and must move some distance through an area depleted
of the ion with which it reacts before it meets the part of the complex which is diffusing backwards. When this meeting takes place, precipitation again occurs; and the process is repeated.

5. Other Diffusion Theories of Liesegang Ring Formation.

Several minor diffusion theories have been advanced. Many of these apply Fick's law of diffusion, which is expressed by the relationship

\[ dS = -Dq \frac{dc}{dx} dt \]

when \( dS \) is the quantity of substance which passes in time \( dt \) through a diffusion cylinder of cross section \( q \) under a concentration gradient \( \frac{dc}{dx} \); \( D \) is the diffusion coefficient and is constant for a given substance (125, p. 1022).

McGuigan (126) explains the formation of rings by diffusion of silver nitrate into a potassium dichromate-gelatin gel as follows:

"Ag\(_2\)CrO\(_4\) is formed and a clear zone results in the gelatin by the attraction of the chromate to the silver. Beyond this zone of influence, the chromate is fixed and remains so unless an attraction force is exerted. The AgNO\(_3\) now wanders on through the ring into the clear zone until it approximates the chromate gelatin sufficiently close to exert an attraction which again draws the chromate and forms another ring and clear zone. At the same time the chromate exerts a pull on the silver and the ring is formed where the forces are balanced. Again it may be presumed that to start the chromate moving will require a greater force than to keep it moving after the start is made; consequently the second ring
is separated from the first. With each succeeding ring the concentration of the silver is less and this also will operate to remove the succeeding rings farther apart."

Fricke (127) develops an explanation of Liesegang ring formation based on Fick's diffusion equation, the influence of the separation of part of the diffusing substances in the precipitate upon the diffusion gradients, and the concept of the metastable region. His results are complicated by the admitted necessity for considering such secondary factors as adsorption, electrolyte precipitation and the solubility influence of salts resulting as by-products.

Watanabe (128) shows that Fick's law of diffusion does not hold for certain cases of diffusion into gels. When ammonium hydroxide is allowed to diffuse into tubes containing copper sulfate or zinc sulfate in a gel, the ratio \( x/\sqrt{\tau} \) (where \( x \) = distance the precipitate penetrates in time \( \tau \)) is not constant, as it should be if Fick's law holds, but decreases with time. If ferrous sulfate is allowed to diffuse into a gel containing sodium sulfide, on the other hand, the value \( x/\sqrt{\tau} \) increases with time. But for all cases the relationship

\[
x/\sqrt{\tau} = \left[ (Z-z)/Z \right] \cdot k
\]

holds (\( k \) = initial velocity of diffusion, and \( Z = \))
time required for the maximum penetration of the precipitate into the gel). In this case, diffusion rates are assumed to be modified by reactions taking place within the gel; for this reason Fick's law does not hold without the indicated modification.

Steopoe (129) considers that three factors contribute to ring formation: 1) Diminution of the viscosity of the gel, caused by a slight increase in temperature due to the heat of reaction; 2) Diffusion of the water added with the second reactant; and 3) The greater velocity of diffusion of one reacting ion compared with the other (Ag⁺-ion compared with CrO₄²⁻-ion, in the type example).

Another theoretical modification seeking to show diffusion due to concentration differences as the main cause of Liesegang ring formation has been advanced by Traube and Takehara (130), who also believe that a secondary factor is the formation of a membrane of the precipitate, which causes partial cessation of diffusion.

The relation between time of formation and radii of rings has been investigated by Jablczynski and Kobryner (131). They find the relationship

\[ r_o^2 r - \frac{1}{3} r^3 = - \left( \frac{kDC_0}{\pi s} \right) T + Q \]

where \( r_o \) and \( r \) are the radii of rings at the periphery of a disk and at \( r \), respectively; \( C_0 \) is the concentration
of the diffusing reagent (silver nitrate diffusing into potassium dichromate-gelatin gel in the case studied) on the periphery;  \( S \) is the thickness of the disk;  \( T \) is the time; and  \( D \) is a constant, the diffusion coefficient of silver nitrate.  \( D \) may be expressed in terms of the radii of the concentric rings.

\[
D^{n-2} = \frac{(r_n - r_{n-1})}{(r_2 - r_1)}
\]

where \( r_1, r_2 \ldots r_n \) are the radii of the first, second \ldots \( n \)th rings.  Jablczynski (132) further considers the case of diffusion in one direction, as in a tube, and of diffusion in a plane, assuming that the velocity of the formation of the rings is directly proportional to the rate of diffusion.  For the case of diffusion in a tube (one dimensional diffusion) he obtains the expression

\[
\frac{h^2}{t_n - t_1} = K
\]

where \( h_1 \) and \( h_n \) are the distances from the base of the tube to the rings formed after one and \( n \) seconds, respectively, and \( t_1 \) and \( t_n \) are the times of formation of these rings.  It should be noted here that diffusion is taking place upward from the bottom of the tube which is dipping into the solution of the diffusing reagent (silver nitrate).  If diffusion is taking place inward from the periphery of a disk,
the relationship becomes
\[
\frac{(r_n - r_1)^3}{t_n - t_1} - 3R_0^2 (r_n - r_1) = K_n
\]
in which the radius \( r \) is substituted for the corresponding \( h \) of the previous equation, \( t \) has the same meaning, and \( R_0 \) is the inner radius. It is also shown that the ratio of the distances between the rings is a constant:
\[
\frac{h_3 - h_2}{h_2 - h_1} = A.
\]

This work is based on measurements of rings formed by the diffusion of silver nitrate into a gelatin gel containing potassium dichromate. In a later article, Jablczynski (131) reports that the velocity of silver nitrate diffusion and the velocity of ring formation both follow the equation given for one dimensional diffusion, above, when the silver nitrate is allowed to diffuse into a small trough filled with potassium chromate-gelatin gel. The value of \( K \) for the diffusion is found to be 0.00693; the value of \( K \) for ring formation is 0.00605.

Ganguly (133) calculates the distribution of concentrations of silver nitrate and potassium chromate in a gelatin gel, using Fick’s diffusion law, and, by correlation of these calculations with experimental observations, concludes that certain layers of the gel must contain silver chromate in a peptised
form, while other layers contain precipitated silver chromate.

The diffusion of lead nitrate solution into gelatin, agar and agar-gelatin gels containing potassium dichromate has been reported by Moravek (134). The increase in distance of precipitation from the point of contact of the diffusing solution with the gelatin gel, with time is found to follow a parabolic equation, but the length of the semi-latus rectum of the resulting parabola depends upon the normality of the lead nitrate, and follows no obvious relationship. When the rate of diffusion in gelatin and gelatin-agar gels is plotted against the concentration of the lead nitrate, two maxima are obtained, while in agar gel the rate of diffusion is directly proportional to the concentration of the lead nitrate. Moravek attributes this behavior to the formation of compounds between the gelatin and the potassium dichromate contained in the gel. It is observed that the form of the curve in such cases is affected by the concentration of potassium dichromate in the gel.

Linck (135) and Pannach (136) have studied diffusion of silver nitrate, lead chromate and lead dichromate in gels. Ghosh (105) reports on the diffusion of lead nitrate solution into potassium iodide. His theory of
precipitation is based on the diffusion rates of the reacting substances, as well as on the probable depletion of areas by precipitation. It is to be remembered, however, that Ghosh does not uphold Ostwald's theory of supersaturation, since precipitation is observed to be rhythmic, even in the presence of particles of the compound precipitated.

Bull and Veil (137) find that the velocity of diffusion of the penetrating solution varies as the square root of the time, and that a temporary retardation of diffusion is produced by the formation of each ring. They further report (138) that the principal rings are formed over a preceding system of very fine secondary rings, the spacing of which increases with their distance from the drop; the distribution of these rings shows a periodic fluctuation. The comment of the present writer is that it is difficult to reconcile any theory involving a simple relationship between rate of diffusion and time of formation of the principal rings with the prior formation of a secondary system of rings. Apparently a simple diffusion theory does not tell the whole story, although it is obvious to even the casual observer that rate of diffusion of the entering electrolyte must play an important part in the actual spacing
of the rings, whatever theory one decides to accept as most nearly approaching the true explanation of the formative mechanism of Liesegang structures.

6. Membrane Theories of Liesegang Ring Formation.

It is held by Fischer and McLaughlin (139) that the first precipitated ring acts as a semipermeable membrane through which it is at first impossible for the entering electrolyte to diffuse; but presently holes appear, diffusion becomes possible and eventually a new precipitated membrane is formed, when the retardation and subsequent advance of the diffusion wave takes place again. It has already been mentioned that Traube and Takehara (130) consider the formation of a membrane by the precipitate to act as a secondary factor in ring formation by causing partial cessation of diffusion. Membrane theories are not generally looked upon with favor, however, as many cases are known in which the rings are obviously composed of large crystals, not closely packed. In such cases, the presence of a retarding membrane is clearly not a factor in ring formation, and it is to be questioned, in the opinion of the present writer, whether there is any substantial evidence for membrane formation in any case of periodic precipitation.

a. By Metathesis of Reactants in Solution.

Reference has already been made to the work of Ostwald (98) who postulates that no precipitation can take place until the metastable limit of saturation is exceeded. In so-called metastable solutions, supersaturation can be relieved by introduction of some of the solid phase, but not by mechanical shock, while in labile solutions spontaneous crystallization occurs.

Miers (140), in 1907, supports Ostwald's theory. Miers gives graphs for several inorganic salts; the boundary between the metastable and labile regions is a smooth curve, parallel to the saturation curve, and about ten degrees below it. The curves are based on data obtained by shaking supersaturated solutions sealed in glass tubes and noting the temperature of spontaneous crystallization.

The subsequent investigations of Young and co-workers (141, 142, 100) show that if a metastable limit exists at all, it is, for all practical purposes, coincident with the saturation curve. Young and van Sicklen (100) show that when a sufficiently great
mechanical shock is provided water can be made to crystallize in the absence of ice at a temperature slightly less than 0.02° below the melting point of ice.

Morse (70) maintains that rapid change in concentration also releases supersaturation:

"At points not far from the center of diffusion, the rate of change of concentration of the substance diffusing from the center is, at the moment of precipitation, of the order of five to ten per cent per second. Out near the edge of the slide it is still as much as one per cent per second."

"In periodic precipitation, quiet diffusion brings about:
-- rapid approach to saturation;
-- rapid formation, through and beyond saturation, of the substance of the precipitate;
-- rapid increase in degree of supersaturation.

As already mentioned, the rate of change of concentration of the diffusing substance is such that, within the radius of the preparation used, the degree of supersaturation for a substance of solubility $1 \times 10^{-5}$ mols/liter increases by a hundred per cent in a few seconds.

"The above is offered in explanation of the appearance of crystals which form spontaneously in a ring of precipitate at a measureable distance ahead of existing solid particles."

Ring formation is explained by the supersaturation theory, the only new point here being the method of release of supersaturation. The work of Miss Abbott (69) supports that of Morse.

b. Theory of Periodic Precipitation by Reaction between Gases.

Koenig (48) explains the formation of bands of ammonium chloride by reaction between gaseous ammonia and hydrogen chloride:
"Suppose that we were to start with the two flasks containing equal volumes of ammonia and hydrochloric acid at the same temperature and pressure. The gases diffuse out into the air of the connecting tube till they meet. In the case cited this would be a little beyond the middle of the connecting tube nearer the hydrochloric acid containing flask. They will diffuse into each other till the concentration is such that solid NH₄Cl is formed. The sharp heavy band is deposited where the ammonia and hydrochloric acid have the greatest concentration. Small amounts of HCl and NH₃ on either side of the band rise to the light fog that is between the bands of NH₄Cl. The space for some distance is cleared of the interacting gases. They again diffuse toward each other and meet at some point nearer the less rapidly diffusing gas, the HCl in this case. They diffuse into each other. The point of highest concentration will be where they met the second time and here the second ring will be deposited with its thin fog on either side. And so the process continues."

Karrer (74), working with vials of ammonium hydroxide and hydrochloric acid inclosed by an inverted bottle, concludes that the cellular partitions observed in the upper portion of the vial containing the hydrochloric acid are due to a "lateral temperature gradient of rather marked degree." He says:

"Within the vial each cell marks the boundaries of vertical and horizontal convection currents, the necessary elements for the formation of which are a lateral temperature gradient and a vertical density gradient."

8. Theory of Rhythmic Crystallization.

The general theory of rhythmic crystallization from the melt, or from solution, is that stated by Hedges (9, p. 74) as follows:

"-- The really essential condition, however, is one mobile boundary, for the periodic effect is obtained
at a boundary of water. It seems clear, therefore, that the phenomenon depends on the ability of the liquid to heap itself onto the adjoining crystals. The observations made indicate that when the first crystal forms, the surrounding liquid is immediately attracted to it by surface tension, increasing the height of the crystal wall above the level of the surface of the film, whilst the liquid film in the immediate vicinity becomes correspondingly thinner. This very thin film crystallises with extreme rapidity, generally in an arborescent form, until the ridge of liquid of normal thickness is reached, when a new ring of large crystals forms. The next layer of liquid immediately becomes drawn up by these crystals, and so the process continues."

This theory is regarded by Fischer-Treuenfeld (89) as an adequate explanation of the rhythmic solidification of sulfur from the melt.

Vorländer and Ernst (75), referring to rhythmic crystallization of organic substances from the melt, report that a crystal felt is first formed at the point where crystallization begins. This crystal felt exerts capillarity upon the surrounding liquid, causing the liquid to stream in from all sides; the felt is thus built up vertically as well as horizontally, while the surface of the surrounding liquid sinks. A short rest period ensues, when the capillary action of the crystal felt and the adhesive action which results from the partial cooling of the liquid on the glass slide exactly counterbalance each other. At this point large crystals grow out from the crystal felt into the liquid. The liquid retreats
from them (a phenomenon usual in crystallization), and for lack of material, the crystals stop lateral growth. The solid crystal edge now exerts capillarity on the surrounding liquid and a new crystal felt is formed in a ring surrounding the first mass and at an interval from it.

It might be noted here that Hughes (91) has counted rings from sulfur melts, and finds that by plotting the logarithm of \( N \), the number of rings counted from the center, against the logarithm of \( r \), the distance of the outermost ring counted from the center, a straight line is obtained. The general equation for the lines so obtained is

\[
\log N = a \log r + \log K
\]

where \( N \) and \( r \) are defined as above, \( a \) is the slope of the line to the axis of \( \log r \), and \( \log K \) is the intercept on the axis of \( \log N \).

Dippy (88) finds that Hughes' equation is "borne out reasonably well in a number of instances of measurements made upon rhythmic bands of 3:5-dichloro-4-methyldiphenyl." Dippy believes that a supercooling of the melt is necessary for the occurrence of rhythmic crystallization, and that the differences in height between crests and troughs may be explained by consideration of the effect of
the latent heat of crystallization. His theory is not yet fully developed nor properly substantiated by experimental evidence.

Contrary to the theory upheld by Dippy is the conclusion of Garner and Randall (85), that the rhythmic solidification exhibited by melts of myristic, lauric, undecolic and decoic acids is due to the formation of a solid skin which wrinkles, giving a waved surface. They ascribe the formation of the skin to differences between the temperatures of solidification of the material in the liquid-air and liquid-glas surfaces.

The spiral formations sometimes observed in rhythmic crystallization phenomena have been of great interest to investigators. Hedges (82) says:

"Where crystallisation starts from a central nucleus, I have not observed among the specimens an example of the immediate development of a spiral, but I have a specimen of camphor-sulphonic acid, crystallised from ethyl acetate solution, in which a true spiral succeeds two concentric rings surrounding the nucleus of crystallisation. Moreover, examination shows that a disturbance has been caused at the point where the spiral begins by the presence of another nucleus in the vicinity."

Hedges notes, however, that it seems probable that true spiral crystallization usually occurs when crystallization begins from the periphery of the drop and travels inward, rather than when it begins at a central nucleus and radiates outward.
Ghosh and Prakash (59), discussing the spirals obtained by drying ferric phosphate and ferric arsenate gels, believe that the formation of spirals on glass surfaces probably depends on the crystallization force which is brought into prominence by the contact of two firm surfaces, namely the gel surface and the glass surface.

