

1933

Studies in periodic crystallization in the absence of a gel

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STUDIES IN PERIODIC CRYSTALLIZATION
IN THE ABSENCE OF A GEL

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STUDIES IN PERIODIC CRYSTALLIZATION
IN THE ABSENCE OF A GEL

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MASSACHUSETTS STATE COLLEGE
AMHERST
Julia Elizabeth Abbott

Thesis submitted for the degree of
Master of Science

MASSACHUSETTS STATE COLLEGE, Amherst

May 1933

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I. INTRODUCTION

The formation of banded precipitates in gels (Liesegang rings) has long been a subject of much investigation. Recently it has come to be recognized that similar structures formed in the absence of a gel may be closely related to Liesegang rings. There is strong experimental evidence to show that both phenomena occur in capillary spaces.

There has been a general feeling that rhythmic crystallization may depend either upon total absence of impurities or upon the presence of specific impurities; and, furthermore, that conditions of crystallization may greatly modify, or even destroy, the rhythm produced.

These studies in the periodic crystallization of inorganic salts in the absence of a gel have been made in order to furnish experimental evidence to support an answer to the question: Is the phenomenon under investigation dependent upon certain specific and unvarying factors, or will it consistently appear under widely varying conditions? In other words, the critical circumstances under which certain periodicity occurs were sought.

II. REVIEW OF LITERATURE

A. The Liesegang Phenomenon.

1. Definition and Occurrence.

The Liesegang phenomenon may be defined as the series of concentric rings of precipitate produced by the interaction of solutions in a gel.

A large number of experiments resulting in the formation of banded structures have been described in the literature. Accordingly it seems probable that, given the requisite conditions, any pair of salts forming an insoluble precipitate can be made to give a banded effect upon metathesis in gelatin, agar, or silica gel.

The general method is simple. A dilute solution of one of the reagents is added to the medium while in the sol condition. A fairly concentrated solution of the other reagent is brought in contact with the mixture after it has set. Diffusion occurs within the gel, and a periodic precipitation phenomenon results.

2. Early Work on the Subject.

The first discovery of periodic precipitates is generally attributed to G. Runge, the author and printer of "Der Bildungstrieb der Stoffe," 1855, (62.). He found

that solutions of metallic salts allowed to permeate through sheets of porous paper reacted at their boundaries giving a banded appearance and life-like forms.

In 1879 Ord (57) described the rhythmic banding of calcium oxalate. In 1892 Lupton (47) knew of the phenomenon thought by many to have been discovered by Liesegang (39, 40) in 1896. As none of the earlier workers engaged in a systematic study of their discoveries, the active interest of Liesegang has caused him to be regarded as the pioneer in the field. While staining histological specimens by Golgi's method, he discovered that if a drop of fairly strong silver nitrate solution was placed on a sheet of gelatin containing a small amount of potassium dichromate, the precipitate was not evenly distributed, but appeared in a series of concentric rings. Liesegang rings, as such formations are commonly called, were early compared to naturally banded structures common in biological and geological specimens. Consequently they have been studied by workers in widely varying fields. A great interest has been shown in the study of chemical reaction in colloidal media because of its biological significance.

The literature on the Liesegang phenomenon and related topics is extensive; a bibliography of approximately five hundred titles has been compiled by Hedges (32). It includes work appearing in the year of its publication, 1932, and

covers the field in a very comprehensive way. The fact that more than one-half of the titles belong to work of the last ten years shows that the early work, however significant, was not particularly extensive.

3. Work on the Influence of Various Factors.

a. Concentration.

The fact that the distance between successive bands of precipitate increases as the reaction proceeds has been explained by experimental work making it evident that concentration affects spacing. The concentration of the diffusing agent is lowered by the progress of the reaction, so that a greater distance must be traversed before the critical concentration is reached and the precipitate is deposited.

As a rule the distances between rings decreases when the concentration of the gel and of the reagents increases. There are, however, several cases cited by Hedges (32) as exceptions to this rule. The same cases are exceptions to the rule that the distance between successive bands increases as the reaction proceeds.

According to Bradford (7), publishing in 1920, the concentration of the electrolyte contained in the gel

has a much greater influence on the spacing than has the concentration of the one diffusing into the medium.

Stansfield (65) in 1917 expressed the opinion that ring formations are best obtained by the use of a concentrated diffusing agent and a dilute reactant in the gel. Equal concentrations give an apparently continuous layer of precipitate which the microscope shows to be finely banded.

Köhler (36) reported in 1916 that the rings are imperfectly developed or blurred when the concentrations of reagents are not correct.

b. Temperature.

Popp (59), in 1925, performed an experiment which showed clearly the effect of heat on the formation of bands. He kept one side of the gel at 0° and the other at 20° C., and observed that the distance between rings increased as the temperature was lowered. In this case increase in temperature caused increase in the rate of diffusion, and consequently the precipitate formed and was deposited at shorter intervals.

It has been suggested that some of the periodicity appearing in laboratory materials may be caused by variations in temperature. Frequently there is a fairly regular drop in the temperature of the room during the night.

In 1928, Hedges and Henley (33) referred to temperature difference as a possible cause for a spiral structure of magnesium hydroxide. Equal volumes of 5 per cent magnesium chloride and 2 per cent agar had been mixed and allowed to set in a test tube. The spiral precipitate resulted upon the diffusion into the gel of ammonia (d. 0.880). The report of the result follows:

'It was observed that spiral precipitation was not caused directly by helicoid diffusion, but that layers of precipitate reaching half-way across the test-tube were formed alternately on opposite sides, and at different levels; later, these joined to form a spiral. Such an effect might be caused by temperature difference, due to the exposure of one side of the tube to a draught, thus allowing diffusion on one side to start ahead of the other. When the bands became more than about 1 cm. apart they no longer joined but remained half-way across the tube on alternate sides. Even when a spiral is formed instead of a concentric ring system on a glass plate the diffusion does not really take a spiral course; it is merely that diffusion has lagged behind at some portion of the periphery.'

c. Light.

There is evidence that in some cases, at least, light modifies periodic precipitation, and that periodic exposure to light may cause periodic structures to develop. There has been, however, some confusion among workers between effects of light itself and the effects of the temperature changes caused by the light. Liesegang, in 1923, (44) suggested that heat and not light may have been the cause of the variations in band formation reported in 1921 by

Hatschek (31). Hatschek had observed and studied differences in periodic structures of lead chromate and dichromate in agar where the results obtained in the dark were strikingly different from those obtained on exposure to light. By screening one side of the gel and illuminating the other ordinary and anomalous structures could be produced in the same gel.

Cluzet and Kofmann (14), 1931, reported that the formation of Liesegang rings from silver nitrate, potassium dichromate, and gelatin was unaffected by visible light, X-rays, or radium rays, but ^{was} retarded by ultra-violet light.

Other workers with light-sensitive substances find that visible light is extremely important. That colloidal gold and colloidal platinum are light-sensitive is well-established experimentally. Davies and Sivertz (16) in 1926 obtained diurnal bands of colloidal platinum by the reduction of platinic chloride in tubes exposed to ordinary daylight. No bands formed when the illumination was continuous. Davies (15) had reported work with colloidal gold four years earlier (1922). He kept the tubes containing the silica gel and gold in the dark for nine days without obtaining bands, but upon the exposure of the tube to a powerful beam of light for an hour, a band appeared. It is believed that a change in light was the essential factor in producing periodicity in this case.