It is probable, in the opinion of the present writer, that the rhythmic crystallization of substances as different in their crystal habits as the organic acids and sulfur, may depend upon varying factors, some of which are more obviously in control in the case of crystal felts, such as those formed by the organic acids, while others are predominently controlling in the case of more distinctly massive crystals, such as those formed by sulfur. It seems reasonable that capillarity should be one of these factors, and equally reasonable that the degree of supercooling of the melt should be another. Further research is needed to establish conclusively the presence or absence of other forces influencing the phenomenon.

While spiral formation is interesting and does undoubtedly often occur, the present writer favors the opinion that it is a modified case of crystallization in concentric circles, due probably to interruption of ring formation at some point.
F. Periodic Structures in Nature.

Many natural structures show periodicity of one kind or another, but few of these periodic structures can properly be classified as due to periodic precipitation, or to simple rhythmic crystallization. The rings in tree trunks are undoubtedly due to external factors influencing growth and may be dismissed from the present consideration. (For discussion and bibliography, see Hedges (9, pp. 90-1).) For similar causes it appears unnecessary to discuss here the concentric bands in starch grains (see Hedges (9, pp. 91-2)). There are, however, many biological structures which may be more closely related to Liesegang rings and rhythmic crystallization phenomena. Kuster (143) finds an analogy to Liesegang rings in certain striped feathers, in striped coloring of cat's skin, and in striped skins of many fishes; while Gebhardt (144) studies bands and 'ocelli' on insects' wings from this standpoint. Leduc (145) notes the laminar structure of the cornea and Raehlmann (146) refers to a periodic structure in the retina.

Periodic layering in bones has been studied by Liesegang (147). The same author also notes the layered structure of gall stones and of urinary calculi (148), while the concentric layering of
urinary calculi is also commented upon by Schade (149), who shows excellent photographs of the rings. Weiser and Gray (150), in 1933, state that:

"The concentric rings in the 'common gall stones' of inflammatory origin are not the result of the deposition of alternate light and dark colored layers but are a manifestation of the Liesegang phenomenon. The colloidal bile pigments diffuse into a mass of cholesterol crystals, hydrophilic colloids and lime and the calcium-bile complex is deposited in concentric bands. The term 'layered stone' as applied to the 'common gall stone' is a misnomer."

In 1913, Liesegang notes (151) that an iridescent film is produced by the diffusion of sodium phosphate into a gel containing a calcium salt; the film can be hardened by formaldehyde, and Liesegang suggests the possibility of the production of artificial pearls in this manner. Before the year is out, however, Küster (152) replies to Liesegang with evidence that the film is iridescent due to the folding of a very fine surface membrane, not to any laminated structure. As early as 1814, on the other hand, Brewster (153) explains that the iridescent colors of mother-of-pearl are due to two factors, - a grating effect on the surface, and an interference effect caused by a thin film of calcium carbonate. In 1917, Pfund (154) again points out that the iridescence of mother-of-pearl can be ascribed to "(a) diffraction of light due to a grating-like structure of the terminal edges of successive laminae; (b) interference
of light due to reflection from numerous parallel laminae of sensibly equal thickness. The average thickness of many of these laminae is reported to be 0.4μ to 0.6μ. Lord Rayleigh (155) agrees with these views, but shows that the second effect is due to alternate layers of calcium carbonate and conchiolin, rather than to layers of calcium carbonate only. Clément and Rivière (156) report a method for the precipitation of calcium carbonate in an albuminous medium in the form of a diffraction grating which gives a physical structure resembling mother-of-pearl and having the same property of iridescence. Ganguly (157) reports studies on the deposition of calcium carbonate from a thin layer of an aqueous solution of calcium bicarbonate containing gelatin. He finds:

"For any given initial concentration of calcium bicarbonate there is a range of gelatin concentrations which yield translucent layers showing the iridescent colours characteristic of mother-of-pearl."

Banding and striping in plants is quite common. It is of interest to note that Bhatnagar and Sehgal (158) find that the concentric colored rings in the red beet are spaced similarly to those produced by precipitation of mercuric iodide or of potassium dichromate in the beet which has had its coloring matter extracted with acid. These bands are also
similar in spacing to Liesegang rings obtained in the usual way. The banded distribution of pigments in leaves of many plants is noted by Küster (159).

Möller (160) shows that periodic structures of the Liesegang ring type can be produced by the diffusion of silver nitrate into certain plant tissues, such as wheat grains and leaves of some plants. Excellent photomicrographs accompany his article. Seidel (161) reports similar precipitation in the root fibers of wheat, oat and rice. He pictures a case of precipitation in the root hairs of Chenopodium chiloca. Similar structures in nerve fibers are reported by Macallum and Menten (162). Both these authors and Rabl (163) maintain that the Frommann lines in nerve are not preexistent, but are Liesegang structures due to the diffusion of the silver nitrate into the chlorides already present in uniform distribution in the nerve fibers. A similar phenomenon is the periodicity observed by Lloyd and Moravek (19) in the trichomes of Pelargonium and other plants when treated for the microchemical detection of potassium. The specimen is treated with sodium cobaltihexanitrite, excess reagent removed by washing, and the specimen then treated with ammonium sulfide to blacken the cobalt salt. Black bands of the cobalt sulfide are produced within the cellulose walls. Hedges (9, pp. 88-9) refers to
other similar cases of production of periodic structures in biological media, as well as to the problems of "fairy rings", i.e., concentric rings or spiral growths of moulds or bacteria on their substrate (pp. 92-3).

Periodic geological structures are not uncommon. One must be careful not to confuse true cases of rhythmic precipitation, such as agates, with banding due to seasonal deposition, such as is seen in salt beds and gravel banks. The rings found in agates and in malachite have been discussed by Liesegang (164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174). He shows (164, 167, 170, 173) that structures with bands, tubes and pseudoclases similar to those shown by agates can be produced artificially in gels, by typical Liesegang reactions. Heinz (175) also obtains bands and tubes similar to those found in agates by the interaction of silicic acid sols and salt solutions. But Linck and Heinz (176) maintain that the banding of agate is due to the alternate action of silicic acid and of salts, the former during the dry season, the latter during the wet season of the year. Liesegang (166) suggests that most agates are formed by the diffusion of iron oxide into silica gel. This gel is not solid opal, but a soft, more hydrous substance. The iron may be originally evenly distributed throughout the gel, or may enter as a colloidal solution from surrounding
rocks. The precipitation is probably caused by sodium or potassium silicates adsorbed by the silica. He later notes (169) that only some agates in porphyries are due to rhythmic precipitation of a preexisting silicic acid gel, while in others it must be assumed that the silicic acid is present in sol form (i.e., as waterglass). Liesegang considers horizontally banded agates as a separate case (166); these are assumed to be really stratified, and to be produced by the intermittent introduction of small portions of gel into a cavity. Jablczynski (132), on the other hand, finds by measurement that the spacings of rings in agates do not correspond to the spacings of rings produced in gels.

Endell (177) reports a tubular rhythmic rust formation in meteoric iron from the Cañon Diablo. Storz (178) notes rhythmic banding of certain South African stones, and attributes this banding to the formation of alternate zones of hardness or of color, due to rhythmic changes of external conditions during the formation of the stone. Hartman and Dickey (179) apply the theory of Liesegang structures to the banded structures occurring in the iron formations of the Lake Superior region; they conclude that these structures have been brought about by slow diffusion of soluble ferrous salts through a
gel formed by the interaction of basic nitrogenous substances, carbon dioxide, or carbonates with sodium silicate, giving rise to irregularly spaced bands of varying thicknesses of insoluble ferrous carbonate separated by silica. Other examples of periodic geological structures are cited by Hedges (9, pp. 97-8).

The crimp in wool and other natural fibers is discussed by Hedges (9, pp. 93-7) with bibliography. This phenomenon is so little akin to the work undertaken by the present writer that it will not be considered here.

This brief discussion of natural periodic structures cannot be expected to cover the field with any thoroughness, but the present writer hopes it is sufficient to show the fundamental and very broad importance of the Liesegang phenomenon and related fields.
III. PURPOSE OF THIS WORK:

From the discussion of the literature, it is apparent that no systematic study of the influence of variations in temperature and in concentration on rhythmic crystallization from solution has been reported. Such a study seems desirable in view of the known effects of such variations on Liesegang structures and the close resemblance of rhythmic crystallization structures to Liesegang rings.

The work of Miss Abbott (69), already reviewed in some detail, indicates that specific impurities may cause great variation in spacing of bands in rhythmic crystallization, or may even prevent the formation of banded structures under otherwise favorable circumstances. Confirmation of these results and extension of data in this direction also appear desirable, especially since specific impurities are known to play an important part in the production of Liesegang rings.

Consequently the present investigation was undertaken to extend the existing knowledge concerning effects of temperature and concentration upon the phenomenon of rhythmic crystallization. Later it seemed
advisable to extend the work done by Miss Abbott on the effect of specific impurities.
IV. EXPERIMENTAL WORK.

A. Apparatus.

Ordinary white non-corrosive microscope slides were used for all work, unless otherwise specified.

A Freas electric oven with constant temperature control was used during the investigation of the effect of temperature upon rhythmic crystallization.

The microscope used for examining the structures obtained was a Zeiss, type number 5710, with mechanical stage, polarizer and analyzer. This instrument made possible magnifications between 56x and 940x with the oculars and objectives supplied. The condenser was of the swing-out type, with iris-cylinder diaphragm. A micrometer eye-piece was used for measurements; this was first calibrated against a standard stage micrometer; the usual tube length, 160 mm., was used. Table I gives the results of calibrations.

Table I

<table>
<thead>
<tr>
<th>Objective used</th>
<th>Reading on micrometer eye-piece</th>
<th>Reading on stage micrometer</th>
<th>Value of one division on micrometer eye-piece</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30</td>
<td>38</td>
<td>0.013 mm.</td>
</tr>
<tr>
<td>C</td>
<td>35</td>
<td>18</td>
<td>0.005 mm.</td>
</tr>
<tr>
<td>E</td>
<td>24</td>
<td>5</td>
<td>0.002 mm.</td>
</tr>
</tbody>
</table>

Calibration of Micrometer Eye-piece.

(Draw tube at 160 mm.; 100 divisions on stage micrometer equal 1 mm.)
When the solution and slides were maintained at a certain temperature, the following apparatus was used. A liter beaker was filled with water (water and sodium chloride, when 100°C. was the desired temperature). This was placed on a ringstand at a convenient height to be heated by a Bunsen burner. In the water (or salt solution) were suspended a thermometer and a Pyrex test tube, the latter containing the solution of which the crystallization was under investigation. Dipping into the solution in the test tube were a second thermometer, and the curved pipet by which the solution was later to be transferred to the slide. The water in the beaker was agitated during heating either by an electric stirrer or manually by a glass ring of suitable size, with glass handle. The solution within the test tube was agitated by moving the pipet and thermometer. The curved pipet was necessary to place liquid on the slides in the oven, since there was not room for the use of the ordinary straight type pipet.
B. Methods and Results.

1. Preparation and Cleaning of Slides.

Many of the slides, during the first part of the investigation, were cleaned by the method suggested by Chamot and Mason (180, p. 174); i.e., the slide was cleaned in water, or other appropriate solvent, then a film of Bon Ami was rubbed on, allowed to dry, and removed with a clean dry cloth. Care must be taken, when cleaning by this method, lest small particles of Bon Ami remain on the slide.

Later it was found more satisfactory to soak the slides for some days in chromic acid cleaning solution, after which they were rinsed many times in distilled water, drained from the last rinsing by touching one end of the slide firmly to a pile of ordinary filter papers. In this way the possibility of leaving pieces of lint upon the slide, after wiping, was eliminated. Though Laug (180a) found traces of dichromate remaining after similar treatment of glassware, Miss Abbott (69) has shown that this has no influence upon rhythmic crystallization on slides so cleaned.
2. Investigations on the Effects of Temperature and Concentration on Rhythmic Crystallization from Solution.

a. Method.

The solution to be used, heated to the desired temperature, was transferred to slides, at the same temperature, by means of the curved pipet. One moderate sized drop was placed on each slide. The slides were maintained at the desired temperature for some time before the drops of solution were placed on them, until crystallization was complete, and often for some time longer.

Slides to be maintained at room temperature were placed in a quiet place, viz., the electric oven, a quiet corner of the constant temperature room, or, in a few cases, in a locker drawer. Room temperature was noted several times during the crystallization, in each case, and its constancy assured.

All salts used were C.P. grade.

b. Effects of Temperature and Concentration on Rhythmic Crystallization of Cadmium Sulfate.

The rhythmic crystallization of cadmium sulfate had been indicated by work reported by Sir David Brewster (73). This salt was, therefore, chosen as a subject for preliminary study. The slides were made at constant temperature, in an electric oven, by
the method already described. The salt used was Baker's Analyzed C. P. Data are tabulated in Table II. Polarized light was found best for observation of rhythm.

In Table II, tests 1 and 4 were run at room temperature (25°C.) using a solution containing five grams of cadmium sulfate per one hundred cubic centimeters of solution. These slides were all vitreous, although some showed small areas with spider-web-like banding. A few slides in test 4 showed irregular periodicity, and one had a few regular periods of 0.005 mm. It was observed that these slides showed no periodicity when first made, but when examined after several hours, imperfect rhythm had appeared. Mellor (181, Vol. IV, p.616) reports the existence of the mono-, hexa-, hepta- and octotri-hydrates of cadmium sulfate (CdSO₄·H₂O, CdSO₄·6H₂O, CdSO₄·7H₂O, and CdSO₄·2H₂O, respectively). It was thought that one of the higher of these hydrates might first form, which, on evaporation, gave a lower hydrate; during the recrystallization, from one hydrated form to another, it seemed possible that the periodicity might become evident. In an endeavor to hasten the formation of the lower hydrate, test 2 was run using ten cc. of a solution containing five grams cadmium sulfate per one hundred cc. of
Table II

Data on Rhythmic Crystallization of Aqueous Solutions of Cadmium Sulfate.

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration</th>
<th>Temp.</th>
<th>No. slides</th>
<th>Results.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 gm./100 cc.</td>
<td>Room.</td>
<td>6</td>
<td>Vitreous.</td>
</tr>
<tr>
<td></td>
<td>soln. 0.2398 M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10 gm. 0.2398 M CdSO₄ + 2 cc. 6N H₂SO₄</td>
<td>Room. 16</td>
<td>Three show indistinct rhythm in dendrites; other thirteen show periodicity distinctly on coarse dendrites.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>10 cc. 95 gm./100 cc. soln. (1.199 M)CdSO₄ + 2 cc. 6N H₂SO₄</td>
<td>Room. 10</td>
<td>Many small spherules. Good rhythm on all slides; spacing of bands irregular.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.2398 M CdSO₄</td>
<td>25°C. 10</td>
<td>Largely vitreous with few circular crystals showing spider-web-like banding. Few periods of 0.005 mm. observed on one slide; few irregular larger periods on other slides.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.199 M CdSO₄</td>
<td>25°C. 10</td>
<td>Spider-web-like banding in all. Periods of 0.02 mm. and 0.04 mm. most common.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.2398 M CdSO₄</td>
<td>52°C. 20</td>
<td>Six slides largely vitreous; others show rhythm; several show spiral rhythm. Vitreous slides often show several small areas of imperfect rhythm. Periods of 0.0025 mm., 0.005 mm. and 0.0175 mm. most common, often spirally crosshatched. Reexamined next day; no change observed.</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Concentration</td>
<td>Temp.</td>
<td>No. slides</td>
<td>Results</td>
</tr>
<tr>
<td>-----</td>
<td>---------------</td>
<td>-------</td>
<td>------------</td>
<td>---------</td>
</tr>
<tr>
<td>7</td>
<td>1.199 M CdSO₄</td>
<td>52°C</td>
<td>20</td>
<td>Two slides with poor periodicity; others show periodicity in varying degrees of excellence. Some spider-web-like banding; several cases of rhythm like shingling. Some coarse rhythm. Periods of 0.0025 mm., 0.005 mm., 0.0075 mm. and 0.0125 mm. most common.</td>
</tr>
<tr>
<td>8</td>
<td>0.2398 M CdSO₄</td>
<td>100°C</td>
<td>20</td>
<td>Sixteen slides with excellent periodicity; four with thicker material showing poor rhythm. Periods most frequently observed are 0.0025 mm., 0.005 mm. and 0.0075 mm. Only a few cases show very regular periodicity; these most commonly show periods of 0.005 mm.</td>
</tr>
<tr>
<td>9</td>
<td>1.199 M CdSO₄</td>
<td>100°C</td>
<td>19</td>
<td>Good periodicity in ten slides; the other nine show evidences of rhythm, but the material is too thick to show rhythm well under the microscope. Crests 0.005 mm., 0.010 mm. and 0.025 mm. apart are most common. Three slides show zigzag modification, the crests approximately 0.01 mm. apart.</td>
</tr>
</tbody>
</table>
solution to which was added 2 cc. of 6 N sulfuric acid. The slides so made showed distinct periodicity on coarse dendrites. A similar set, test 3, was run, using the same amount of acid, added to ten cc. of a solution containing twenty-five grams cadmium sulfate per one hundred cc. of the solution. All these slides showed good rhythm; there were many small spherules, such as described by Sir David Brewster (73).