Investigations with silver salts gave interesting results. A rhythmic precipitate of silver oxide was said by Mathur and Dhar (48) to disappear on exposure to light. Dhar and Chatterji (19) stated that the rhythmic precipitation of silver chloride and of silver iodide took place in the light but not in the dark. Tryhorn and Blacktin (68) said that both silver dichromate and mercuric iodide crystallized from the gel more readily in the light than in the dark.

d. The Gel.

Although the gel itself cannot be assumed to be chemically inert, the breaking down of the theory of the specificity of the gel has supported the idea that only the physical properties of the medium are important.

The literature contains reports of failure to obtain rings of a certain precipitate in one medium when another medium had been successfully used. More recent work shows that in practically every case this failure was not due to the nature of the gel, but rather to the technique employed. 'A difficulty in the experimental work,' writes Bradford, (7), 'is the narrowness of, frequently, both the concentration limits, between which good bands are obtained. For this reason it is possible

to make a series of experiments with substances, capable of forming beautiful strata, without obtaining any.'

McGuigan and Brough (49) published in 1923 an article in which they suggested that the part of the gel in the formation of periodic precipitates is simply to prevent turbulence. They regard periodic precipitation as the normal course, and still more general is their remark, 'There is some evidence that all chemical action may be periodic.'

It is well established that the gel is not indispensable in the formation of periodic precipitates. Diffusion in capillary tubes, in reaction media of kaolin, sand, and pulverized calcium carbonate, and between glass plates gives structures not essentially different from those obtained in gels. A more detailed treatment of this will be given under the discussion of periodicity in the absence of a gel. It is relevant² to the topic at hand, however, that capillary spaces seem to be the important factor in every medium. This leads to a consideration of the structure of a gel and the mechanism involved in diffusion.

Bechhold and Zeigler (2) in 1906 showed that Graham's conclusion that a simple salt diffuses in a gelatin gel at practically the same rate as in water

holds for dilute gels, but not for more concentrated ones. Hedges' comment is: 'Actually such a behaviour is quite in accordance with the present-day views of the structure of gels, for in the more concentrated gels the channels of water between the particles are so thin as to offer considerable resistance to the movement of the dissolved molecules. An idea of the size of these channels can be gained from measurements of the vapour pressure of the liquid contained in the gel, and the value $3 \text{ m } \mu$ has been calculated for a silicic acid gel.' ($\text{m } \mu = 10^{-6} \text{ mm.}$)

In 1921, Burton and Bell (12) made an observation of some significance. The gelatin containing one reagent was allowed to set on a rubber sheet and then was stretched. After the addition of the second reagent, periodic bands formed, but not as rings. Concentric ellipses appeared with the major axes in the direction of the stretching force. This indicates to the writer that diffusion along the major axis was more rapid than in other directions because of the increase in the distance between particles and consequent widening of the channels through which the diffusing salt had to pass. Also the inner electrolyte would be moved with the gelatin, and as a result its concentration per unit of area along the major axis would be diminished.

Variations in the structure of the Liesegang phenomenon have been shown to be caused by lack of homogeneity in the gel. In 1920 Hatschek (30) reported the formation of twin-rings and screw-like formations of calcium phosphate in gelatin. An examination of his report has revealed to the writer that the gelatin used was soaked for a much shorter time than that used for less spectacular experiments and was consequently not homogeneous.

The formation of spirals, rosettes, mineral trees, and innumerable other variations has been described, but it is the opinion of the writer that in every case these anomalies indicate variations in the rate of diffusion, and are fundamentally Liesegang rings modified by distortion.

e. Impurities.

In 1914, Liesegang (43) discovered that small quantities of acid and of gelatose are necessary in gelatin for the formation of well-defined rings of silver dichromate. Hatschek (30) found the same substances to be important factors in the production of calcium phosphate bands in a ten per cent gelatin gel.

Distortion of Liesegang rings by substances which are volatile or emit volatile products, such as minced

onions, garlic, asafoetida, and formaldehyde, has been reported by two independent workers. (64; 66).

The use of tap water known to contain a small amount of chlorine was found by Foster (26, 27) in 1919, to produce rings of silver dichromate in groups of three instead of singly when Liesegang rings were being made in gelatin. Miss Foster has published some very clear photographs of her results in the report of her investigations.

Schleussner (63) published in 1922 his discovery of the fact that the chloride and phosphate impurities in gelatin produce a series of rings of silver salts, which can be observed by the aid of a lens, lying between the bands of silver dichromate. Pure gelatin is said to give a continuous precipitate. Kiegel and Reinhard (60) in 1927, showed that the addition of small quantities of sodium chloride to pure gelatin caused the Liesegang phenomenon to take place.

f. Summary of the Literature on the Influence of Various Conditions on the Liesegang Phenomenon.

1. Concentration is extremely important since it has been shown to affect the spacing and the sharpness of the bands. Only concentrations within fairly narrow limits, as a rule, give periodic precipitates.

2. Temperature affects rate of diffusion and consequently the distance between bands.
3. Light causes periodicity in some substances and makes no apparent difference in others. Silver salts are modified in their periodicity by light changes.
4. The gel is important in providing stabilizing capillary spaces in which the reaction is free from turbulence.
5. Impurities make great differences in the production of the Liesegang phenomenon. There is some evidence that impurities are necessary for the formation of rings in gelatin.

4. Theories Advanced to Explain the Liesegang Phenomenon.

a. The Supersaturation Theory.

The essence of the supersaturation theory is the assumption that a highly supersaturated solution and not a solid precipitate is the immediate product of metathesis in capillary spaces. When crystal nuclei form, the supersaturated solution diffuses toward them from all sides, leaving areas containing none of the scarcer electrolyte. The more plentiful electrolyte must pass through a considerable area of relative depletion before it has diffused far enough to encounter the inner salt in quantities sufficient to bring about another supersaturation followed by crystallization.

Although there has been considerable criticism of the theory from time to time, many of the objections have been withdrawn in the light of further investigation, and there is today a considerable group of workers supporting Ostwald, the chief exponent of the supersaturation theory. Shortly after Liesegang made his discovery, Ostwald (58) advanced this theory. His own description of the process whereby the rings are formed as quoted by Hedges (32) follows:

'Durch die Diffusion des Silbersalz^{es} in die chromathaltige Gelatine bildet sich in der Gelatine bald eine Lösung, welche in bezug auf Silbersalz übersättigt ist. Der Niederschlag erfolgt aber nicht sofort, sondern erst, nachdem die metastabile Grenze überschritten ist. Dies geschieht natürlich gleichzeitig in einem Kreise, der mit dem Tropfenkreise konzentrisch ist. Um den entstandenen Niederschlag lagert sich das Silberchromat, in bezug auf welches die Umgebung des Ringes übersättigt ist und verstarke ihn; dies dauert so lange, bis das lösliche Chromat aus der Nahe entfernt, in den Niederschlag gegangen ist. Alsdann wandert das Silbersalz über den Ring hinaus, übersättigt ein neues, ferner liegendes kreisförmiges Gebiet und der gleiche Vorgang wiederholt sich. Da die Silberlösung beim Weiterdiffundieren immer verdünnter wird, so wird die kritische Konzentration, bei welcher die Ausscheidung beginnt, immer später erreicht, und der neue Ring entsteht erst in einem weiteren Abstände, als der zwischen seinen Vorgängern betrug.'