Since the slides made with addition of sulfuric acid (tests 2 and 3) showed no better rhythm than those made with cadmium sulfate solution alone, when the latter were examined after standing for a few hours (test 4), all subsequent slides were made without addition of the acid.

Test 5 was made at 25°C., using a solution containing twenty-five grams of cadmium sulfate per one hundred cc. of the solution. All these slides showed a spider-web-like banding; i.e., there were two sets of "cracks." One set radiated from the center of crystallization, while the other set consisted of portions of concentric circles cut off between the radiating "cracks." The circular sets did not coincide between two pairs of radiating "cracks," but period lengths were, in general, approximately the same, the lack of coincidence
apparently being due to the fact that concentric cracks started sooner (nearer the crystallization center) between certain pairs of radiating cracks than between other pairs. The periods observed in test 5 were not regular, but the spacings most frequently observed were 0.02 mm. and 0.04 mm. This is four to eight times the magnitude of the most common spacing observed when a solution only one-fifth as concentrated was allowed to crystallize at the same temperature.

In test 6, the dilute solution of cadmium sulfate was again used (five grams of the salt per one hundred cc. of the solution), but crystallization took place at a constant temperature of 52°C. Six of the twenty slides made were largely vitreous, but these showed small areas of imperfect rhythm; the other fourteen slides showed good periodicity, with periods of 0.0025 mm., 0.005 mm. and 0.0175 mm. most common. The 0.005 mm. spacing coincides with the spacing most commonly observed when the same solution crystallized at room temperature. The slides made at 52°C., however, often show spiral, periodic crosshatching marks across the main periods, which thus assume much the appearance of a finely banded barber's pole. This is apparently a case of very fine secondary rhythm. This set of slides showed no change when allowed to stand a day after the first
observations were made; all rhythmic "cracking" had appeared within a few hours of the first crystallization.

Test 7 was also run at 52°C., but with the stronger solution, which contained twenty-five grams cadmium sulfate per one hundred cc. of solution. In this test, all slides showed some periodicity; only two were poor, while eighteen showed good to excellent rhythm. There were some cases of spider-web-like banding, as well as several instances in which the bands were slipped in small radial sections to give a shingled effect. These slides also exhibited some "coarse rhythm," as the present writer prefers to designate the typical rhythm figured by Hedges (9) and others; this rhythm is much coarser than the rhythm ordinarily obtained and studied during these investigations, and is inclined to be very much less regular in its spacing. The most common periods observed in test 7 were those of 0.0025 mm., 0.005 mm., 0.0075 mm. and 0.0125 mm. This spacing does not differ materially from that obtained with the solution of one-fifth the concentration under the same conditions (test 6), but is much smaller than that obtained with the same (concentrated) solution at 25°C.

The dilute solution of cadmium sulfate (five grams per one hundred cc. of solution) was used for test 8; crystallization was allowed to take place at
a constant temperature of 100°C. Sixteen of the twenty slides showed excellent periodicity; the material on the other four was too thick for proper observation and periodicity was either poor or obscured by the massiveness of the crystalline material. Periods of 0.0025 mm., 0.005 mm. and 0.0075 mm. were most frequently observed; in the few cases where rhythm was regular, the periods of 0.005 mm. were most common. This same period was common in slides of the same solution made at 25°C. and at 52°C.

Test 9 was also run at 100°C., but in this case the concentrated solution (twenty-five grams cadmium sulfate per one hundred cc. of solution) was used. Nine slides gave heavy crystalline masses and good rhythm could not be observed; the other ten slides showed excellent periodicity. Periods of 0.005 mm., 0.01 mm. and 0.025 mm. were most common. Three slides showed a zigzag modification, with periods of approximately 0.01 mm. The spacing in these slides tended to be greater than in those made at the same temperature with the more dilute solution (test 8), and is also, on the average, greater than in the slides made with the concentrated solution at 52°C. (test 7), though it is, on the other hand, finer than in the slides of the concentrated solution at
room temperature (test 5).

In all tests, polarized light gave the clearest distinction of rhythm. By observation with crossed nicols, it was evident that the crystals in the crests were oriented so that they lay longitudinally along imaginary lines radiating from the local center of crystallization. Where two areas of crystallization met, the line of meeting was sharply defined. All measurements of spacing of periods were made from edge to corresponding edge between "cracks".

The tests on cadmium sulfate served as preliminary trials, only, as this compound did not exhibit well defined typical rhythmic crystallization. The evidence from the tests run, however, is that a marked difference of temperature at which slides are allowed to crystallize does not produce any great difference in the distance between crests. A concentrated solution has a maximum spacing, at least, greater than that of a dilute solution allowed to crystallize at the same temperature, though in some areas identical spacing may be observed in both cases. The irregularities occurring in the rhythm, such as shingled effect, zigzag modification, spirals and secondary rhythm, arose from unknown causes, but since they were visibly similar to almost identical modifications found in the Liesegang phenomenon, it is suggested that their causes might be analogous.
It would appear, then, that the spirals observed were due to temporary obstruction of crystallization at one side of the center of crystallization. The zigzag structures and the shingled effect were similar to modifications reported by Küster and were, doubtless, due to an inequality in the starting time of crystallization upon different sides of the crystal nucleus. The secondary rhythm was rather unusual in not being parallel to the primary rhythm, but was possibly due to periodic precipitation from a center within a primary crest, coincident in time with the primary precipitation.

c. Effects of Temperature and Concentration on the Rhythmic Crystallization of Potassium Dichromate.

Since none of the typical rhythm obtained by Miers (74) and by Hedges (9) had been obtained, preliminary experiments were undertaken on the rhythmic crystallization of potassium dichromate from aqueous solution; this was the salt most often used for illustration by the investigators mentioned. Table III gives the data obtained in these preliminary experiments.

In test 1, a drop of a saturated solution of potassium dichromate was placed upon a slide, which was then gently warmed over the small flame of a
pilot type modified Bunsen burner. The typical coarse rhythm illustrated by Miers (74), who used this method, was obtained. In one case, the rhythm was very irregular, while in the other case it was extremely regular, with a period of 0.15 mm.

The technique of test 1 was repeated in test 2, but a dilute solution of potassium dichromate was substituted for the saturated one used in test 1. The slides of test 2 also showed coarse rhythm, and in several areas where it was well defined the period was again found to be 0.15 mm.

In test 3, a drop of a dilute solution of potassium dichromate was placed upon each slide. The slides were then allowed to stand, undisturbed, at room temperature, until crystallization was complete. Coarse rhythm was found to be present in all eight slides, and the common, regular periods were 0.15 mm. and 0.065 mm.

A solution of 0.5 gm. potassium dichromate (C.P. Baker’s Analyzed) per one hundred cc. of solution was then made up. This solution was used for tests 4, 5 and 6, all run at room temperature, but at different times. Each of these tests included six slides. In all eighteen slides rhythm was present. All slides showed periods of 0.04 mm. and 0.065 mm.; sets 5 and 6 showed periods of 0.15 mm., while set 6 had many areas with periods of 0.025 mm. While some
### Table III

Data on Preliminary Experiments on Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

<table>
<thead>
<tr>
<th>No.</th>
<th>Soln. used.</th>
<th>Temp.</th>
<th>No. slides.</th>
<th>Results.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Saturated $K_2Cr_2O_7$ soln.</td>
<td>Warmed on slides</td>
<td>2</td>
<td>Coarse rhythm present; one slide irregular, the other very regular with 0.15 mm. spacing from edge of crest to corresponding edge of next crest (period).</td>
</tr>
<tr>
<td>2</td>
<td>Dilute $K_2Cr_2O_7$ soln.</td>
<td>Warmed on slides</td>
<td>5</td>
<td>Coarse rhythm present; several well defined areas show 0.15 mm. periods, as in test 1.</td>
</tr>
<tr>
<td>3</td>
<td>Dilute $K_2Cr_2O_7$ soln.</td>
<td>Room temp.</td>
<td>8</td>
<td>Coarse rhythm present; periods of 0.15 mm. and 0.065 mm. very common.</td>
</tr>
<tr>
<td>4</td>
<td>0.5 gm. $K_2Cr_2O_7$ per 100 cc. soln. (0.0170 M)</td>
<td>Room temp.</td>
<td>6</td>
<td>Coarse rhythm present. Periods of 0.04 mm. and 0.065 mm. very common; very irregular in many areas.</td>
</tr>
<tr>
<td>5</td>
<td>0.0170 M $K_2Cr_2O_7$</td>
<td>Room temp.</td>
<td>6</td>
<td>Periodicity imperfect; periods of 0.04 mm., 0.065 mm. and 0.15 mm. most frequently observed.</td>
</tr>
<tr>
<td>6</td>
<td>0.0170 M $K_2Cr_2O_7$</td>
<td>Room temp.</td>
<td>6</td>
<td>Excellent coarse rhythm; 0.025 mm., 0.065 mm., 0.04 mm. and 0.15 mm. commonly observed periods.</td>
</tr>
<tr>
<td>7</td>
<td>0.1360 M $K_2Cr_2O_7$</td>
<td>Room temp.</td>
<td>4</td>
<td>Thicker precipitates than in those made with the more dilute soln.; rhythm less definite and less regular. Periods of 0.15 mm. and 0.195 mm. most common.</td>
</tr>
<tr>
<td>8</td>
<td>0.1360 M $K_2Cr_2O_7$</td>
<td>Room temp.</td>
<td>3</td>
<td>Largely dendritic. Some periods 0.065 mm., 0.15 mm. and 0.5 mm., but poorly defined.</td>
</tr>
<tr>
<td>9</td>
<td>0.1360 M $K_2Cr_2O_7$</td>
<td>Room temp.</td>
<td>6</td>
<td>Many dendrites; very fine rhythmic banding visible with use of polarized light. Coarse rhythm present. Periods of 0.15 mm. common.</td>
</tr>
</tbody>
</table>
of these periods were very small, the rhythm was all of the type
described by Miers (74) and by Hedges (9) as far as was
observed. That is, ridges of typical potassium di-
chromate crystals, often dendritic in nature, were
arranged regularly about a common center; these ridges
were separated from one another by open spaces or by areas
in which lay very few crystals. This type of rhythm is
designated by the present writer as "coarse" rhythm.

Tests 7, 8 and 9 were run at room temperature,
using a solution containing four grams of potassium
dichromate (C.P. Baker's Analyzed) per one hundred cc.
of the solution. As might be expected, all the slides
in these tests showed thicker precipitates than those
run with the more dilute solution. All showed
many dendrites. The rhythm was often indefinite
and irregular. Periods of 0.15 mm. were observed
on all three sets of slides; set 7 showed periods of
0.195 mm., also, while set 8 showed periods of 0.065 mm.
and 0.5 mm. In set 9, it was noticed that a very
fine, very regular rhythmic banding was distinguishable
with the use of polarized light. This is hereafter
referred to as "fine" rhythm, to distinguish it from
the "coarse" rhythm already mentioned. Fine rhythm
is easily overlooked unless polarized light is used;
it consists of very narrow alternating bands of
thickly crystalline areas and thinly crystalline areas.
While detail is not readily observable, it appears as though the thick areas (crests) are composed of numerous very fine potassium dichromate crystals all similarly oriented, i.e., with the long axes coinciding with imaginary lines drawn outward from the center of crystallization, while the thin areas (troughs) are composed of similar crystals lying at right angles to those in the crests. This structure has been suggested by Miss Abbott (69) who first observed fine rhythm in slides of potassium dichromate. She found similar rhythm, though with different periods, given by ammonium and sodium dichromates.

Typical coarse rhythm often shows irregular spacing, i.e., the period size changes rapidly within comparatively small areas. The fine rhythm first observed by Miss Abbott (69) and confirmed by the present writer, is, on the other hand, usually extremely evenly spaced over large areas. Whereas coarse rhythm, in many cases, looks like mere evaporation rings, the fine rhythm is distinct over extremely large areas of a typical slide and looks far too regular to be the result of evaporation only. The presence of fine rhythm is, therefore, taken by the present writer to be the final criterion of rhythm or lack of rhythm on any given slide.

Subsequent observations have shown that one
cause of coarse rhythm is a massing of material during crystallization. Slides standing on edge were inverted after crystallization had started, so that crystallization proceeded against the force of liquid flowing down toward the crystal mass. Coarse rhythm resulted in every case.

A systematic study of the effect of temperature and concentration on the rhythmic crystallization of potassium dichromate from aqueous solution was now undertaken. Observations were made with regard to both fine and coarse rhythm. Data are tabulated in Table IV. Each set consisted of twenty slides, made at a definite temperature, in the manner described under the section on methods and apparatus; the concentrations employed were 0.05 gm. potassium dichromate per one hundred cc. of solution, 0.5 gm. of potassium dichromate per one hundred cc. of solution and 4 gms. potassium dichromate per one hundred cc. of solution. Each of these solutions was run at room temperature (23°C. or 25°C., as specified), at 50°C., and at 100°C.

The slides in set 1 were made with a solution of 0.05 gm. potassium dichromate per one hundred cc. of solution at 25°C. Six of these slides showed small circular crystals, apparently nuclei which grew only slightly before the supply of salt was exhausted. Only one of the twenty slides showed good
### Table IV.

**Data on Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Soln. used.</th>
<th>Temp.</th>
<th>No. slides</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05 gm. $K_2Cr_2O_7$ per 100 cc. solution (0.0017 M)</td>
<td>25°C.</td>
<td>20</td>
<td>Six of these slides show small circular crystals. One slide shows good coarse rhythm; in the other nineteen coarse rhythm is poor and irregular or entirely absent. Eight slides show well defined fine rhythm of 0.01 mm. period (with crest and trough each 0.005 mm.), or of 0.005 mm. period (0.0025 mm. width of crest and trough, each). In every slide there is fine rhythm crossed by fine rhythm approximately at right angles; the fine rhythm is, in each direction, of the 0.01 mm. period type. (This will be designated as &quot;x-rhythm&quot;).</td>
</tr>
<tr>
<td>2</td>
<td>0.0017 M $K_2Cr_2O_7$</td>
<td>25°C.</td>
<td>20</td>
<td>These slides are largely dendritic. Three show rudimentary coarse rhythm; four show simple fine rhythm, while all twenty show x-rhythm. Periods of fine and x-rhythm are 0.005 mm. (crest and trough each 0.0025 mm.).</td>
</tr>
<tr>
<td>3</td>
<td>0.0017 M $K_2Cr_2O_7$</td>
<td>50°C.</td>
<td>20</td>
<td>These slides tend to be dendritic, with massive circular crests at edges. Three slides show evidence of inferior coarse rhythm. Seven slides show good fine rhythm, and all twenty have areas of x-rhythm. The common period of fine and x-rhythm is 0.005 mm. (crest and trough each 0.0025 mm.).</td>
</tr>
<tr>
<td>4</td>
<td>0.0017 M $K_2Cr_2O_7$</td>
<td>100°C.</td>
<td>20</td>
<td>Largely irregular semi-massive crests Nineteen slides show ordinary type fine rhythm (period 0.01 mm., crest and trough each 0.005 mm.), and all twenty slides show areas of x-rhythm.</td>
</tr>
<tr>
<td>No.</td>
<td>Soln. used.</td>
<td>Temp.</td>
<td>No.</td>
<td>Results</td>
</tr>
<tr>
<td>-----</td>
<td>-------------</td>
<td>-------</td>
<td>-----</td>
<td>---------</td>
</tr>
<tr>
<td>5</td>
<td>0.5 gm. $\text{K}_2\text{Cr}_2\text{O}_7$ per 100 cc. soln. (0.0170 M)</td>
<td>23°C.</td>
<td>20</td>
<td>Coarse rhythm in varying degrees of excellence. 0.026 mm., 0.065 mm. and simple multiples of 0.065 mm. are most common widths of crests, with spacings between crests usually of approximately the same width as the crests. Fourteen of these slides show excellent fine rhythm, the crests lying between the crests of the coarse rhythm and parallel to them. The periods of fine rhythm are commonly 0.01 mm., occasionally 0.02 mm., with equal division between crest and trough. $X$-rhythm of period 0.013 mm. is noticeable on one slide.</td>
</tr>
<tr>
<td>6</td>
<td>0.0170 M $\text{K}_2\text{Cr}_2\text{O}_7$</td>
<td>50°C.</td>
<td>20</td>
<td>Slides tend to be dendritic and massive. Six slides show large numbers of very small circular crystals. Fifteen slides show irregular coarse rhythm. Eleven slides show well defined fine rhythm, with period of 0.01 mm. (crest and trough each 0.005 mm.); one case of period 0.015 mm. (crest and trough each 0.0075 mm.)</td>
</tr>
<tr>
<td>7</td>
<td>0.0170 M $\text{K}_2\text{Cr}_2\text{O}_7$</td>
<td>50°C.</td>
<td>20</td>
<td>Thirteen of these slides show numerous small circular crystals. Fourteen show irregular coarse rhythm; an equal number show fine rhythm, often very good over small area, period 0.01 mm. (crest and trough each 0.005 mm.).</td>
</tr>
<tr>
<td>8</td>
<td>0.0170 M $\text{K}_2\text{Cr}_2\text{O}_7$</td>
<td>100°C.</td>
<td>20</td>
<td>These slides have large massive scalloped circular crests, which look much like the start of a heavy system of coarse rhythm, but only one shows well developed coarse rhythm. Four slides have numerous small circular crystals. Fifteen of the slides have well defined areas of fine rhythm. The usual period is 0.01 mm. (crest and trough each 0.005 mm.); periods with 0.005 mm. crest and 0.01 mm. trough; and 0.01 mm. crest and 0.005 mm. trough are present on at least four slides.</td>
</tr>
<tr>
<td>No.</td>
<td>Soln. used.</td>
<td>Temp.</td>
<td>No.</td>
<td>Results.</td>
</tr>
<tr>
<td>-----</td>
<td>-------------</td>
<td>-------</td>
<td>-----</td>
<td>----------</td>
</tr>
<tr>
<td>9</td>
<td>4 gms. $K_2Cr_2O_7$ per 100 cc. soln. (0.1360 M)</td>
<td>25°C.</td>
<td>20</td>
<td>All slides dendritic; little or no rhythm evident in fifteen slides; five slides show characteristic fine rhythm with period 0.01 mm. (crest and trough each 0.005 mm.).</td>
</tr>
<tr>
<td>10</td>
<td>0.1360 M $K_2Cr_2O_7$</td>
<td>50°C.</td>
<td>20</td>
<td>These slides tend to be dendritic and massive. Ten slides show numerous small circular crystals. Coarse rhythm is evident on fifteen slides; fine rhythm is present on eight slides. The coarse rhythm is usually very irregular. The fine rhythm has periods of 0.01 mm. (crest and trough each 0.005 mm.).</td>
</tr>
<tr>
<td>11</td>
<td>0.1360 M $K_2Cr_2O_7$</td>
<td>50°C.</td>
<td>20</td>
<td>These slides are largely dendritic. All show more or less numerous small circular crystals. The rhythm, fine and coarse, is irregular and difficult to measure. (Drops were large.)</td>
</tr>
<tr>
<td>12</td>
<td>0.1360 M $K_2Cr_2O_7$</td>
<td>100°C.</td>
<td>20</td>
<td>All twenty slides show massive scalloped circular crests. Three have a few small circular crystals. There are no definite examples of either coarse or fine periodicity.</td>
</tr>
</tbody>
</table>
coarse rhythm; in the other nineteen coarse rhythm was irregular and poor or entirely absent. Eight slides, on the other hand, showed fine rhythm, well developed, while all twenty of the slides had well defined areas of fine rhythm crossed by a second system of fine rhythm approximately at right angles to the first; this modification, of crossed rhythms, will henceforth be designated as 'x-rhythm' by the present writer. Some of the simple fine rhythm and all of the x-rhythm showed periods of 0.01 mm., in which crest and trough were each 0.005 mm. wide. A part of the fine rhythm showed periods of 0.005 mm., with crest and trough each 0.0025 mm. wide.

Set 2 was run as a check on set 1, at a later date, using the same solution and temperature (25°C.). These slides were largely dendritic. Only three of the twenty slides showed even rudimentary coarse rhythm; four showed simple fine rhythm and all twenty had good areas of x-rhythm. The periods in both fine and x-rhythm were 0.005 mm., with crest and trough each 0.0025 mm. This period is one of those observed in the fine rhythm in set 1, and is exactly one-half the common period for x-rhythm of set 1.

In set 3 the solution of 0.05 gm. potassium dichromate per one hundred cc. of solution was again used; twenty slides were made at a constant temperature of 50°C. These slides tended to be dendritic, with
massive circular crests at the edges of the drops. There was very inferior coarse rhythm on three slides. All twenty slides had areas of x-rhythm, though only seven showed large areas of simple fine rhythm. The common period of both simple fine and x-rhythm was 0.005 mm., with crest and trough each 0.0025 mm. This is the period that was most common at 25°C. when the same concentration of potassium dichromate was employed.

The same solution of potassium dichromate used in sets 1, 2 and 3 was used in set 4, run at 100°C. Much of the material in these slides gathered in large irregular semi-massive crests. Nineteen of the twenty slides showed simple fine rhythm of period 0.01 mm., crest and trough each 0.005 mm., and there were areas of x-rhythm on all twenty slides.

The four sets just considered show the influence of temperature upon the crystallization of the solution used. As the temperature rose, dendrites became less common, and massive circular crests at the edge of the drop became more common. The amount of simple fine rhythm present was greatest in the slides run at 100°C., and did not much vary in those run at 50°C. from that in those run at 25°C. All slides at all the temperatures used showed areas of x-rhythm. The periods observed in the four sets
of slides were of two orders only, 0.005 mm. and 0.01 mm. Temperature did not seem to affect the period of fine rhythm.

Sets 5, 6, 7 and 8 were made with a solution containing 0.5 gm. potassium dichromate in 100 cc. of solution. This solution was ten times as strong as that used in making the first four sets of slides. Set 5 was made at 23°C. All twenty slides showed some coarse rhythm, but much of it was extremely imperfect and irregular. The most common widths of crests in the coarse rhythm were 0.026 mm., 0.065 mm. and simple multiples of the last, with the spaces between crests usually of approximately the same width as the crests. There was excellent fine rhythm in fourteen of these slides; the crests of fine rhythm lay between those of coarse rhythm and parallel to them; the period of the fine rhythm was commonly 0.01 mm., more rarely 0.02 mm., with the period width equally divided between crest and trough. One slide showed x-rhythm, period 0.013 mm.

Set 6 was also made with solution containing 0.5 gm. potassium dichromate in one hundred cc. of solution, but this set was run at 50°C. All slides showed massive crests as well as numerous dendrites. Six of these slides showed large numbers of very small circular crystals, much like those observed on an equal number of slides of set 1. Irregular coarse
rhythm was observed in fifteen of the twenty slides. Eleven slides showed well defined fine rhythm, period 0.01 mm., and there was one case of fine rhythm of period 0.015 mm., with crest and trough of equal width, in both types of periods.

Set 7 was a check on set 6, made at a later date, with the same solution at the same temperature. Small circular crystals were noticeable on fourteen of these slides. Coarse rhythm was not marked. Fourteen slides showed fine rhythm, often extremely good in small areas. The period was most commonly 0.01 mm., with crest and trough each 0.005 mm.

The solution of 0.5 gm. potassium dichromate in one hundred cc. of solution was again used in test 8; these twenty slides were made at a constant temperature of 100°C. In each case a large massive scalloped circular crest formed about the edge of the drop; this crest looked much like the beginning of a system of coarse rhythm, but only one slide showed well developed coarse rhythm. Four slides showed numerous small circular crystals. Fifteen slides had well defined areas of fine rhythm, the usual period being 0.01 mm. (crest and trough each 0.005 mm.). Periods of 0.015 mm. (crest 0.005 mm. and trough 0.01 mm., or crest 0.01 mm. and trough 0.005 mm.) were present on at least four slides.
Considering sets 5 to 8, inclusive, it is seen that the tendency to form heavy crests increased with increase in temperature. Dendrites were more common at lower temperatures than at 100°C. Coarse rhythm was common and fairly regular at 23°C, irregular and somewhat less common at 50°C, and entirely absent, except for the massive outmost crest, at 100°C. Fine rhythm was present at all temperatures used, and the amount present did not seem to vary greatly with the temperature. Periods of 0.01 mm. were found common at all temperatures investigated. Periods of 0.02 mm., at 23°C., and of 0.005 mm., at 100°C., were also observed. Only one case of x-rhythm was noted; this was on a slide made at 23°C.; the period was 0.013 mm.

The slides in sets 9 to 12, inclusive, were made with a solution containing four grams potassium dichromate in one hundred cc. of solution. This solution was eight times as concentrated as that used in making sets 5 to 8, inclusive, and eighty times as concentrated as that used in making sets 1 to 4, inclusive. Set 9 was run at 25°C. All twenty of these slides were dendritic; in only five slides were there areas of good rhythm. The areas of fine rhythm observed had a period of 0.01 mm., with crest and trough each 0.005 mm.
Set 10 was made with the same solution at 50°C. These slides tended to be dendritic and massive. Small circular crystals were numerous on ten slides. Coarse rhythm was evident on fifteen slides, but was usually very irregular. Eight slides showed fine rhythm, with period of 0.01 mm., crest and trough each 0.05 mm. This is the same period observed in slides of the same solution made at 25°C. Set 11 was run as a check on set 10, at a later date; these twenty slides were made at the same temperature (50°C.) and of the same solution (four grams potassium dichromate in one hundred cc. of solution) as those of set 10. The drops put on slides in set 11 were large and resulted in heavy, dendritic masses. All slides showed more or less numerous small circular crystals. Both fine and coarse rhythm were present, but both were irregular and difficult to measure.

Set 12 was made with the solution of four grams of potassium dichromate per one hundred cc. of solution, at 100°C. All twenty slides showed massive scalloped circular crests. Three slides had a few small circular crystals. There were no good examples of either coarse or fine rhythm. While fine rhythm was well marked in slides of this solution made at 25°C., or at 50°C., the slides at 100°C. did not show fine rhythm. This was probably due to the fact that
practically all the material on these slides was, in every case, drawn into the outer scalloped crest, leaving very little solution to crystallize thinly enough to show clear evidences of any kind of rhythm. This was the last set run at constant temperature, with only one drop of solution on each slide.

If all the data in Table IV are considered, it appears at once that coarse rhythm was often irregular and never constant enough to serve as the criterion of periodicity. In considering the occurrence of fine rhythm recorded in Table IV, a summary of occurrence and period size may be of value. Such a summary is set forth in Table V. From the data in this table it becomes plain that temperature and concentration differences, within the wide limits studied, have no influence upon the production of fine rhythm from aqueous solutions of potassium dichromate, providing only that the solution is not so strong, and the temperature not so high, that crystallization proceeds rapidly with the formation of heavy crests which, by their massiveness, prohibit the detection of rhythm which might be present (see set 12). The periods most commonly observed were those of 0.005 mm. and 0.01 mm; these were constant over wide areas on slides made at varying temperatures, with varying concentrations of the
Table V.

Rhythmic Crystallization of Potassium Dichromate. Fine Rhythm.

<table>
<thead>
<tr>
<th>No.</th>
<th>Gm. K₂Cr₂O₇</th>
<th>Molar-temp.</th>
<th>Period</th>
<th>Crest. Trough.</th>
<th>X-rhythm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>per 100 cc.</td>
<td></td>
<td></td>
<td>period</td>
</tr>
<tr>
<td></td>
<td></td>
<td>solution.</td>
<td>sizes</td>
<td>common.</td>
<td>sizes common.</td>
</tr>
<tr>
<td>-----</td>
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</tr>
<tr>
<td>1,2</td>
<td>0.05</td>
<td>0.0017</td>
<td>25°C.</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0025</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>0.0017</td>
<td>50°C.</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0025</td>
<td>0.0025</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>0.0017</td>
<td>100°C.</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.0170</td>
<td>23°C.</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.02</td>
<td>0.01</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>6,7</td>
<td>0.5</td>
<td>0.0170</td>
<td>50°C.</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.015 0.0075 0.0075)</td>
<td>Common within narrow limits.</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>0.0170</td>
<td>100°C.</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.015</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.005 0.01)</td>
<td>0.005</td>
</tr>
<tr>
<td>9</td>
<td>4.0</td>
<td>0.1360</td>
<td>25°C.</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>10,11</td>
<td>4.0</td>
<td>0.1360</td>
<td>50°C.</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>12</td>
<td>4.0</td>
<td>0.1360</td>
<td>100°C.</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>
solution. In general, the crest and trough were of equal width; where this was not the case, it appears that the crest was that of one period, while the trough was that of another period either one-half or double the width of the first. All observed periods were either 0.005 mm. in width or some simple multiple of this width.

X-rhythm was, with one exception, observed only in slides made with the least concentrated solution, sets 1 to 4, inclusive. The periods were 0.005 mm. and 0.01 mm., as in fine rhythm. These areas seem, indeed, to be merely places in which a simple fine rhythm area was crossed by another area of fine rhythm. In one slide of the solution containing 0.5 gm. potassium dichromate per one hundred cc. of solution, run at 23°C., an instance of x-rhythm was observed; this had a period of 0.013 mm. Due to difficulties in measuring, this may have been a slight variation from the 0.015 mm. period noticed in simple fine rhythm. As only one area was observed, no exhaustive study could be made; it is possible, of course, that uncontrolled factors, peculiar to that one slide, caused that particular case of x-rhythm with its anomalous period width.

In summary, it may be said that rhythmic crystallization is of two types, coarse rhythm and fine rhythm. Coarse rhythm is less constant in period than fine rhythm and cannot, in the judgment of the present
writer, be taken as the criterion for absence or presence of rhythm; fine rhythm is of much more constant period, large areas, in fact, showing an extremely constant spacing. It is also noticeable that different slides show large areas with the same constant period for fine rhythm, and this characteristic period is uninfluenced by the temperature at which the slide is made, nor does it depend upon the concentration of the solution used. Only when the solution is comparatively highly concentrated does the thickness of the deposited mass hide the fine rhythm, and then most readily when the slide is made at a high temperature, which causes the rapid formation of one or two massive crests, containing nearly all of the material, rather than the slower formation of a series of crests, or of a comparatively evenly distributed crystal mass. Only when the mass is thin enough to transmit light can the differences in thickness, termed crests and troughs by the present writer, be clearly observed. It is of particular significance that all periods of well defined fine rhythm observed in the crystallization of potassium dichromate are of approximately the same width or are simple multiples of the basic period. This has also been observed by Miss Abbott (69), who further notes that the simple period for ammonium dichromate is different from that
for potassium dichromate, while both of these periods differ from the basic period of sodium dichromate. Miss Abbott did not, however, investigate slides made with dilute solutions or at low temperatures.

3. Effect of Type of Interface on the Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

Experiments were carried out to demonstrate the effect of the type of interface upon the rhythmic crystallization of potassium dichromate. Results are tabulated in Table VI. The potassium dichromate solution used had a concentration of four grams per one hundred cc. of solution. When successive drops of the potassium dichromate solution were allowed to diffuse into distilled water placed beneath a cover slip on a slide, no rhythm resulted. These conditions were planned to simulate those under which rhythmic precipitation by metathesis takes place. (See 58.) The upper interface was liquid to glass.