Liesegang's attitude toward the theory is note-worthy. In 1907, (42), he performed an experiment which seemed to make the theory untenable. After a set of typical rings of silver dichromate had been preparedⁿ the usual way, in a layer of gelatin on a glass plate, a drop of potassium dichromate was placed where the drop of silver nitrate had been before its diffusion. This diffused and reacted

with the excess silver nitrate remaining in the gel. The formation of a second series of rings was thought to indicate that a supersaturated solution did not precede the formation of rings, as the presence of crystals in the first set of bands was assumed to make supersaturation impossible. Upon discovering that the two sets of rings were at different levels in the gelatin, he withdrew his criticism.

Hatschek in 1914 (28, 29) raised the same objection upon obtaining stronger evidence. Using a test-tube with the precipitate occurring as discs at various levels below the surface of the gel, he let potassium dichromate diffuse downward in such a way that the existing precipitate would be encountered. Again a second series of precipitates were seen. Hatschek went further and prepared bands of lead iodide in a gel containing small crystals of that substance.

Some years later, however, Dhar and Chatterji (19) published the results of experiments showing that silver chromate in gelatin is not coagulated or precipitated by crystalline silver chromate, even after several days, thus showing Hatschek's work to be inconclusive.

There has followed the suggestion of Hedges that planted crystals probably have surfaces sufficiently

different from those of crystals produced in the reaction mixture to account for their failure to grow. In other words, the supersaturation may persist until new nuclei are formed because the crystals added are not chemically clean or for some other reason do not attract the excess solute.

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 it 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.

The supersaturation theory is supported by the fact that the effect of neutral salts on the spacing of silver dichromate bands can be explained by the lowering of the metastable boundary of supersaturated solutions.

This explanation was set forth by Avdalian (1) in 1928.

b. The Coagulation Theory.

Opposed to the supersaturation theory there stands the coagulation theory developed by Dhar and Chatterji (18, 19, 20, 21), about 1923, and postulating that the substance of which the rings are formed exists first in a colloidal state and not as the solute of a supersaturated solution. Excess of the diffusing agent is assumed to be the cause of the coagulation process by which the precipitate is brought down in some cases, and the soluble product of the reaction seems to be the cause in others.

In 1920, Williams and Mackenzie (7) showed that silver chromate produced in gelatin did not behave as a protected colloid, but as a crystalloid, and that its precipitation followed the usual rules of the solubility product. In fact, the evidence supporting Dhar and Chatterji's assumption about the colloidal nature of the solution is inconclusive, and probably not generally applicable.

c. The Adsorption Theory.

The theory that assigns to adsorption the major part in causing periodicity in Liesegang rings was advanced by Bradford (3, 4, 5, 6, 7, 8, 9, 10) in a series of articles beginning in 1916 and continuing through 1929. The solute in the gel is assumed to be adsorbed by the finely divided precipitate. The specific

surface or the degree of dispersion of the precipitated matter is an important factor. Bradford has obtained periodicity in systems previously thought to be necessarily continuous, by modifying the degree of dispersion while other factors remained constant.

The theory has been criticized by workers whose experimental results do not support it. Quantitative investigation by Dhar and Chatterji (22) in 1929, showed that silver chromate adsorbs very little potassium chromate. Although the percentage of silver ions approached 5%, there was scarcely any adsorption of chromate ions. Furthermore, small crystals with large specific surfaces are necessary for extensive adsorption, but a number of periodic structures have been obtained, according to Hedges (32), where the precipitate was in the form of relatively large crystals and the specific surface was so small that the adsorption must have been negligible.

B. Crystallization of Substances from Solutions Containing Colloids.

1. In the Presence of Gelatin.

In 1906, Liesegang (41) found that potassium dichromate in ten per cent gelatin solution crystallized in bands when the drying progressed slowly from one end to the other.

About ten years later Küster (37, 38) described the periodic crystallization of copper sulphate, tri-sodium phosphate, and other inorganic salts from solutions containing gelatin.

Rohonyi (61), publishing in 1913, reported that in freezing thin films of gelatin solution he observed the formation of concentric rings of ice.

2. In the Presence of Colloids Other Than Gelatin.

Hedges (32), discussing this subject in 1932, said: 'The presence of hydrophilic colloids appears to favour periodic crystallisation.....According to du Noüy, (56), the presence of colloids causes periodic crystallisation of sodium chloride at certain concentrations. Von Weimarn (70) describes the crystallisation of lithium chloride in concentric rings from a viscous, colloidal solution containing degradation products of cellulose.'

C. Periodic Structures Formed in the Absence of a Gel.

1. Periodic Structures Formed in a Reaction Mixture.

Reference has been made by the writer to the fact that periodic precipitates have been found in many instances where capillary spaces existed entirely independent of a gel. The investigations cover a period of thirty years and involve a number of workers.

In 1903, Morse and Pierce (53) reported that rhythmic precipitation took place in pure water solution. This is generally taken to be the first report of this fact. In 1911, Vanzetti (69), and in 1913 and 1914 Dreaper (24, 25,) reported the formation of bands of many crystalline substances in glass capillary tubes containing diffusing reagents. In 1919, Traube (67) got bands of precipitate in plaster of Paris. In 1923, three groups of workers also reported results of this nature. Notboom (55) placed a drop of dilute potassium iodide under a cover-glass on a microscope slide and a drop of concentrated lead nitrate at the edge of the cover-slip, and obtained very even bands of lead iodide in the capillary spaces. McGuigan and Brough (49) placed a moistened crystal of silver nitrate on a plate on which a thin film of potassium dichromate had dried, and they found ordinary rings of silver dichromate resulting. Liesegang and Watanabe (45) reported periodic precipitation in reaction media of sand, kaolin, and pulverized calcium carbonate.

Other isolated examples of no great importance precede the work of Morse (52). In 1930, Morse, who with his co-worker Pierce had been the first to publish on the subject of periodic precipitates in the absence of a gel, published an extensive investigation of the

phenomenon in ordinary aqueous solution. As this work is related to the research of the writer, it will be reviewed in considerable detail.

After a brief historical sketch, Morse gives the scope of the paper thus:

'This paper offers data on thirty-six cases of periodic precipitation in aqueous solution; indicates the rather general nature of the phenomenon; presents a number of microphotographs of typical precipitates; considers the bearing of the data on theories which have been offered, and suggests a general explanation of the results observed in pure water solutions.'

As for Morse's experimental procedure, microscope slides were bored so that there was a hole in the center. A drop of one of the solutions was placed on the slide and covered by a cover-glass. Then a drop of the other solution, more concentrated than the first, was placed over the hole, on the other side of the slide. At times, in place of the concentrated solution, a dilute solution was placed over the hole and a crystal of the solid salt was placed in the drop of solution. Plugs of macerated filter paper were sometimes placed in the holes to make diffusion more nearly free from disturbances.

Morse observed about forty cases of periodicity in the precipitates out of about two hundred cases 'rather hastily examined.'

The precipitates were:

Silver cyanide	Lead cyanide	Mercurous chloride
iodate	iodate	hydroxide
chromate	chloride	iodate
bichromate	iodide	carbonate
tungstate	hydroxide	arsenate
phosphate	sulfide	
arsenate	oxalate	Mercuric oxide
	sulfate	sulfide
Cupric sulfide	tungstate	carbonate
chromate	arsenate	phosphate
Barium sulfate	Thallous iodide	Manganous hydroxide
carbonate	chromate	carbonate
Caesium alum	Cadmium hydroxide	

In the above list Morse finds no basis for classification.