When water and potassium dichromate solution were allowed to diffuse into each other on an un-covered slide, however, coarse and fine rhythm resulted. The upper interface in this case was liquid to air.

A portion of the potassium dichromate solution was spread on a slide by the method used in 'blood-
Table VI.

Effect of the Type of Interface on the Rhythmic Crystallization of Potassium Dichromate.

Made with a soln. of 4 gms. $K_2Cr_2O_7$ per 100 cc. soln. (0.1360 M)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>Liquid-air.</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Water placed</td>
<td>3</td>
<td>Liquid-glass.</td>
<td>No rhythm.</td>
</tr>
<tr>
<td></td>
<td>between</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cover slip and</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>slide; five</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>successive</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>drops $K_2Cr_2O_7$ soln.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>added, each</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>drying before</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>next was added.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Drop of water</td>
<td>1</td>
<td>Liquid-air.</td>
<td>Coarse and fine rhythm present.</td>
</tr>
<tr>
<td></td>
<td>and drop of</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$K_2Cr_2O_7$ soln.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>allowed to</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>diffuse into</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>each other and</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>dry on uncovered</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>slide.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$K_2Cr_2O_7$ soln. spread</td>
<td>1</td>
<td>Liquid-air.</td>
<td>Coarse and fine rhythm present.</td>
</tr>
<tr>
<td></td>
<td>on slide by</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot;blood-streak&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>method.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$K_2Cr_2O_7$ soln. run between two slides and allowed to dry; slides pulled apart and examined.</td>
<td>2</td>
<td>Liquid-glass.</td>
<td>No rhythm.</td>
</tr>
</tbody>
</table>
streaking. A drop of solution was placed near one end of the slide. A second slide was pressed firmly against the first, at an angle of about 60°, so that the liquid spread along the line of contact of the two slides. The second slide was then drawn along the first, leaving a thin smear of the solution, which was allowed to dry spontaneously. Coarse and fine rhythm resulted. The upper interface was liquid to air.

Potassium dichromate was run between two slides and allowed to dry before the slides were pulled apart. There was no rhythm. The upper interface was liquid to glass.

These experiments substantiate the opinion that a mobile interface must be present for rhythmic crystallization from solution to take place.

4. **Rhythmic Crystallization of Cadmium Iodide.**

Preliminary tests with a solution of cadmium iodide indicated that this salt would exhibit rhythmic crystallization. The cadmium iodide was made by refluxing spongy cadmium metal with iodine in aqueous solution; excess iodine was boiled off and the salt allowed to crystallize from the mother liquor. This salt is given the formula Cd(CdI₄) and
is considered to be the cadmium salt of iodo-cadmic acid, \( H_2(CdI_4) \) (182, p. 148). In the preliminary tests, several cases of convex cones, built up step-wise, much like the old-fashioned straw bee-hives, were observed when a solution of cadmium iodide saturated at room temperature was allowed to crystallize at 100°C. Dilute solution, warmed on the slide, gave good rhythm with basic period of approximately 0.013 mm. Rhythmic crystallization of this salt has not hitherto been reported.

Five slides of a solution of cadmium iodide, saturated at room temperature, were prepared by the method described by Miss Abbott (69). All of these slides showed good coarse rhythm; the evident irregularity was no greater than that often observed in slides of potassium dichromate made by the method of Miers (74). The irregularity appeared, however, very great until a careful inspection showed that the periods reoccurred in groups. A similar phenomenon has been reported by Miss Foster (46, 47) in connection with Liesegang phenomena.

Five slides of a solution of recrystallized cadmium iodide, saturated at room temperature, were prepared and examined. These slides were similar to those obtained with the sample had not been recrystallized. The two samples had been prepared
at different times, by different workers, and served as checks upon each other.

There is no doubt that cadmium iodide exhibits the phenomenon of rhythmic crystallization from aqueous solution. The rhythm is of the kind described as "coarse", and consists of regularly recurring groups. There is enough irregularity to make exact measurements of spacing very difficult. Typical hexagonal crystals of the salt are always present in large numbers; rhythm is most often near the edges of the slide and parallel to them.

5. Investigations on the Effects of Specific Impurities on Rhythmic Crystallization of Potassium Dichromate.

a. Introduction.

The review of literature has shown the general belief that specific impurities may often, if not always, play an important part in rhythmic crystallization. It was demonstrated by Miss Abbott (69) that potassium dichromate would crystallize rhythmically even in the presence of comparatively large amounts of acid or of base. On the other hand, extremely pure solutions of potassium dichromate also exhibited excellent rhythmic crystallization. Miss Abbott found, however, that the presence of potassium chloride in the ratio of one part of the chloride to four parts
of the dichromate did materially affect the clearness of the periodicity. She attributed this effect to the dissimilarity in crystal habit of the two salts.

b. Method.

The method of obtaining rhythmic crystallization employed by Miss Abbott (69) was more rapid and quite as satisfactory as the one used by the present writer in the investigation of the effects of temperature and concentration on rhythmic crystallization, and was, therefore, used for making slides for the study of the effect of specific impurities on rhythmic crystallization. The method consists of heating the solution to be tested to the boiling temperature in a beaker; the slide is then dipped in, quickly removed and allowed to drain and dry. Miss Abbott recommends allowing crystallization to take place in the vapors rising from the boiling solution. In each case, the present writer made three slides of a set of five in this manner, but allowed the material on the other two slides to crystallize after the slide had been removed from the solution, drained by touching the edge to a pile of filter paper and set on edge to dry. The conditions of drying had no noticeable effect on the resulting crystallization.
Potassium dichromate was selected as the salt to be studied, because its normal periods are well known and any deviation from the normal could be easily detected. As specific impurities, potassium chloride, sodium chloride, calcium chloride, potassium nitrate, potassium sulfate and ferric chloride were used. These, as well as the potassium dichromate, were all C.P.

c. Effect of Potassium Chloride on the Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

The most distinct rhythmic crystallization of potassium dichromate was obtained when a concentrated solution of the salt was used. A 0.5 M solution of potassium dichromate is nearly saturated at boiling, and was, therefore, chosen as the solution to be used. For easy comparison, a 0.5 M solution of potassium chloride was also used. The results of this investigation are shown in Table VII. Preliminary tests has shown that the 0.5 M potassium dichromate solution constantly gave fine rhythm, with the usual periods 0.015 mm. and 0.03 mm. Set 1 was made using a solution of seventy cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M potassium chloride. All five slides were dendritic. There was some coarse
Table VII

Effect of Potassium Chloride on the Rhythmic Crystallization of Potassium Dichromate.

<table>
<thead>
<tr>
<th>No. Soln. used</th>
<th>No. slides</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 70 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M KCl.</td>
<td>5</td>
<td>Dendritic. Some coarse rhythm. Fine rhythm distinct in many areas.</td>
</tr>
<tr>
<td>2 60 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M KCl.</td>
<td>5</td>
<td>Thickly dendritic. Some fine rhythm.</td>
</tr>
<tr>
<td>3 50 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M KCl.</td>
<td>5</td>
<td>Potassium dichromate largely dendritic on potassium chloride crystals. Some indications of fine rhythm.</td>
</tr>
<tr>
<td>4 40 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M KCl.</td>
<td>5</td>
<td>Potassium dichromate largely dendritic on potassium chloride crystals. Very faint traces fine rhythm in small areas.</td>
</tr>
<tr>
<td>5 30 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M KCl.</td>
<td>5</td>
<td>Finely dendritic. Some evidences of crude coarse rhythm. No fine rhythm.</td>
</tr>
<tr>
<td>6 20 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M KCl.</td>
<td>5</td>
<td>Potassium dichromate built in very fine dendrites on potassium chloride crystals. No rhythm.</td>
</tr>
<tr>
<td>7 10 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M KCl.</td>
<td>5</td>
<td>Potassium dichromate built in very fine dendrites on potassium chloride crystals. No rhythm.</td>
</tr>
<tr>
<td>8 0.5 M KCl</td>
<td>5</td>
<td>One case crude coarse rhythm. No other indications of rhythm.</td>
</tr>
</tbody>
</table>
rhythm, and many areas of distinct fine rhythm.

Set 2 was made using a solution of sixty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M potassium chloride. The slides of this set were thickly dendritic. Some fine rhythm was present.

The first clear indication of the effect of the chloride came in set 3, made using fifty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M potassium chloride. In these slides the potassium dichromate was largely dendritic on well developed crystals of potassium dichromate. While there were some indications of fine rhythm, its presence was not obvious. In set 4, made using forty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M potassium chloride, the effect was more pronounced. Again the potassium dichromate was largely dendritic on the potassium chloride crystals. There were only extremely faint traces of fine rhythm, and those in very small areas.

Set 5 was made using thirty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M potassium chloride. The potassium dichromate was built in fine dendrites upon the potassium chloride crystals. While there were some evidences of crude coarse rhythm, there was no indication of fine rhythm.
Set 6 was made using twenty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M potassium chloride; set 7 was made using ten cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M potassium chloride. In both these sets the potassium dichromate formed very fine dendrites built upon the potassium chloride crystals. Neither set showed rhythm of any kind.

Set eight was run as a check, using only 0.5 M potassium chloride. There was one case of crude coarse rhythm, but otherwise no indications of rhythm were to be observed.

In summary, these tests showed that a two to one ratio of chloride ion to dichromate ion had a slight effect upon the rhythmic crystallization of potassium dichromate, while a ten to three ratio of chloride ion to dichromate ion completely inhibited the rhythmic crystallization of potassium dichromate. When large amounts of the chloride were present, potassium dichromate built dendritically upon cubic crystals of potassium chloride. Fine rhythm was not found when all of the dichromate was used in building dendrites. Since coarser dendrites of the dichromate appeared, under the influence of the potassium chloride, coincident with the disappearance of fine rhythm, it seems probable that potassium
chloride inhibited fine rhythm formation by modifying the arrangement of the potassium dichromate crystals.

d. Effect of Sodium Chloride on the Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

Table VIII contains data showing the effect of varying amounts of sodium chloride, present as a specific impurity, upon the rhythmic crystallization of potassium dichromate from aqueous solution. The possible crystalline products from a solution containing sodium, chloride, potassium and dichromate ions are sodium chloride, potassium chloride, sodium dichromate and potassium dichromate. The effect of potassium chloride upon the rhythmic crystallization of potassium dichromate has been discussed in the last section. Miss Abbott (69) showed that sodium dichromate crystallized rhythmically, with a period smaller than that of the potassium salt. Effects not obviously due to either potassium chloride or sodium dichromate might, then, be tentatively ascribed to the presence of sodium chloride.

Set 1 was made as a preliminary check on the 0.5 M potassium dichromate used. While there were some dendrites, there were large areas of excellent fine rhythm, of period 0.03 mm., with crest and trough
Table VIII.

Effect of Sodium Chloride on the Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

<table>
<thead>
<tr>
<th>No. Soln. used</th>
<th>No. slides</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0.5 M (K_2\text{Cr}_2\text{O}_7)</td>
<td>5</td>
<td>Some dendrites. Much excellent fine rhythm, period 0.03 mm. (crest and trough each 0.015 mm.).</td>
</tr>
<tr>
<td>2 150 cc. 0.5 M (K_2\text{Cr}_2\text{O}_7), 10 cc. 0.5 M NaCl.</td>
<td>5</td>
<td>Some dendrites. Few areas coarse rhythm. Excellent fine rhythm, period 0.03 mm.</td>
</tr>
<tr>
<td>3 150 cc. 0.5 M (K_2\text{Cr}_2\text{O}_7), 50 cc. 0.5 M NaCl.</td>
<td>5</td>
<td>Dendritic. Some coarse rhythm. Good fine rhythm, periods 0.03 mm. (crest and trough each 0.015 mm.) and 0.045 mm. (crest 0.03 mm., trough 0.015 mm.).</td>
</tr>
<tr>
<td>4 150 cc. 0.5 M (K_2\text{Cr}_2\text{O}_7), 100 cc. 0.5 M NaCl.</td>
<td>5</td>
<td>Many dendrites. Some poorly defined coarse rhythm. Very good fine rhythm, period 0.03 mm. (crest and trough each 0.015 mm.).</td>
</tr>
<tr>
<td>5 80 cc. 0.5 M (K_2\text{Cr}_2\text{O}_7), 100 cc. 0.5 M NaCl.</td>
<td>5</td>
<td>Dendritic. Coarse rhythm present. Much fine rhythm.</td>
</tr>
<tr>
<td>6 70 cc. 0.5 M (K_2\text{Cr}_2\text{O}_7), 100 cc. 0.5 M NaCl.</td>
<td>5</td>
<td>Largely dendritic. Coarse rhythm present. Much fine rhythm.</td>
</tr>
<tr>
<td>7 60 cc. 0.5 M (K_2\text{Cr}_2\text{O}_7), 100 cc. 0.5 M NaCl.</td>
<td>5</td>
<td>Dendritic, with fine dendrites. Coarse rhythm present. Much fine rhythm.</td>
</tr>
<tr>
<td>8 50 cc. 0.5 M (K_2\text{Cr}_2\text{O}_7), 100 cc. 0.5 M NaCl.</td>
<td>5</td>
<td>Largely dendritic. Some coarse rhythm. Much fine rhythm.</td>
</tr>
<tr>
<td>No.</td>
<td>Soln. used.</td>
<td>No. slides.</td>
</tr>
<tr>
<td>-----</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>9</td>
<td>40 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M NaCl.</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>30 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M NaCl.</td>
<td>5</td>
</tr>
<tr>
<td>11</td>
<td>20 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M NaCl.</td>
<td>5</td>
</tr>
<tr>
<td>12</td>
<td>10 cc. 0.5 M K₂Cr₂O₇, 100 cc. 0.5 M NaCl.</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>0.5 M NaCl.</td>
<td>5</td>
</tr>
</tbody>
</table>
each 0.015 mm. This behavior was normal and the solution was, therefore, used in the subsequent tests.

Set 2 was made using one hundred fifty cc. of 0.5 M potassium dichromate with ten cc. of 0.5 M sodium chloride. There were some dendrites and a few areas of coarse rhythm. There was much excellent fine rhythm, period 0.03 mm.

In set 3 a solution of one hundred fifty cc. of 0.5 M potassium dichromate with fifty cc. of 0.5 M sodium chloride was used. The slides were dendritic and showed some coarse rhythm. There was good fine rhythm of periods 0.03 mm., crest and trough each 0.015 mm., and 0.045 mm., crest 0.03 mm. and trough 0.015 mm.

Set 4, made with a solution of one hundred fifty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M sodium chloride, showed many dendrites. There was some poorly defined coarse rhythm; the fine rhythm was very good, with period of 0.03 mm.

Set 5 was made using a solution of eighty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M sodium chloride. The slides were dendritic, with some coarse rhythm and much fine rhythm.

For making set 6, a solution of seventy cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M sodium chloride was used. The slides were largely
dendritic. There was some coarse rhythm and much fine rhythm.

Set 7 was made using sixty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M sodium chloride. The slides were covered with very fine dendrites. Coarse rhythm was present; there was much fine rhythm.

Set 8 was made using fifty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M sodium chloride. The slides were largely dendritic, with some coarse rhythm and much fine rhythm.

A solution of forty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M sodium chloride was used for making set 9. The slides were composed largely of dendritic crystals of potassium dichromate growing out from cubic crystals, probably of sodium chloride. There was some rather irregular coarse rhythm and some poorly defined fine rhythm.

The slides of set 10 were made using thirty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M sodium chloride. Small dendrites of potassium dichromate were built out from cubes of sodium chloride. There were only very faint indications of fine rhythm.

In set 11, made of twenty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M sodium chloride, the potassium dichromate occurred as small crystals built out in all possible directions from cubic sodium chloride crystals. There was some obscure coarse rhythm,
obviously due to drying effects, but no fine rhythm was present in the slides of this set.

Set 12 was made using ten cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M sodium chloride. These slides were much like those of set 11; the potassium dichromate crystals were built upon sodium chloride crystals, as in the last set, and again coarse rhythm, due to drying effects, was observed. No fine rhythm was present.