Thirty-one illustrations are discussed systematically. Most of these are examples of true periodicity produced by quiet diffusion, but several are artifacts. Mechanical shock, however slight, causes in some otherwise continuous precipitates a sharp ring. A second tap will cause a second band, and unless great care is taken an artificial periodic structure is formed which may be very misleading. Morse's comment is: 'It is difficult to explain how shock can act otherwise than to increase the general agitation and movement in the wave front, unless the effect of shock is to release supersaturation.'

Confusion arises from the drifting and consequent trapping of particles, which may result in bands of great regularity. In the phenomenon Morse is discussing, there is no motion of particles; each particle remains

where it first appears, and grows. The necessity for leaving no traces of dirt on the glass surfaces was also emphasized by Morse.

Gelatin, even when only very small amounts are present, causes great variation in the formations. Morse reports that a quarter of one per cent of gelatin completely destroys periodicity in lead iodide.

Morse has condensed the results of his investigations with water solutions as follows:

1. No gel or other colloid is necessary for periodic precipitation;
2. The precipitates obtained in water are "coarsely crystalline," compared with the particles which make up semipermeable membranes and with particles which measurably adsorb electrolytes;
3. The majority of the precipitates are not measurably more soluble in the solution resulting from the metathesis than they are in pure water;
4. Substances of all degrees of solubility form periodic precipitates;
5. The crystals which make up periodic precipitates are of various habit; they grow like crystals and exhibit no phenomena analogous to what is broadly termed coagulation (see for example Figs. 3 and 23);
6. The crystals which make up periodic precipitates are not started by seeding from crystals already present; they appear at points in the solution distant from any existing particle of the solid phase;
7. Preliminary measurements indicate that rings in water follow the same rule of constancy of the ratio of the separation of successive rings $\left(\frac{r_2}{h_2} - \frac{h_2}{r_1} = K \right)^*$ as do ring systems in gelatin.
8. There is strong evidence that the solution is supersaturated with the substance of the precipitate at the time the ring appears.'

Morse explains these results in a way which seems to the writer to be adequate, simple, and worthy of being briefly summarized here. His initial criticism

* Here h_n represents the distance of the nth ring from the center.

of the supersaturation theory as set forth by Ostwald (58) is in connection with the concept of the metastable limit. In 1899, Ostwald said that precipitation did not take place until the metastable limit was exceeded. During the next ten years there was a general acceptance of the idea that supersaturated solutions were of two kinds. In the so-called metastable solutions supersaturation could not be relieved by mechanical shock, but only upon the introduction of some of the solid phase. In the so-called labile solutions spontaneous crystallization occurs. Miers (50) in 1907 published graphs of several inorganic salts showing that he believed the boundary between the metastable and the labile regions to be a smooth curve parallel to the saturation curve and lying about ten degrees below it. He worked with supersaturated solutions sealed in glass tubes, and shook the tubes at intervals. Only at certain temperatures did he get spontaneous crystallization. He accordingly supported Ostwald's idea that a metastable limit existed at which shaking first gave crystals.

Subsequent work, however, has proved that no such definite distinction can be made. If the metastable limit exists at all, it lies so close to the saturation curve that for all practical distinctions they coincide. The difficulty with the work of Miers was that the shaking was not adequate to start crystallization; hammers giving

sharp blows to drops of water were used by Young and van Sicklen (72) publishing in 1913. They showed that with a sufficiently great mechanical shock water could be made to crystallize in the absence of ice, even when the degree of supercooling was very small. Work has been done with sugar solutions, and other substances, and all of the results support the conclusions of Young and van Sicklen.

Morse accepts the ideas of the more recent workers, and adds to them. Just as great mechanical shock releases supersaturation, so, according to Morse, does rapid change in concentration. The following is his own statement of his ideas:

'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 1×10^{-4} 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 measurable distance ahead of existing solid particles.'

Having thus accounted for the release of supersaturation, Morse explains the distance between the rings in the commonly accepted way. The concentration falls to the saturation point and stays there until diffusion has carried the stronger electrolyte into a region containing enough of the inner reagent to form a supersaturated solution of the precipitate. Then the rapid change in concentration is again brought about with the consequent release of supersaturation in the formation of another ring of crystals separated from the first by the area in which no supersaturation occurred.

2. Periodic Crystallization from the Melt.

The investigation of periodic crystallization from the melt preceded that of other phenomena discussed here by a comparatively long time. In 1853, Sir David Brewster (11) published the results of investigations with thin layers of molten substances. Later it was established that many substances, particularly organic ones, formed rhythmic structures when cooling.

In 1932, Dippy (23) observed this phenomenon in thin films of piperonal, perpinol hydrate, vanillin, phenyl benzoate, phenanthrene, cinnamic acid, thymol, and 3, 5-dichloro-4-methylphenyl. He reported that unless an air interface was present crystallization was

continuous. Other workers have reported that when the crystals formed between glass plates, periodicity was not observed. Hedges (32) says that the essential condition is one mobile boundary, for a boundary of water will not interfere as does glass.

Hughes in 1929 worked with thin films of molten sulphur. The discovery that rings were formed in the freezing of sulphur was reported in 1915. Measurements made by Hughes (35) gave information as to their spacing.

Plotting the logarithm of N , the number of rings counted from the center, against the logarithm of r , the distance of the rings from the center, Hughes obtained a straight line. The general equation for these lines is:

$$\log N = a \log r + \log K$$

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

Hughes developed technique for obtaining these rings, and succeeded in getting eighty-nine rings or arcs in one direction. Crystallization proceeded from the center toward the periphery in this case.

Theories offered to explain this type of crystallization are applicable to crystallization from solutions and will be discussed in connection with that topic.

3. Periodic Crystallization from Solution.

In 1853, Sir David Brewster, (11) whose work with melts has already been mentioned, studied periodic crystallization from the aqueous solution. The literature contains little or no reference to further work on the subject during the rest of the nineteenth century.

Sir Henry Miers (51) in 1908 reported the rhythmic crystallization of potassium dichromate from aqueous solutions on a microscope slide. The details of his method will be given later in connection with the experimental work of the writer, since it was in part concerned with the periodic crystallization of dichromates.

Linck and Korinth (46) in 1928 studied rings of sulphur formed by crystallization from its solution in carbon disulphide.

Hedges and Meyers (34) in 1925 made some observations with aqueous solution of chrome alum and again barium nitrate. The distance between the rings decreased with thinner films and with increasing rate of crystallization.

Hrynalovski (34 a, 34 b) about 1926 studied the rhythmic crystallization of potassium alum. The same kind of crystallization in potassium sodium tartrate has been photographed by Buckley.

Hedges (32) suggests a theory for the formation of bands of crystals in thin films whether from the melt or from solution. He supposes that when the first crystals form, the surrounding liquid is immediately attracted to it and held there by surface tension. The liquid feeds the crystals until they are higher than the film. The liquid film becomes correspondingly thinner as the crystals in its midst grow. Then this very thin film crystallizes with extreme rapidity, and the crystals extend, usually in an arborescent form, until the liquid of normal thickness is reached. Then a new ring of large crystals grows.

In support of this explanation Hedges has written: Various other features support this view, which was originally reached by direct observation of the process. The periodic structure did not form at either high or low rates of crystallisation, but did so at intermediate rates. When the rate of crystallisation is high, the liquid is not drawn up by the crystals with sufficient speed to make the trough of a wave, and when crystallisation is slow, the liquid has time to spread out to an even layer. The thinnest films do not crystallise periodically, doubtless because of the difficulty of drawing so thin a film away from the underlying surface.

III. EXPERIMENTAL WORK

A. The Problem.

A review of the literature shows that considerable work has been done on the effects of changes in conditions upon those processes which usually result in the formation of periodic precipitates in gels. The problem underlying the research reported in this thesis was to discover the results produced when processes known to give periodic structures in the absence of a gel were carried on under widely differing conditions of concentration, temperature, and other factors.

The writer was further interested in contributing to the facts already known whatever she could learn about optimum conditions for the production of specific periodic structures, and to evolve or confirm an adequate theory.

These studies involved work with dichromates crystallizing from aqueous solution, and with lead iodide precipitated by the metathesis of lead nitrate and potassium iodide.

B. Apparatus.

Glass microscope slides were used as the surfaces on which the crystal formed periodic structures. Details of their preparation for use will be given later.

A vacuum desiccator was used whenever a dustfree atmosphere seemed particularly desirable.

The microscope used in the examination of the slides was a Zeiss microscope, type number 5710, with large mechanical stage, polarizer, and analyzer. This type is equipped with swing-out condenser with iris-cylinder diaphragm. Magnifications between 56 and 940 were possible.

The use of the micrometer eye-piece for measuring distances between bands was preceded by the calibration of the scale against a standard stage micrometer, the tube length being the usual one, 160 mm.

C. Methods and Results.

1. The Preparation and Cleaning of Slides.

New microscope slides were obtained for use in the experimental work under discussion. The first method used was that suggested by Chamot and Mason (13). It consisted in rubbing the slides with a thin paste of Bon Ami, and then removing it, either before or after it had dried, with a cloth entirely free from grease.

Since the presence of surface films has been found by other workers to cause or to influence greatly the formation of periodic structures, the use of Bon Ami was abandoned early in the work, and the following method was used. New chromic acid cleaning solution was prepared, and the slides to be cleaned were soaked in it at least 12 hours. Usually they were soaked several days.

The chief purpose was to remove the sodium ions from the surface of the glass, because their presence has been thought to increase the adsorption of the negative ions of the solution on the glass, and in this way to affect the precipitate.

Thorough rinsing of the slides followed the decantation of the cleaning solution. Distilled water was renewed until no color of the dichromate ion remained. A test for acid showed that this was not sufficient rinsing, so the slides were kept in hot water at least an hour, rinsed again, and kept in distilled water until used.

In order that the possibility of contamination from drying cloths might be avoided, the slides were used wet whenever this was possible. Upon several occasions, they were removed from the fresh distilled water with forceps, placed on edge in a vacuum desiccator, allowed to dry, slipped into a horizontal position, and used without being touched. For other experiments, clean folded cheese-cloth from packages was used to absorb the water, the pads being touched by the hands on one side and by the glass on the other.

Care was taken at all times to have the slides scrupulously clean or contaminated intentionally by a specific substance. There is, however, no evidence ~~from~~

from the experimental results that Bon Ami was not as good for cleaning as chromic acid; the formation on the two sets of slides were very similar at all times.

2. The Periodic Precipitation of Lead Iodide.

a. Brief History.

It has been reported in the review of the literature that Notboom and Morse worked independently on the formation of bands of lead iodide. In 1923, Notboom, (55), got results from the diffusion of a concentrated aqueous solution of lead nitrate into a thin film of potassium iodide upon a microscope slide. In 1930, Morse (52) repeated the work. Both workers published photographs showing bands of various widths, but neither discussed measurements or the effects of changes in concentrations.

b. General Method Used.

A drop of one reagent was placed on a clean microscope slide, and a square cover-glass was carefully lowered over the drop so that air was excluded. A few moments were allowed for the liquid under the glass to spread evenly. Then at the end of the cover glass nearer the center of the slide a drop of the second reagent was placed, and allowed to spread without interference from the experimenter. When measurements were to be made, the slides were not touched until the liquid had entirely evaporated from under the glass.

c. Types of Cover-Glasses.

Work was begun with ordinary round or square, thin cover-slips. The periodicity seemed to occur in the part of the slide farthest away from the initial precipitate, so that it seemed well to extend the area of the field. Square cover-glasses were placed in series, and material diffused from the far edge of one under two or even three slides. But this set-up was complex, and it was hoped that better results could be obtained by simpler means.

A method not unlike that used by Morse was worked out independently. A hole was bored, not in the slide, but in the round cover-glass, and the drop of the second reagent was placed over the hole. No plugs were used. The fragility of the cover-slips, and the limited area between their centers and their edges, made this method seem unfitted to give any extensive periodicity.

Some of the cover-slips, broken in an attempt to bore holes for the work described above, were used to allow diffusion to proceed from a narrow crack. The pieces were placed with their broken edges parallel and slightly apart. Some periodicity was observed, but in very small areas.

In all of the above experiments there was observed considerable disturbance of the rhythm at the edges.

As evaporation was taking place there, the concentrations were constantly changing, and conditions were not controlled. It was therefore thought that cover-glasses having a large area and a minimum perimeter would be desirable. In the absence of large cover-slips, whole microscope slides were used as covers with excellent results. These, however, presented some practical difficulty in handling, as the edges did not coincide. Adjustment of the mechanical stage of the microscope made one slide move along the other destroying the bands.

Finally, microscope slides were cut in half, and used as cover-glasses with entirely satisfactory results throughout the rest of the work with lead iodide.

d. Use of Surfaces Other Than Glass.

The question arose whether or not the glass surface was necessary for the formation of bands of lead iodide. It was suggested that attempts be made to get the same results in the absence of glass. Cellophane was suggested. Accordingly two pieces of cellophane were held together by a drop of potassium nitrate solution, and a drop of lead iodide was added at the edge. The examination with the microscope showed that a periodic precipitate had

formed, but when further examination was made it was discovered that the precipitate was not on the cellophane, but in it. Washing and rubbing did not remove the precipitate. It was then decided that unintentionally a substance comparable to those used in the Liesegang phenomenon had been used, and the results, however interesting, were of no significance in the present investigation.

Next, blades of stainless steel paring knives were chosen as desirable substitutes for glass. Stainless steel seemed desirable because it is probably more nearly homogeneous than glass, its surface being free from highly charged particles. Experiments failed at first because of the difficulty of keeping the blades in position. The use of rubber stoppers as weights and supports finally solved the difficulty. The examination of a blade with appropriate lighting and a lower power lens showed periodicity of the precipitate.

e. Thickness of the Film.

Several months after certain slides had been prepared, an attempt was made to reproduce the results under exactly the same circumstances. Solutions of the same strength were prepared, and it was thought that the

technique was unchanged. Three drops of 0.6 N potassium iodide solution were placed on a slide; a half of a slide was placed over the drops; a drop of lead nitrate was placed at the edge of the cover-glass, and then a second drop and soon a third drop. Whereas the earlier precipitate had been distinctly banded, these were continuous. With eight widely varying concentrations of lead nitrate, only one slide showed any periodicity. On it 0.2 N lead nitrate had been used.