As a final check on the 0.5 M sodium chloride solution, set 13 was run with this solution alone. The usual regular cubic crystals were resultant. There were, on the five slides, two instances of small areas of irregular coarse rhythm. No fine rhythm was present.

Inspection of the various sets of slides in this series showed that the period of fine rhythm did not decrease; it may be concluded from this that sodium dichromate was not formed to any large extent. Fine rhythm persisted only slightly longer in the series in which sodium chloride was used as impurity than in that in which potassium chloride was used. When the chloride ion was introduced as potassium chloride, a ratio of chloride ion to dichromate ion of two to one caused slight decrease in fine rhythm to result, while a ratio of ten to three caused entire absence of fine rhythm. When both chloride and sodium ions
were introduced, a ratio of sodium and of chloride ions to dichromate ion of five to two caused appreciable decrease in the amount of fine rhythm present, while a ratio of ten to two caused complete absence of fine rhythm. Within the ratios used, a difference between two to one (four to two) and five to two is not very great, however, nor is the difference between ten to three and ten to two highly significant. Within rough limits the two series check each other and one could conclude that the chloride ion was the constant and sole cause of lack of formation of fine rhythm in both series.

It is perhaps worthy of notice that sodium chloride and potassium chloride are both less soluble than potassium dichromate at 100°C. Later (see section g, below) a series of solutions was run with calcium chloride as the foreign salt; this salt is nearly twice as soluble (molar solubility) as either of the chlorides just considered.

e. Effect of Potassium Nitrate on the Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

For the investigation of the effect of the nitrate ion on the rhythmic crystallization of potassium dichromate, potassium nitrate was introduced. The results are recorded in Table IX. Set 1 was the check on the
### Table IX.

Effect of Potassium Nitrate on the Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

<table>
<thead>
<tr>
<th>No. Soln. used</th>
<th>No. slides</th>
<th>Results.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0.5 M K₂Cr₂O₇</td>
<td>5</td>
<td>Many dendritic areas. Fine rhythm on all slides; periods 0.045 mm. (crest 0.03 mm., trough 0.015 mm.) and 0.03 mm. (crest and trough each 0.015 mm.).</td>
</tr>
<tr>
<td>2 150 cc. 0.5 M K₂Cr₂O₇, 10 cc. 0.5 M KNO₃</td>
<td>5</td>
<td>Largely dendritic. Large areas fine rhythm; periods 0.03 mm. (crest and trough each 0.015 mm.) and 0.045 mm. (crest 0.03 mm., trough 0.015 mm.).</td>
</tr>
<tr>
<td>3 150 cc. 0.5 M K₂Cr₂O₇, 20 cc. 0.5 M KNO₃</td>
<td>5</td>
<td>Largely dendritic. Coarse rhythm, poorly defined. Fine rhythm present, period 0.03 mm.</td>
</tr>
<tr>
<td>4 150 cc. 0.5 M K₂Cr₂O₇, 30 cc. 0.5 M KNO₃</td>
<td>5</td>
<td>Largely dendritic; dendrites show long, stout axes in may cases. Fine rhythm present; periods 0.03 mm. (crest and trough each 0.015 mm.), 0.045 mm. (crest 0.03 mm., trough 0.015 mm.; or crest 0.015 mm., trough 0.03 mm.) and 0.06 mm. (crest and trough each 0.03 mm.).</td>
</tr>
<tr>
<td>5 150 cc. 0.5 M K₂Cr₂O₇, 40 cc. 0.5 M KNO₃</td>
<td>5</td>
<td>Largely dendritic; long stout axes often present. Coarse rhythm poorly defined. Fine rhythm present; period 0.03 mm. (crest and trough each 0.015 mm.).</td>
</tr>
<tr>
<td>6 150 cc. 0.5 M K₂Cr₂O₇, 50 cc. 0.5 M KNO₃</td>
<td>5</td>
<td>Largely dendritic, with long central axes. Poorly defined coarse rhythm. Fine rhythm present; periods 0.03 mm. (crest and trough each 0.015 mm.) and 0.075 mm. (crest 0.06 mm., trough 0.015 mm.).</td>
</tr>
<tr>
<td>7 150 cc. 0.5 M K₂Cr₂O₇, 60 cc. 0.5 M KNO₃</td>
<td>5</td>
<td>Largely dendritic, with long axial crystals. Coarse rhythm extremely slight. Fine rhythm present, largely obscured by overlying dendrites; period 0.03 mm.</td>
</tr>
<tr>
<td>8 150 cc. 0.5 M K₂Cr₂O₇, 70 cc. 0.5 M KNO₃</td>
<td>5</td>
<td>Dendritic with long, strong central axes. No fine rhythm. Some evidences very irregular coarse rhythm.</td>
</tr>
</tbody>
</table>
0.5 M potassium dichromate used. All slides showed fine rhythm, with periods 0.045 mm. and 0.03 mm. Potassium nitrate had been examined for fine rhythm previously, and none had been found.

Set 2 was made using one hundred fifty cc. of 0.5 M potassium dichromate with ten cc. of 0.5 M potassium nitrate. The slides were largely dendritic but with large areas of fine rhythm of periods 0.03 mm., crest and trough each 0.015 mm., and 0.045 mm., crest 0.03 mm. and trough 0.015 mm.

In the next set, 3, made with one hundred fifty cc. of 0.5 M potassium dichromate and twenty cc. of 0.5 M potassium nitrate, there was also considerable fine rhythm, period 0.03 mm. There was some poorly defined coarse rhythm, and there were many dendrites.

In set 4, made using one hundred fifty cc. of 0.5 M potassium dichromate with thirty cc. of 0.5 M potassium nitrate, there were many dendrites, often with long stout axes. Fine rhythm was present with period 0.03 mm., 0.045 mm. and 0.06 mm.

A solution of one hundred fifty cc. of 0.5 M potassium dichromate with forty cc. of 0.5 M potassium nitrate was used for making set 5. The slides were largely dendritic, often with long stout central axes in the dendrites. There was some poorly defined
coarse rhythm and good areas of fine rhythm, period 0.03 mm.

Set 6, made using one hundred fifty cc. of 0.5 M potassium dichromate with fifty cc. of 0.5 M potassium nitrate, has many dendrites with long central axes. There was some poorly defined coarse rhythm. Fine rhythm was present, periods 0.03 mm. and 0.075 mm.

The fine rhythm was diminished in set 7, made with one hundred fifty cc. of 0.5 M potassium dichromate with sixty cc. of 0.5 M potassium nitrate. The typical long axes appeared in the dendrites. Coarse rhythm was slight, and fine rhythm, period 0.03 mm., was slight and largely obscured by the dendrites.

Set 8 was made using one hundred fifty cc. of 0.5 M potassium dichromate with seventy cc. of 0.5 M potassium nitrate. There were many dendrites with long, strong central axes. There were some evidences of very irregular coarse rhythm, but fine rhythm was entirely absent in this set.

Definite curtailment of fine rhythm did not appear until set 7, when the ratio of nitrate ion to dichromate ion was two to five (six to fifteen), while in set 8, with corresponding ratio seven to fifteen, fine rhythm was entirely suppressed. The ratio of chloride to dichromate ion necessary for complete suppression of fine rhythm was approximately
ten to three. The nitrate ion, therefore, is shown to be far more effective than the chloride ion in the inhibition of rhythmic crystallization of potassium dichromate from aqueous solution.

f. Effect of Potassium Sulfate on the Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

Potassium sulfate was used as a specific impurity to determine the effect of the presence of the sulfate ion upon the periodic crystallization of potassium dichromate. The data are shown in Table X. Set 1 shows the usual check on the 0.5 M potassium dichromate used. There was good fine rhythm on all slides, period 0.015 mm. There was also some good coarse rhythm, period 0.06 mm.

For making set 2, a solution of one hundred fifty cc. of 0.5 M potassium dichromate with ten cc. of 0.5 M potassium sulfate was used. The slides tended to be dendritic. They showed good fine rhythm, period 0.015 mm., and some good coarse rhythm, period 0.075 mm.

Set 3 was made using a solution of one hundred fifty cc. of 0.5 M potassium dichromate with twenty cc. of 0.5 M potassium sulfate. There were many dendrites and some irregular coarse rhythm. There
Table X.
Effect of Potassium Sulfate on the Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

<table>
<thead>
<tr>
<th>No.</th>
<th>Soln. used.</th>
<th>No. Slides</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5 M K₂Cr₂O₇</td>
<td>5</td>
<td>All slides show good fine rhythm, period 0.015 mm. Some good coarse rhythm, period 0.06 mm.</td>
</tr>
<tr>
<td>2</td>
<td>150 cc. 0.5 M K₂Cr₂O₇, 10 cc. 0.5 M K₂SO₄</td>
<td>5</td>
<td>These slides tend to be dendritic. Good fine rhythm, period 0.015 mm. Some good coarse rhythm, crest 0.045 mm. space 0.03 mm.</td>
</tr>
<tr>
<td>3</td>
<td>150 cc. 0.5 M K₂Cr₂O₇, 20 cc. 0.5 M K₂SO₄</td>
<td>5</td>
<td>Many dendrites; some irregular coarse rhythm. Much fine rhythm, period 0.015 mm.; one slide shows wide area fine rhythm, period 0.045 mm.</td>
</tr>
<tr>
<td>4</td>
<td>150 cc. 0.5 M K₂Cr₂O₇, 30 cc. 0.5 M K₂SO₄</td>
<td>5</td>
<td>Many dendrites; some irregular coarse rhythm. Several large areas fine rhythm, periods 0.015 mm. and 0.045 mm.</td>
</tr>
<tr>
<td>5</td>
<td>150 cc. 0.5 M K₂Cr₂O₇, 40 cc. 0.5 M K₂SO₄</td>
<td>5</td>
<td>Many dendrites; poorly defined coarse rhythm. Much fine rhythm, periods 0.015 mm. and 0.03 mm.</td>
</tr>
<tr>
<td>6</td>
<td>150 cc. 0.5 M K₂Cr₂O₇, 50 cc. 0.5 M K₂SO₄</td>
<td>5</td>
<td>Many dendrites. Coarse rhythm present, but dendritic and irregular. Fine rhythm very abundant, periods 0.015 mm. and 0.03 mm.</td>
</tr>
<tr>
<td>7</td>
<td>150 cc. 0.5 M K₂Cr₂O₇, 60 cc. 0.5 M K₂SO₄</td>
<td>5</td>
<td>Largely dendritic. Some very irregular coarse rhythm. Many good areas fine rhythm, periods 0.015 mm., 0.03 mm. and 0.045 mm.</td>
</tr>
<tr>
<td>8</td>
<td>150 cc. 0.5 M K₂Cr₂O₇, 70 cc. 0.5 M K₂SO₄</td>
<td>5</td>
<td>Largely dendritic. Large areas fine rhythm, periods 0.015 mm. and 0.03 mm.</td>
</tr>
<tr>
<td>No.</td>
<td>Soln. used</td>
<td>No. slides</td>
<td>Results</td>
</tr>
<tr>
<td>-----</td>
<td>------------</td>
<td>------------</td>
<td>---------</td>
</tr>
<tr>
<td>9</td>
<td>150 cc. 0.5 M 5</td>
<td>Largely dendritic; some poorly defined coarse rhythm. Fine rhythm present, period 0.03 mm.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇, 80 cc. 0.5 M K₂SO₄.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>150 cc. 0.5 M 5</td>
<td>Largely dendritic; some irregular coarse rhythm. Many large potassium sulfate crystals on which potassium dichromate has built. Considerable fine rhythm, periods 0.015 mm. and 0.03 mm.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇, 90 cc. 0.5 M K₂SO₄.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>150 cc. 0.5 M 5</td>
<td>Largely dendritic; some irregular coarse rhythm. Large crystals of the salts often obvious. Large areas fine rhythm, periods 0.015 mm. and 0.03 mm.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇, 100 cc. 0.5 M K₂SO₄.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>150 cc. 0.5 M 5</td>
<td>Largely dendritic; coarse and fine rhythm present, but usually not well defined. Some measureable areas fine rhythm, periods 0.03 mm. and 0.045 mm.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇, 150 cc. 0.5 M K₂SO₄.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>150 cc. 0.5 M 5</td>
<td>Almost completely dendritic, with large crystals. Two poorly defined areas fine rhythm; one area very irregular coarse rhythm. Branching of dendrites is extremely regular, suggesting a new type of rhythm.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇, 200 cc. 0.5 M K₂SO₄.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.5 M K₂SO₄. 5</td>
<td>Dendritic. One area coarse rhythm; otherwise no indications of either fine or coarse rhythm.</td>
<td></td>
</tr>
</tbody>
</table>
was much fine rhythm, period 0.015 mm., and one excellent area fine rhythm, period 0.045 mm. Both these periods for fine rhythm were common in set 4, made with one hundred fifty cc. of 0.5 M potassium dichromate and thirty cc. of 0.5 M potassium sulfate.

A solution of one hundred fifty cc. of 0.5 M potassium dichromate with forty cc. of 0.5 M potassium sulfate was used for making set 5. These slides showed many dendrites. Coarse rhythm was poorly defined, but there was much fine rhythm, periods 0.015 mm. and 0.03 mm. Set 6, made with one hundred fifty cc. of 0.5 M potassium dichromate with fifty cc. of 0.5 M potassium sulfate, also had many dendrites. The coarse rhythm present was dendritic and irregular, but good fine rhythm was very abundant, with periods 0.015 mm. and 0.03 mm.

Set 7 was made using one hundred fifty cc. of 0.5 M potassium dichromate with sixty cc. of 0.5 M potassium sulfate. The slides were largely dendritic. Coarse rhythm was present, but very irregular. There were many good areas of fine rhythm, with periods of 0.015 mm., 0.03 mm. and 0.045 mm. Much like these slides were those of set 8, made with one hundred fifty cc. of 0.5 M potassium dichromate with seventy cc. of 0.5 M potassium sulfate. Large areas of fine rhythm, of periods 0.015 mm. and 0.03 mm.,
were present, although these slides, also, were largely dendritic.

For set 9, a solution of one hundred fifty cc. of 0.5 M potassium dichromate with eighty cc. of 0.5 M potassium sulfate was used. There was some poorly defined coarse rhythm present. The slides were largely dendritic. There was, however, good fine rhythm present, period 0.03 mm.

In set 10, made using one hundred fifty cc. of 0.5 M potassium dichromate with ninety cc. of 0.5 M potassium sulfate, the potassium dichromate crystals were obviously dendritic upon large crystals of potassium sulfate. There was some irregular coarse rhythm; considerable fine rhythm was present, of periods 0.015 mm. and 0.03 mm. Set 11, made using one hundred fifty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.5 M potassium sulfate, also showed large potassium sulfate crystals with large dendrites of potassium dichromate built upon them. There was some irregular coarse rhythm; and large areas of fine rhythm were present, with periods 0.015 mm. and 0.03 mm.

Set 12 was made using one hundred fifty cc. of 0.5 M potassium dichromate with an equal volume of 0.5 M potassium sulfate. The slides were largely dendritic. Coarse and fine rhythms were present, but
usually not well defined. A few measurable areas of fine rhythm showed periods of 0.03 mm. and 0.045 mm. The inhibition of fine rhythm begun here was practically complete in set 13, made with one hundred fifty cc. of 0.5 M potassium dichromate with two hundred cc. of 0.5 M potassium sulfate. These slides were almost completely dendritic, with the branching of the dendrites so regular as to suggest that this might be a type of true rhythm. One areas of very irregular coarse rhythm and two poorly defined areas of fine rhythm were observed on five slides.

As a final check, set 14 was made using 0.5 M potassium sulfate alone. The slides were dendritic. There was no indication of rhythm other than one area of coarse rhythm, doubtless due to drying effects.