At first it was feared that the earlier work had in some way been open to periodic outside influences and was therefore unreliable. But when the work was repeated with one drop of reagent instead of three, excellent periodicity occurred in practically every case. Details of this experiment will be given below. It is cited here to show that the thickness of the film under the cover glass is an important factor.

f. The Effects of Changes in Concentration on the Structure .

A solution of potassium iodide containing 10 grams per 100 c. c., was prepared from Baker's Analyzed salt. This concentration (.6N) was used in all of the following work. A solution containing 51.2 grams of Baker's Analyzed lead nitrate per 100 c. c., was prepared, and

portions of it were diluted so that a series of solutions of the following concentrations was produced:

No. of the soln.	g./l	Normality	Percent saturated
1.	512	3.1	100
2.	256	1.54	50
3.	128	.77	25
4.	64	.38	12.5
5.	32	.19	6.25
6.	16	.096	3.125
7.	8	.048	1.562
8.	4	.024	0.78
9.	2	.012	0.39

From these solutions a series of slides was made in the following way: A drop of potassium iodide was placed on each of nine slides in a row; cover-glasses were slipped back and forth with considerable pressure so that the drop was spread in a very thin film; in most cases, the film became so thin that the two surfaces adhered to each other through capillary attraction of the molecules between them. A short time was allowed for the motion to subside and for the film to adjust itself evenly. Then a drop of one of the nine solutions of

lead nitrate was placed on the slide at the edge of the cover-glass. Capillary action drew some of the lead salt under the glass immediately, so that the thickness of the film increased slightly and the lead nitrate was not entirely dependent upon molecular motion for diffusion. Soon quiet diffusion took place, and continued undisturbed until the slides were dry.

A second series of slides was prepared the following day. The report includes both sets.

A general statement of results will precede the detailed description of the nine groups of slides. In every case, the precipitate was definitely crystalline. In at least one half of the slides the periodicity was easily observed without a lens. It was evident that the spacing between bands was much greater when the slides were made with dilute lead nitrate. Conditions near the edges of the slide always seemed to be abnormal, and the rhythm there was consistently finer than that in areas less affected by evaporation.

Many of the slides upon careful examination revealed four distinct areas. They will be named and described below in some detail.

The first precipitation area was an area of regular, parallel bands of lead iodide and was the first to appear as diffusion took place.

The second area is the complex salt area because it is believed that the disappearance of the first bands of lead iodide was due to the formation of a complex salt. This region developed at the places where precipitation first occurred and gradually extended into the area already covered with crystals in bands leaving only clear spaces there.

The third region lay beyond the first and may be called the area of double precipitation. The rows were like those of the first area except for the size of the crystals which were coarse and seemed to have been built up by a second precipitation of lead iodide. Experiments with potassium iodide diffusing back over the precipitate have given large, well-defined areas of double precipitation, the newly formed lead iodide building on the crystals already laid down. It is thought that this third area occurred in undisturbed slides when the concentration of the potassium nitrate became so much greater than that of the lead nitrate that the potassium salt diffused back toward the lead salt more rapidly than the lead nitrate moved forward. As soon as this concentration of the lead iodide was sufficiently reduced by precipitation, the lead nitrate diffused into the potassium nitrate and formed new bands as it did originally.

The fourth region formed last, lay farthest from the first precipitate, and was clearly defined. Since the bands in this region were widely separated and the few crystals in the bands were far apart, it has been assumed that the precipitate there was formed from relatively dilute solutions. The originally saturated or concentrated solutions had been diluted by metathesis until the amount of precipitate formed was comparable to that formed in slides where only dilute lead nitrate was used.

The results produced in the slides briefly described above follow in greater detail:

Solution 1. When 3 N lead nitrate was used as the diffusing agent, the entire area under the cover-glass was seen to be periodic. The bands were definite, uniform in width and spacing, and could be seen with a hand lens. The crystals in the bands were like grains of sand in shape and uniformity of size.

The first bands dissolved in the concentrated lead nitrate solution diffusing through them, before measurements had been made. The bands remaining in the first precipitation area were measured with the micro-meter eye-piece and showed 40 periods in the first millimeter.

In these fine bands the crystals were small and lay close together. In intermediate regions the distance between crystals and between bands increased with the width of the rows. By far the greatest area was covered by bands lying about 20 to the millimeter. The coarsest rhythm was found to have 12 periods per m. m.

These slides showed all four regions described in the general statement of results. The areas were relatively large and clearly defined.

Solution 2. These slides closely resemble those prepared with solution 1 and described above, although the concentration was only one half that used above. When 1.5 N lead nitrate was used, the spacing varied from 42 to 5 rows per mm. It was possible to measure the periodicity very near the beginning of the precipitation in this case because in two slides there was apparently no area where the lead iodide dissolved. Here the rows were finest. Gradually they increased in size, and the coarsest rows were found about 3 cm. from the finest rows.

Solution 3. When .77 N lead nitrate was used with the .6 N potassium iodide common to all these experiments,

the variations were less striking than those found in the more concentrated mixtures. The finest bands observed measured 20 to the millimeter. The coarsest in the first precipitation area measured 6 per m.m., and the coarsest on the whole slide, 4. These last lay beyond the area of double precipitation, in the region where the amount of precipitated matter was small.

Solution 4. When .38 N lead nitrate was used, the results were very similar to those described under solution 3. The periodicity varied in much the same way, measuring about 18 at the beginning and increasing in width of bands until 5 per m. m., was the typical formation.

Solution 5. With a .19 N solution of lead nitrate the spacing of the bands was as follows: At a corner where evaporation was rapid, 16 per mm.; at the center of the edge at which precipitation took place first, 10 rows per mm.; at the far edge, 5 per mm.; at an unusually depleted place, probably the last to become banded, only 2.5 bands per mm. These slides showed some evidence of the dissolution of bands of lead iodide by one of the reagents present. As the potassium iodide was 3 times as concentrated as the lead salt, it seems probable that this is not the same kind of area as was described in

connection with the more concentrated lead solutions. It is possible that the vacant area at the edge of the cover-glass was one occupied by the lead nitrate alone, and that precipitation in this case, as in cases to be cited later, did not take place until the lead salt diffused into the iodide.

Solution 6. This dilute solution (.1 N) gave no bands finer than 6 per mm. The crystals lay in very definite rows but the rows did not extend over a very wide area, doubtless because the amount of precipitate formed by a drop of dilute lead nitrate was very small. Areas measuring 2.5 to 3 rows per mm. were the most common.

Solution 7. The precipitate formed from a .05 N solution of lead nitrate was almost entirely macroscopic. Twenty-one bands were easily counted without the aid of a lens. The rows were composed of large geometric crystals of apparently slow growth. The bands lay 2 to a millimeter and were remarkably regular. At the region farthest from the entrance of the lead solution the spacing was somewhat wider, but at the opposite end of the structure, 3 bands instead of 2 appeared in one millimeter. The

first bands lay well up under the cover-glass. Apparently the dilute lead nitrate did not precipitate lead iodide until a considerable amount of space had been covered. Then the critical concentration was reached, and precipitation relieved the supersaturation.