The sulfate ion did not begin to modify the rhythmic crystallization of potassium dichromate, according to the data shown, until the ratio of sulfate ion to dichromate ion was approximately one to one. When the ratio was approximately four to three, rhythm was almost completely inhibited. The sulfate ion, therefore, is more effective in inhibiting the formation of fine rhythm than the chloride ion, but less effective than the nitrate ion.
g. Effect of Calcium Chloride on the Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

In the cases in which sodium chloride and potassium chloride were used as specific impurities in potassium dichromate solutions, it was found that the ratios of chloride ion to dichromate ion concentration of ten to two and of ten to three, respectively, caused complete inhibition of fine rhythm. Sodium and potassium ions are in many respects not markedly dissimilar. They are both monovalent and both quite similar in properties. It appeared desirable to try the effect of the presence of a divalent cation, and for this purpose a series of slides was made and examined, using calcium chloride as the specific impurity. Calcium chloride and its hydrates are much more soluble than potassium dichromate. Data are given in Table XI. A 0.25 M solution of calcium chloride was used with a 0.5M solution of potassium dichromate, so that equal volumes of the two solutions would contain equal molar concentrations of the chloride ion and of the dichromate ion, respectively.

The slides of set 1 were made using a solution of fifty cc. of 0.5 M potassium dichromate with ten cc. of 0.25 M calcium chloride. The slides were largely dendritic. There was some good coarse rhythm, and much excellent fine rhythm, periods 0.02 mm. and 0.025 mm.
Table XI.

Effect of Calcium Chloride on the Rhythmic Crystallization
of Potassium Dichromate from Aqueous Solution.

<table>
<thead>
<tr>
<th>No. Soln. used.</th>
<th>No. slides</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 50 cc. 0.5 M</td>
<td>5</td>
<td>Largely dendritic. Some good coarse rhythm. Excellent fine rhythm, periods 0.02 mm. and 0.025 mm.</td>
</tr>
<tr>
<td>K₂Cr₂O₇,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 cc. 0.25 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 50 cc. 0.5 M</td>
<td>5</td>
<td>Dendritic. Some coarse rhythm. Good fine rhythm, periods 0.02 mm., 0.025 mm. and 0.05 mm.</td>
</tr>
<tr>
<td>K₂Cr₂O₇,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 cc. 0.25 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 50 cc. 0.5 M</td>
<td>5</td>
<td>Largely dendritic. Few areas good coarse rhythm. Good fine rhythm, periods 0.03 mm. and 0.01 mm.</td>
</tr>
<tr>
<td>K₂Cr₂O₇,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 cc. 0.25 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 50 cc. 0.5 M</td>
<td>5</td>
<td>Largely dendritic, with some coarse rhythm. Excellent fine rhythm, period 0.015 mm.</td>
</tr>
<tr>
<td>K₂Cr₂O₇,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 cc. 0.25 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 50 cc. 0.5 M</td>
<td>5</td>
<td>Largely dendritic, with some irregular coarse rhythm. Fine rhythm excellent in many areas, period 0.03 mm.</td>
</tr>
<tr>
<td>K₂Cr₂O₇,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 cc. 0.25 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 40 cc. 0.5 M</td>
<td>5</td>
<td>Almost completely dendritic, with small areas good fine rhythm, period 0.035 mm.</td>
</tr>
<tr>
<td>K₂Cr₂O₇,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 cc. 0.25 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 30 cc. 0.5 M</td>
<td>5</td>
<td>Dendritic, with rhythmic branching in dendrites. Some coarse rhythm. No typical fine rhythm.</td>
</tr>
<tr>
<td>K₂Cr₂O₇,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 cc. 0.25 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 20 cc. 0.5 M</td>
<td>5</td>
<td>Rhythmic branching in dendrites. Some indications of coarse rhythm. No typical fine rhythm.</td>
</tr>
<tr>
<td>K₂Cr₂O₇,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 cc. 0.25 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Soln. used.</td>
<td>No. slides</td>
</tr>
<tr>
<td>-----</td>
<td>-------------</td>
<td>------------</td>
</tr>
<tr>
<td>9</td>
<td>10 cc. 0.5 M</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 cc. 0.25 M CaCl₂</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.25 M CaCl₂</td>
<td>5</td>
</tr>
</tbody>
</table>

In set 2, made with fifty cc. of 0.5 M potassium dichromate with twenty cc. of 0.25 M calcium chloride, the results were much like those in set 1. The material was largely dendritic, with some coarse rhythm. Fine rhythm was good, with periods 0.02 mm., 0.025 mm. and 0.05 mm.

A solution of fifty cc. of 0.5 M potassium dichromate with thirty cc. of 0.25 M calcium chloride was used for making set 3. Again the slides were largely dendritic, with a few areas of good coarse rhythm. There was much good fine rhythm, with periods 0.03 mm. and 0.01 mm.

Set 4 was made using fifty cc. of 0.5 M potassium dichromate with forty cc. of 0.25 M calcium chloride. The slides were largely dendritic, with some coarse rhythm. There was considerable excellent fine
rhythm, of period 0.015 mm.

For making set 5, a solution of fifty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.25 M calcium chloride was used. The slides were largely dendritic, with some irregular coarse rhythm. Fine rhythm was excellent in many areas, with period 0.03 mm.

A solution of forty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.25 M calcium chloride was used for making set 6. The slides were almost completely dendritic, with small areas of good fine rhythm, of period 0.035 mm.

Set 7 was made using thirty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.25 M calcium chloride. The slides were dendritic, with rhythmic branching of the dendrites. These slides show a transition from the typical fine rhythm to the open parallel branching often observed in dendrites of potassium dichromate. There was some coarse rhythm, but no typical fine rhythm.

In set 8, made using twenty cc. of 0.5 M potassium dichromate with one hundred cc. of 0.25 M calcium chloride, rhythmic branching of the dendrites was very obvious. There were some indications of coarse rhythm, but no traces of typical fine rhythm.
A solution of ten cc. of 0.5 M potassium dichromate with one hundred cc. of 0.25 M calcium chloride was used for making set 9. There were many typical calcium chloride crystals, and numerous dendrites of potassium dichromate. Some of these dendrites showed rudimentary rhythmic branching. There were obscure indications of coarse rhythm.

Set 10 was a check run on the 0.25 M calcium chloride solution. The crystals were very deliquescent, and were often aligned parallel to each other over large areas. There was, however, no true rhythm of any kind.

The slides of this series were of especial interest in that they showed a transition from the parallel branching of dendrites (set 7) to typical fine rhythm (set 6). This takes us back one step further toward the ultimate cause of fine rhythm. Fine rhythm is due to rhythmic and very regular branching of fine dendrites. Miss Abbott (69) observed the crystals in crest and trough to be lying at right angles to each other; the 'branch' lies at right angles to the parent 'stem'.

When the ratio of chloride ion to dichromate ion was five to two (set 6), fine rhythm was still present, but when this ratio was ten to three (set 7)
fine rhythm was not typical, although the transition type of rhythmic branching of dendrites was observed. When sodium or potassium chloride was used in place of calcium chloride, the ratio of chloride ion to dichromate ion at the point of inhibition of fine rhythm was ten to two or ten to three, respectively. The charge on the cation cannot be an important factor, since the effect of the chloride ion is constant, no matter whether it is introduced with a monovalent cation, as sodium or potassium, or with a divalent cation, as calcium. In any case, a ratio of chloride ion to dichromate ion of ten to three causes inhibition of fine rhythm. There is also further substantiation of the view that the anion alone affects the inhibition of rhythm, in this case, at least, since the ratio of chloride ion to dichromate ion is constant in the presence of sodium ion, calcium ion or excess potassium ion. These results were unexpected in view of the data obtained by Miss Abbott (69).

h. Effect of Ferric Chloride on the Rhythmic Crystallization of Potassium Dichromate from Aqueous Solution.

An attempt was made to introduce a 0.166 M solution of ferric chloride (without added hydrochloric acid) as specific impurity into the 0.5 M potassium dichromate solution. A set was run using
fifty cc. of 0.5 M potassium dichromate with ten cc. of 0.166 M ferric chloride, and fine rhythm was found on all five slides. Another set made using fifty cc. of 0.5 M potassium dichromate with twenty cc. of 0.166 M ferric chloride also showed fine rhythm, but a precipitate, probably basic ferric chloride, formed before slides could be made, obstructing the course of crystallization in many areas. Ferric chloride undergoes hydrolysis with great ease. No further attempts were made to use the ferric chloride solution as specific impurity.

6. Spacing of Periods from the Center of Crystallization.

The spacing of bands has been discussed. Measurements of distances of the bands from the center of crystallization were often difficult, as in some cases the center was surrounded by a large irregular area of undifferentiated precipitate, while in other cases the arcs formed by the crests and troughs were sections of incomplete circles, the centers of which were occupied by dendrites, or were, in some cases, not even on the slide. Measurements were taken in several cases, however, in an attempt to determine whether potassium dichromate gives rhythmic bands which agree with the findings of Jablczynski (132) for Liesegang rings, or of Hughes (91) and Dippy (88).
for rhythmic crystallization of melts. Table XII shows the results of measurements taken as typical during the course of the present investigation.

Jablczynski (132) found the ratio between rings formed by metathesis of silver nitrate and potassium dichromate in gelatin gel to be constant, expressed by

\[
\frac{h_3 - h_2}{h_2 - h_1} = A,
\]

where \( h_n \) is the distance of the \( n \)th ring from the point of entrance of the diffusing silver nitrate solution.

Hughes (91) and Dippy (88), investigating cases of rhythmic solidification from the melt, found that by plotting the logarithm of \( N \), the number of rings counted from the center, against the logarithm of \( r \), the distance of the ring from the center, a straight line was obtained, with the general equation:

\[
\log N = a \log r + \log K
\]

where \( N \) and \( r \) are defined as above, \( a \) is the slope of the line to the axis of \( \log r \), and \( \log K \) is the intercept on the axis of \( \log N \).

In Table XIII a comparison is made between the results recorded in Table XII and those obtained by Jablczynski and by Hughes. In slides 2, 3 and 5, agreement with Jablczynski was perfect, as the
Table XII.
Measurements from Centers.

<table>
<thead>
<tr>
<th>No.</th>
<th>Soln. used.</th>
<th>Distance of successive periods from center of crystallization (mm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150 cc. 0.5 M</td>
<td>0.045; 0.070; 0.095; 0.125; 0.155.</td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇, 100 cc. 0.5 M K₂SO₄.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.5 M.</td>
<td>0.060; 0.075; 0.090; 0.105; 0.120; 0.135; 0.150.</td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇,</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>50 cc. 0.5 M</td>
<td>0.010; 0.015; 0.020; 0.025; 0.030; 0.035; 0.040; 0.045.</td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇, 10 cc. 0.166 M FeCl₅.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>50 cc. 0.5 M</td>
<td>0.020; 0.040; 0.060; 0.100; 0.120; 0.140; 0.160.</td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇, 20 cc. 0.25 M CaCl₂.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>50 cc. 0.5 M</td>
<td>0.015; 0.030; 0.045; 0.060; 0.075; 0.090.</td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇, 40 cc. 0.25 M CaCl₂.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>40 cc. 0.5 M</td>
<td>0.060; 0.095; 0.150; 0.160; 0.200; 0.235.</td>
</tr>
<tr>
<td></td>
<td>K₂Cr₂O₇, 100 cc. 0.25 M CaCl₂.</td>
<td></td>
</tr>
</tbody>
</table>
Table XIII.
Comparison of Results with Those of Jablczynski and of Hughes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Soln. used.</th>
<th>Values of $A; \frac{h_2-B_2}{B_3-B_1} = A$.</th>
<th>Agreement with Jablczynski</th>
<th>Agreement with Hughes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150 cc. 0.5 M $K_2Cr_2O_7$, 100 cc. 0.5 M $K_2SO_4$.</td>
<td>1.00, 1.20, 1.00.</td>
<td>Partial.</td>
<td>Fair.</td>
</tr>
<tr>
<td>2</td>
<td>0.5 M $K_2Cr_2O_7$.</td>
<td>1.00, 1.00, 1.00.</td>
<td>Perfect.</td>
<td>Fair.</td>
</tr>
<tr>
<td>3</td>
<td>50 cc. 0.5 M $K_2Cr_2O_7$, 10 cc. 0.166 M $FeCl_3$.</td>
<td>1.00, 1.00, 1.00.</td>
<td>Perfect.</td>
<td>Almost perfect.</td>
</tr>
<tr>
<td>4</td>
<td>50 cc. 0.5 M $K_2Cr_2O_7$, 20 cc. 0.25 M $CaCl_2$.</td>
<td>1.00, 2.00, 0.50, 1.00.</td>
<td>Partial.</td>
<td>Good.</td>
</tr>
<tr>
<td>5</td>
<td>50 cc. 0.5 M $K_2Cr_2O_7$, 40 cc. 0.25 M $CaCl_2$.</td>
<td>1.00, 1.00, 1.00.</td>
<td>Perfect.</td>
<td>Excellent.</td>
</tr>
<tr>
<td>6</td>
<td>40 cc. 0.5 M $K_2Cr_2O_7$, 100 cc. 0.25 M $CaCl_2$.</td>
<td>1.85, 0.15, 4.00, 0.88.</td>
<td>Negative.</td>
<td>Fair.</td>
</tr>
</tbody>
</table>
value $\frac{h_3 - h_2}{h_2 - h_1} = A$ remained constant. In slides 1 and 4, the value of $A$ was constant for some ratios, but not for all, while in slide 6, $A$ had no constancy.

On plotting the logarithm of the number of rings, counted from the center, against the logarithm of the distance of the rings from the center, all six slides gave statistically straight lines, although slides 3 and 5 were much more nearly perfect than the others. The lines obtained from plotting the data, which are given in Table XIV, are shown on the accompanying graph (p.139). Slides 1, 2 and 3 show a tendency to give a curve from data near the center of crystallization, but many more cases would have to be investigated to prove any significance in this. Such investigation is difficult, as has been pointed out. The agreement with the results obtained by Hughes and by Dippy is, however, very good.

The slides examined were chosen at random from among those in which centers of crystallization were distinct. They are, therefore, a fair sample of results obtained during this investigation. No coarse rhythm was taken for these calculations, as coarse rhythm which exhibits a center has always formed from the outside inwards toward the center.

If slides had been taken exhibiting the usual fine rhythm of extremely constant spacing over wide
areas in large arcs such that the "center of crystallization" would be situated off the slide, no distances from the center could have been measured. If the first period formed had been used as a "center of crystallization" and measurements made from it, however, a regular series like those in slides 2, 3 and 5 would have been found in those numerous cases in which the periods are of equal width over large areas. In such cases, there would again be agreement with the work of Jablczynski and with that of Hughes and of Dippy.
Graph I. Logarithm of number of period plotted against logarithm of distance from center.
It may be concluded that the relationship noticed by Jablczynski holds in many cases, but is not universally true for the phenomenon at present under investigation. By plotting the logarithm of the number of rings counted from the center against the logarithm of the distance from the center, as suggested by Hughes, a statistically straight line is obtained in every case.

C. Discussion of Results.

The experimental work has shown that in such widely different compounds as cadmium sulfate and potassium dichromate rhythmic crystallization is not materially affected by differences in temperature or in concentration of the aqueous solution from which crystallization takes place.

The smallest period observed for both cadmium sulfate and potassium dichromate was 0.005 mm. Others periods were multiples of this width. While there was a comparatively large margin of error in measurements of such low magnitude, the fact that much larger periods were, within the limits of error of the measurements, simple multiples of this basic period makes it probable that the value 0.005 mm. is very nearly correct. The periods noted were,
in every case, those most commonly observed; other periods did occur, but not uniformly or over wide areas. Whatever the force may be which acts over wide areas to produce rhythmic crystallization, it most often, in the cases studied, has a recurrent phase every 0.005 mm. or at some simple multiple of approximately this distance.

There are several possible explanations for the recurrence of a simple period. As most of the work in this investigation was done with potassium dichromate, and as potassium dichromate may be taken as typical of a large number of compounds exhibiting the phenomenon of rhythmic crystallization, the discussion will now be confined to a consideration of this salt. The basic period of rhythm for potassium dichromate was found to be 0.005 mm., regardless of the temperature, concentration of solution used, or impurities present. Even coarse rhythm, although extremely irregular for the most part, usually has periods of multiples of 0.005 mm.