Solution 8. This was the most dilute solution with which periodicity was obtained under these conditions. Its normality was .024, only one-twenty-fifth of that of the potassium iodide used. There were six distinct bands about 1 mm. apart and composed of crystals far apart and sharply defined. The bands were broad and could be seen clearly by the unaided eye.

Solution 9. Only a few widely scattered crystals appeared with this extremely dilute solution. No periodicity could be discovered.

g. Summary of Results of Work with Lead Iodide.

A general method has been adopted and experiments performed to show that:

1. Microscope slides with half slides as cover-glasses are satisfactory though not indispensable surfaces for the periodic precipitation of lead iodide.

2. The thickness of the film is an important factor, probably because capillary spaces give a condition essentially comparable to that in a gel.

3. Whereas other workers have placed the more concentrated solution on the outside, the above experiments have shown that the concentration of the outer solution may be only 4 per cent of that of the inner one. Capillarity was responsible for the intake of the drop in the first place, and diffusion evidently carried it far into the inner region in spite of the great difference in concentrations.

4. 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.

5. 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.

Table I

The Influence of the Concentration of Lead Nitrate
on the Spacing of Bands of Precipitated Lead Iodide.

Concn. KI	Concn. $\text{Pb}(\text{NO}_3)_2$	Number of bands PbI_2 per mm.	
		Maximum	Minimum
.6 N	.012 N	0	0
.6 N	.024 N	1	1
.6 N	.048 N	3	2
.6 N	.096 N	6	3
.6 N	.19 N	16	2.5
.6 N	.38 N	18	5
.6 N	.77 N	20	6
.6 N	1.54 N	42	5
.6 N	3.1 N	40	12

5. The Periodic Precipitation of Other Insoluble Halides.

When other lead halides were tried, no positive results were obtained. Four slides of lead bromide showed no bands. As Morse (52) does not report this substance among the forty with which he succeeded in getting bands, it seems probable that further investigation would give only negative results. The great difference in the solubility of lead iodide and lead bromide at 20° may account for their different habits in precipitating. Lead bromide is more than 12 times as soluble as lead iodide, and the chloride is still more soluble.

Silver nitrate and potassium halides were used in experiments of the same type as those performed with lead salts. Distinct layers were observed in all cases that were moved under the microscope as the reaction proceeded. At first it was believed that this was spontaneous rhythm, but after Morse's remarks on the susceptibility of these silver precipitates to slight shock had been read, the experiments were repeated. Periodicity was entirely absent when nothing disturbed the slides.

4. The Periodic Crystallization of Potassium Dichromate from Aqueous Solution.

a. History.

The periodic crystallization of potassium dichromate was first reported by an English worker, Sir Henry Miers, (51), in 1908. According to Hedges (32) this effect is produced when a drop of saturated potassium dichromate solution on a microscope slide is warmed gently over a flame. The slide is quickly transferred to a microscope stage. Crystallization begins at the edge of the drop and continues periodically. The distance between rings decreases with the thickness of the films. As the rate of crystallization increases the distance between rings decreases.

b. Methods of Obtaining Periodicity.

The method described above may be criticized because it involves motion, strong convection currents, and exposure to contaminated atmosphere. Some of these difficulties have been overcome by methods devised for carrying out this research.

It was discovered early in the work that if a clean microscope slide was placed in a hot solution of potassium dichromate, and removed when the solution was boiling, a film of solid salt appeared upon rapid evaporation,

and in some cases this film showed periodic ridges. If the solution was too dilute, the crystals were piled at the part of the slide to which the liquid withdrew before evaporation could take place. If the solution was too concentrated, the film was so thick that ridges could not be observed. Various concentrations and alterations of technique were tried before optimum conditions were discovered. A solution containing 20 grams per 100 c. c. seemed best, although good results were obtained with solutions varying from this concentration by as much as 5 g. per 100 c. c.

A slight variation of the above method which gave extraordinarily good results follows: Two slides were placed in a solution deep enough to cover more than half of a ^cside. The slides were placed together so that a film of solution was held between them. The slides were removed with forceps, allowed to cool, and then quickly pulled apart. Whole slides have been covered with excellent periodic crystal structures in this way.

Practically the same results can be obtained by dipping a glass rod into a hot, fairly concentrated

solution of the salt, and then quickly drawing the side of the rod across the surface of a hot slide.

A fourth method consisted of placing slides in a vacuum desiccator, adding a drop of dilute solution to each slide, and evacuating the desiccator. This method was used when a dustfree atmosphere seemed desirable.

c. Investigation on the Effect of Impurities on the Rhythmic Crystallization of Potassium Dichromate.

Before any investigation on the effect of impurities could be carried out, it was necessary to observe the phenomenon under conditions as nearly free from impurities as possible. Baker's Analyzed potassium dichromate was recrystallized, and a solution containing 1 gram per liter was prepared with distilled water. Slides cleaned by the method described above were placed on the desiccator tray, allowed to drain and dry, and then slipped into a horizontal position. A drop of the potassium dichromate solution was placed on each of several of the slides, and the desiccator was evacuated. After twenty-four hours crystallization had not taken place, so washed air was let into the desiccator. Immediately crystals formed. Microscopic examination showed them to be periodic. The films were thin and the

periodicity very fine. This showed that under conditions as free from impurities as those just described, periodicity occurs.

This experiment was repeated with commercial sulphuric acid in the bottom of the desiccator so that crystallization would take place without the introduction of air. After 24 hours, examination of the solid that had formed in the vacuum showed that there were broad, vitreous, yellow bands at the edges of the drops. These were cracked and devoid of crystals. Crystallization seems to have started after the vitreous area had formed, and to have spread toward them from the interior. These crystal branches show contiguous crystal groups of a definite pattern, growing smaller as they approach and invade the vitreous area and deplete the area immediately around them. The explanation of this formation is probably that the acid removed water with so little agitation and so gradually that the concentration of the solution increased to the supersaturation stage. With no stimulus for the formation of crystal nuclei, evaporation continued until only a thin film of solid was left spread over the surface of the glass. No periodicity could be found.

Other experiments were performed using the desiccator with about 100 c. c., of fresh C. P. concentrated

sulphuric acid in the lower compartment. Probably the action of this acid was quicker than that of the first acid and not affected by the presence of impurities.

The purpose of the following work was to determine the effect of minute quantities of a specific impurity on the periodic crystallization of potassium dichromate. Clean, wet slides were heated in a .2% Gold Dust soap solution and used without rinsing. They were dried on clean cheesecloth, and marked with a glass pencil. Clean slides were dried, and the two kinds of slides were placed side by side over the porcelain rack in the desiccator. Drops of the dilute potassium dichromate solution (1 gram per liter) were placed on each of the slides, and the pressure was reduced. After 24 hours, they were examined under the microscope, and rhythm was found in practically every drop. Large transparent crystals had grown at the edges of both kinds of slides. In both small unsymmetrical patches of well-ordered ridges appeared in the inner areas. The rhythm was very distinct, and the arcs of crystals could frequently be seen to have a common center. The only difference between the two sets of slides was that those containing Gold Dust had held the drops in shape better than the surfaces having no impurity. This was doubtless due to

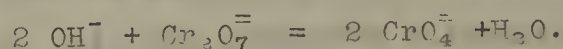
surface tension differences. Evidently the crystal formation was not affected by small amounts of Gold Dust.