When crystallization is taking place on a slide prepared as suggested by Miss Abbott(69), it is possible to observe which areas crystallize with extreme rapidity, and which crystallize more slowly. On observing these areas under the microscope, it is found that the areas which crystallize with most
rapidity are either obviously and finely dendritic or exhibit extremely perfect fine rhythm, often about several centers of crystallization. Areas crystallizing with moderate rapidity are coarsely dendritic, often with periodic branching of the dendrites. The areas which crystallize more slowly are often areas exhibiting coarse rhythm, and if crystallization is comparatively very slow, the rhythm may be so coarse as to be macroscopic. This is the condition attained by warming a drop of liquid, on a slide, over a low flame, as suggested by Miers (63). Crystallization may, however, become so slow as to favor the formation of large crystals of the salt rather than dendrites; in such a case no rhythm results.

During the course of the experiments with solutions of potassium dichromate with calcium chloride, a form transitional between simple rhythmic branching of dendrites and typical fine rhythm was observed. It appears, therefore, that fine rhythm is essentially dendritic material, rhythmically branched, the whole so compacted as to have lost, or modified, its obvious dendritic structure. Miss Abbott (69) has noticed, and the present writer has confirmed the observation, that the crystals lie parallel within a crest or a trough, but that the crystals
of the crest are perpendicular to those of the trough. In rhythmic dendritic branching, each branch is perpendicular to the stem from which it arises. By formation of secondary and tertiary branches, forms very near to the x-rhythm reported in these investigations result.

Trough and crest are not separated by a straight and sudden break; under high magnification, it is easily seen that the transition is not sharp. The distance across a trough or a crest is, therefore, approximate, at best, and between this fact and the difficulty in accurately measuring a distance as small as 0.005 mm., it is not safe to place too much emphasis on the recurrence of 0.005 mm. and its multiples as period widths. These period widths give an indication, however, of the distance between the inner edge, for example, of one zone of supersaturation and the corresponding edge of the next zone.

There is little need to enlarge upon the Ostwald supersaturation theory of rhythmic crystallization as modified by Morse (70) and as applied by Miss Abbott (69). Whatever the initial concentration of the solution, and whatever the temperature at which the slide is prepared, the saturation point must be reached before crystals can form. With the
large surface area exposed for evaporation, the small amount of solution upon a slide must become supersaturated with great rapidity. Release of supersaturation causes rapid forward growth of crystals, the tips of which are constantly pushing into the supersaturated liquid and being bathed by it. As supersaturation is overcome, this rapid growth ceases and a series of crystals is laid down perpendicular to the first. After the release of supersaturation, the bathing liquid is not too concentrated to allow the development of several surfaces rather than, with great rapidity, to build upon a few favored faces. During rapid growth, it is probable that only the surfaces facing against the solution are built upon, and the crystal grows rapidly in the forward direction, pushing the solution out of contact with less favored surfaces. In the next stage, less favored faces have a chance to develop, as the growth is slower. As potassium dichromate has no water of crystallization, the release of supersaturation not only removes the salt from solution, but also leaves an excess of water behind, and rapid diminution in concentration must result. The sudden deposition of material on faces in contact with the solution must cease within a short interval, both of time and of space. A space
interval ensues in which the crystals are built slowly and form at right angles to those formed rapidly. This growth continues for some time, during which supersaturation is being built up by evaporation at a distance from the crystals. When the crystal growth reaches this next area of supersaturation, rapid growth again ensues, with the formation of another area of forward pointing crystals. The cycle is repeated again and again, resulting in typical fine rhythm. Rhythmic branching of dendrites must take place in much the same manner when crystallization is somewhat less rapid and larger crystal masses can form.

When crystallization takes place slowly enough for coarse rhythm to form, diffusion may be sufficient to deplete the area of slow growth to such an extent that few crystals, or none, are formed in this region.

The recurrence of regular periods is not surprising. A series of conditions is repeated regularly in time and space; periodicity is the obvious result.

The most constant relationship discovered is in accord with the work of Hughes (91); when the logarithm of the number of rings counted from the center is plotted against the logarithm of the distance from the center, the resulting line is always straight (within experimental limits).
The influence of added salts upon the rhythmic crystallization of potassium dichromate is apparently due to the effect of the anion introduced. Table XV shows the radii of cations and anions of the salts introduced and the ratio of the molar concentration of the introduced anion to potassium dichromate that was necessary to prevent fine rhythm formation in each case.

Table XV.
Ionic Sizes.

<table>
<thead>
<tr>
<th>Salt introduced.</th>
<th>Radius cation (Å)</th>
<th>Radius anion (Å)</th>
<th>Ratio molar concn. anion to molar concn. K₂Cr₂O₇ to prevent rhythm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>1.00</td>
<td>1.80</td>
<td>10:2</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>1.33</td>
<td>1.80</td>
<td>10:3</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>1.05</td>
<td>1.80</td>
<td>10:3</td>
</tr>
<tr>
<td>Potassium sulfate</td>
<td>1.33</td>
<td>1.65</td>
<td>4:3</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>1.33</td>
<td>1.26</td>
<td>1.4:3 (7:15)</td>
</tr>
</tbody>
</table>

The chloride ion was effective in the same amount, within experimental limits of error, when added as sodium chloride, potassium chloride or calcium chloride. In every case, a ratio of chloride ion to potassium dichromate of ten to two or three
was sufficient to prevent the formation of fine rhythm.

When sulfate ion was introduced as potassium sulfate, a ratio of sulfate to dichromate of four to three prevented the formation of fine rhythm. The sulfate ion was two and one-half times as effective in preventing the formation of fine rhythm as was the chloride ion. The nitrate ion was even more effective, for a ratio of nitrate to dichromate of seven to fifteen, or one and four-tenths to three, was found to prevent the formation of fine rhythm.

The radius of the chloride ion is 1.80 Å, that of the sulfur to oxygen grouping in the sulfate ion is 1.65 Å, and the radius of the nitrogen to oxygen grouping in the nitrate ion is 1.26 Å. The radius of the oxygen ion is 1.35 Å (183). If the approximate radius of the sulfate ion may be calculated as radius of sulfur to oxygen group increased by the radius of the oxygen ion, the result is 3.00 Å. Similarly the approximate radius of the nitrate group may be figured as 2.61 Å. The nitrate ion would then be intermediate in size between the chloride and sulfate ions. These calculations are of doubtful validity, but if they are at all indicative of the ion sizes, there can be no direct relationship between ion size and the effect of the ion on rhythmic crystallization.
It seems probable to the present writer, however, that the size of the anion of the added salt is a factor influencing rhythmic crystallization. When potassium dichromate crystallizes from solution, there must be some faces which have a different spacing between the potassium ions presented to the solution from that of others. If it is assumed that the anions introduced are attracted by these exposed potassium ions, it appears that the size of the anion should have some influence upon rhythmic crystallization. A small anion would have to be held in greater numbers to cover the surface sufficiently to prevent further normal growth of a face, while fewer individuals of a larger species of anion might accomplish the same end. If enough foreign anions were held by the potassium ions on a crystal face, other faces would grow at the expense of that face, and the course of crystallization would be altered. This alteration in the course of crystallization would lead to inhibition of the formation of fine rhythm, for it is clear upon microscopic investigation that the orientation of the crystal growth is a factor in the appearance of rhythm.

It is impossible, at present, to say definitely that the size of the foreign anion does, or does not, materially affect rhythmic crystallization.
Since the concentration of the anion of the foreign compound was the deciding factor in the inhibition of rhythmic crystallization, the effect was in some way exerted upon, or through, the potassium ions of the potassium dichromate. It is desirable, therefore, to consider the different ways in which the foreign anion might affect the potassium ion.

It is possible for an anion to affect the rate of diffusion of a cation. It is apparent, however, that the foreign anion did not affect rhythmic crystallization by changing the rate of diffusion of the ions involved, since period widths did not vary materially throughout the course of the investigation. Had the rate of diffusion of the potassium ion been changed, the distance of one point of supersaturation from the next point of supersaturation would have been changed. The constancy of period widths under varying conditions shows that change in rate of diffusion of the potassium ion cannot be the explanation of the effect of the anion introduced.

Degree of ionization, or activity, cannot be a factor in the efficiency of salts in inhibiting rhythm, since salts with monovalent cation and anion, as potassium chloride and sodium chloride, are no more effective than calcium chloride, with divalent cation and monovalent anion, although salts with both
ions monovalent have a higher degree of ionization than salts having one divalent ion and a monovalent ion. Complete ionization, or its equivalent, must be assumed for potassium chloride, sodium chloride and calcium chloride under the conditions maintained, since in no other way can the equal action of equivalent concentrations of these three chlorides be explained.

If the inhibition of rhythm is due to cessation of growth on certain crystal faces, this cessation might, in turn, be caused by more or less close adsorption of the foreign salt upon the potassium dichromate. If this were true, there should be some correlation between the comparative molar solubility of potassium dichromate and of the foreign salt, and the amount of foreign salt necessary to inhibit rhythm. Table XVI gives the molar solubilities of the salts used, and of sodium dichromate, which might have resulted from metathesis of sodium chloride and potassium dichromate (although the typical potassium dichromate period width present in slides made from mixed solutions of these salts indicates that sodium dichromate was not formed). In every case, the anhydrous form, or the hydrated form which crystallizes at the temperature indicated, is given.
Table XVI.
Solubilities of Salts (184).

<table>
<thead>
<tr>
<th>Salt.</th>
<th>Temperature (°C.)</th>
<th>Moles soluble in 1000 gms. water.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl$_2$·6H$_2$O</td>
<td>25°</td>
<td>7.38 ± 2%</td>
</tr>
<tr>
<td>CaCl$_2$·2H$_2$O</td>
<td>100°</td>
<td>14.2 ± 2%</td>
</tr>
<tr>
<td>KCl</td>
<td>25°</td>
<td>4.81 ± 0.5%</td>
</tr>
<tr>
<td></td>
<td>100°</td>
<td>7.51 ± 0.5%</td>
</tr>
<tr>
<td>K$_2$Cr$_2$O$_7$</td>
<td>20°</td>
<td>0.390 ± 5%</td>
</tr>
<tr>
<td></td>
<td>30°</td>
<td>0.616 ± 5%</td>
</tr>
<tr>
<td></td>
<td>100°</td>
<td>3.30 ± 5%</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>25°</td>
<td>3.74 ± 2%</td>
</tr>
<tr>
<td></td>
<td>100°</td>
<td>24.50 ± 2%</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>25°</td>
<td>0.690 ± 1%</td>
</tr>
<tr>
<td></td>
<td>100°</td>
<td>1.382 ± 1%</td>
</tr>
<tr>
<td>NaCl</td>
<td>25°</td>
<td>6.145 ± 0.2%</td>
</tr>
<tr>
<td></td>
<td>100°</td>
<td>6.70 ± 0.2%</td>
</tr>
<tr>
<td>Na$_2$Cr$_2$O$_7$·2H$_2$O</td>
<td>20°</td>
<td>6.90 ± 2%</td>
</tr>
<tr>
<td></td>
<td>30°</td>
<td>14.76 ± 2%</td>
</tr>
<tr>
<td>Na$_2$Cr$_2$O$_7$</td>
<td>100°</td>
<td>16.60 ± 2%</td>
</tr>
</tbody>
</table>

At 100°C., the temperature at which the slides held in steam were allowed to crystallize, potassium dichromate is less soluble than calcium chloride, potassium chloride, potassium nitrate or sodium chloride, but more soluble than potassium sulfate. Potassium sulfate ranks between the chlorides and potassium nitrate in effectiveness in inhibiting fine rhythm. Calcium chloride is nearly twice as soluble as either potassium or sodium chloride, and has approximately twice the effectiveness of
either of these salts, but in view of the rest of the evidence this is probably not significant. In contrast to the relationship at 100°C., at 25°C. calcium chloride is only slightly more soluble than sodium chloride, and is not twice as soluble as potassium chloride. Solubility of the foreign in relation to solubility of the crystallizing salt is not the decisive factor in inhibition of rhythm.

The solubility of sodium dichromate is much greater than that of potassium dichromate or of sodium chloride at all temperatures between 20°C. and 100°C.; this substantiates the evidence that sodium dichromate does not crystallize from solutions of sodium chloride and potassium dichromate.

Rhythmic crystallization does not appear to be peculiar to any one type of crystal. While the cubic crystals of sodium chloride and of potassium chloride did not exhibit fine rhythm, they did show cases of coarse rhythm, probably due to drying effects. Cubic crystals do not become dendritic in habit, under ordinary circumstances, and fine rhythm cannot, therefore, result. In some experiments on percrystallization of sodium chloride, through a collodion bag, the present writer obtained hollow pyramids of sodium chloride, built out for more than one centimeter from the surface of the bag. The stepwise
manner in which these crystals were built up was highly suggestive of fine rhythm, although almost macroscopic in many cases.

Potassium dichromate crystallizes in the monoclinic as well as in the triclinic system, but the monoclinic form is not stable, and changes to the triclinic form at high temperatures (120°C.), as pointed out by Stedehouder and Terpstra (185).

Goszner and Muszgnug (186) show that potassium dichromate, triclinic, and ammonium dichromate, monoclinic, are very similar in crystal structure, even though they do not belong to the same crystal system. These similarities may account for similarities in rhythmic crystallization of these two salts, observed and reported by Miss Abbott (69), who also reported the rhythmic crystallization of sodium dichromate, which, like ammonium dichromate, is monoclinic.

Crystals of the monoclinic or triclinic systems are capable of forming complex dendritic growths. Such growths have been shown to be closely related to the phenomenon of typical fine rhythm.

Cubic crystals, such as those of sodium chloride or potassium chloride, hexagonal crystals, as those of cadmium iodide, and rhombic crystals, as formed by potassium nitrate, do not grow into dendrites with great facility. These types of crystals
exhibit coarse rhythm, but do not, under ordinary circumstances, form fine rhythm.

The type of rhythm exhibited by a salt depends upon the crystal habit of the salt, and upon the conditions under which crystallization takes place.
V. SUMMARY.

The literature relative to rhythmic crystallization has been reviewed. Various aspects of the Liesegang phenomenon, and theories advanced for its explanation, have been discussed, as this phenomenon is a special case of rhythmic crystallization.

Technique for the investigation of effects of differences in temperature and concentration of solution upon rhythmic crystallization of compounds from aqueous solutions has been developed and applied to an investigation of the rhythmic crystallization of cadmium sulfate and of potassium dichromate.

It has been shown that differences in temperature and in concentration do not, within wide limits, materially affect the rhythmic crystallization of cadmium sulfate or of potassium dichromate from aqueous solution. When there was much material present, it was found that the salt crystallized in thick layers which made observation of rhythm difficult. High concentrations of the salts, allowed to crystallize at high temperatures, were found to give many cases of large crystal masses, apparently devoid of rhythm.

The necessity for the presence of a mobile interface for rhythmic crystallization of aqueous solutions of potassium dichromate has been demonstrated.
The rhythmic crystallization of cadmium iodide from aqueous solutions has been reported.

The effect of foreign salts upon the rhythmic crystallization of potassium dichromate from aqueous solution has been investigated. The foreign salts used were potassium chloride, sodium chloride, potassium nitrate, potassium sulfate, calcium chloride and ferric chloride. It has been shown that the molar concentration of the foreign anion is the chief factor in the inhibition of fine rhythm. The chloride ion has been shown to be less effective than the sulfate ion, which, in turn, is less effective than the nitrate ion in suppressing fine rhythm of potassium dichromate. The mechanism by which this inhibition of fine rhythm is brought about has been discussed and a possible solution suggested.

The spacing of periods from the center of crystallization has been measured and the results compared with those reported by Jablczynski for Liesegang rings and with those obtained by Hughes and by Dippy in solidified melts. Potassium dichromate fine rhythm has been shown to have partial agreement with the rule found by Jablczynski, and complete agreement, within experimental limits, with the rule found by Hughes.
The mechanism of the formation of fine, and of coarse rhythm has been discussed, and a satisfactory explanation, based on Ostwald’s theory, as modified by Morse and adapted by Miss Abbott, has been arrived at.

The universality of coarse rhythm has been pointed out, and the relationships between fine rhythm, crossed rhythm (x-rhythm) and coarse rhythm have been explained. The dependence of rhythm formation upon conditions during crystallization has been evaluated, and the relationship between type of rhythm obtained and crystal habit of the crystallizing compound has been explained.
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(Alternate Opinion)

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