An attempt to use different solvents was not fruitful because of the insolubility of the salt. When alcohol is added to an aqueous solution at room temperature, a fine precipitation of the solid salt occurs. At high temperatures an oxidation-reduction reaction occurs, and the nature of the solution becomes very complex. The results of the following experimental work show, however, that the complexity of the reaction mixture does not seriously interfere with the formation of crystal ridges.

To 200 c. c. of a solution known to give excellent periodic crystallization when pure, there was added 25 c.c. of alcohol in 5 c.c. portions. The general method used was that of dipping slides into the hot solution and allowing them to cool in the air. The first 5 c.c. portion made no apparent difference in the behaviour of the crystals. The other portions made a difference in the rapidity with which the evaporation took place, but no difference in the structure of the crystal bands.

Soon after the alcohol had been added, the color of the solution changed, a precipitate formed, and it was evident that a reaction was taking place. After two hours, the potassium dichromate still crystallized in a typically periodic way. When, after two weeks, the solution was again heated and the slides made from it were like the first, it was concluded that potassium dichromate crystallized independently, and is not affected by the reaction products formed by its action upon alcohol.

Attempts to study the crystallization of potassium dichromate in solutions of widely varying hydrogen ion concentration failed because of the chemical action of the hydroxyl ion on the dichromate ion according to the equation



The addition of solid sodium hydroxide pellet by pellet until 1 gram had been added to 20 grams of potassium dichromate in 100 c.c. of water did not affect the periodic formations. This was enough to change about 1/5 of the dichromate to normal chromate. In reality, then, the results of this experiment show that the presence of considerable amounts of sodium chromate and potassium chromate does not affect the crystallization of the salt under investigation.

Potassium chromate alone did not crystallize rhythmically. It was therefore concluded that it had not part in the formation of the bands observed.

The addition of acids to potassium dichromate is comparable to the addition of bases as far as chemical breakdown is concerned. Small quantities of acid made very little difference. The addition of concentrated hydrochloric acid in large quantities to a solution of potassium dichromate broke up the periodicity by causing an entirely different type of crystallization to occur. The film was vitreous and contained large, light yellow, geometric crystals. It is probable that the reaction had been sufficient to destroy all of the dichromate, forming dichromic acid and potassium chloride and so the results were of no particular significance in the investigation at hand.

Since the properties of potassium dichromate are such that changes in solvents and variations in pH are limited, there remained as a possibility only the addition of salts to the solution. Here the possibilities were far less limited than in the preceding work, but as the phenomenon is thought to be due to supersaturation,

investigation of the results of the addition of salts was limited to salts having a common ion.

The effect of potassium chloride upon the crystallization of potassium dichromate was studied by the microscopic examination of slides prepared from the following solutions. To a solution of potassium dichromate containing 20 g. / 100 c. c. there was added 1 gram of solid potassium chloride. Several slides were made and labelled. Then a second gram of potassium chloride was added and more slides were made. This process was repeated until 5 grams had been added. The first four sets of slides were practically unaffected by the presence of the chloride, but the fifth set had only very faint periods. It appeared that the presence of the chloride was interfering with the crystal habit of the dichromate. Potassium chloride crystallizes in the cubic system; potassium dichromate in the triclinic. This difference may explain the faintness of the periodicity.

Sodium dichromate has not only a common ion, but also a common crystal habit with potassium dichromate. A solution of sodium dichromate containing 20 g. per 100 c. c. and a solution of potassium dichromate of the same concentration were prepared and gradually mixed.

10 c. c. of the sodium dichromate solution was added to 50 c.c. of the solution of the potassium salt. Slides were dipped in the solution and allowed to dry rapidly. A second 10 c. c. portion of the sodium salt solution was added to the mixture, and more slides were made. This was done five times, so that a solution of equal quantities of potassium and sodium dichromate resulted. The periodicity persisted, but the periods became closer as the percentage of the sodium ions increased. Another difference, observed upon the addition of sodium dichromate, was the tendency of the crystals to grow in a thin layer in definite circles with a well-defined center. Apparently there was no great tendency to form crystal nuclei. These results led to the investigation of the crystallization of sodium dichromate alone.

5. The Periodic Crystallization of Other Dichromates.

a. History.

The literature contains no record of the discovery of the periodic crystallization of either sodium or ammonium dichromate.

b. Work with Sodium Dichromate.

The fact that sodium dichromate did not interfere with the periodic crystallization of potassium dichromate when

the two salts were present in equal quantities led to the investigation of the habits of the sodium salt when crystallizing alone. At first no periodicity was observed, when the method used for the preceding work was followed. It was discovered, however, that if the crystallization was speeded up with heat from a flame, periodicity occurred in thin films. In no case was the periodicity as persistent as that found in potassium dichromate. Fifteen concentric arcs close to a crystal center were the maximum number of periods seen in any one group. The optimum concentration seemed to be about 10 g. per 100 c. c. The method which succeeded when others failed was the one described above, involving 2 slides with a thin film of liquid between them. When the slides were slipped apart, they were held over a flame until evaporation brought about crystallization on the sides that had been together. A carefully adjusted light was necessary for the detection of the arcs under the microscope.

c. The Work with Ammonium Dichromate.

When ammonium dichromate was used in place of potassium dichromate, in aqueous solutions cooling on

slides, bands of much the same nature formed. The first slide showed periodicity, and there seemed to be no necessity for any modification of the method used for potassium dichromate.

It is of interest to note that the size of the cation attached to the dichromate radicle seems to have influence on the rhythm. Potassium and ammonium ions are of the same size, and potassium dichromate and ammonium dichromate showed similar banding; the sodium ion is smaller, and sodium dichromate showed finer but less continuous rhythm. The addition of sodium dichromate to potassium dichromate in increasing amounts gave increasingly fine rhythm. The introduction of hydrogen ion, a very small ion, into a solution of potassium dichromate tended completely to destroy the periodicity.

IV. CONCLUSIONS

A. Theory.

An attempt to understand the mechanism of the formation of the crystals which make up rhythmic structures preceded any attempt to formulate a theory. In the case of the periodic precipitates of insoluble halides, especially of lead iodide, the crystals were easily seen with a magnification of not more than 180. The outlines of the crystals of lead iodide were clear, and it was assumed that nothing would be gained by examination of them with an oil-immersion lens.

The structure of the periodic formation in the case of potassium dichromate crystallizing from aqueous solution was not clear, although the ridges were well defined at a magnification of 56. Upon examination of the bands of crystals under an oil-immersion lens giving a magnification of 940 with a number 4 ocular, the structure was discovered. What appeared as the crest of the ridge was a row of dendrites parallel to each other and of similar size and shape. Between the crests and at a lower level (as the necessity for changing the focus indicated) lay rows of dendritic crystals running parallel to each other, but perpendicular to those in the crests.

It is the opinion of the writer that the banded effect was due to the difference in the structure of the alternating areas, and that this difference was, in turn, due to different rates of growth in the two regions. The rate of growth depended upon concentration, and it seems probable that the periodic structure was a reflection of periodicity in concentration. This is entirely in agreement with the opinions of the workers who have postulated supersaturation as the cause of rhythmic crystallization.

It has been pointed out in detail in the review of the literature that Morse (52) modified the supersaturation theory by emphasizing a time element. His theory, in brief, is that rapid changes in the concentration of the solution bring on periodic structures when slow changes result in continuous structures, even though supersaturation is present in both cases. Morse advanced this theory to explain results obtained from the diffusion of solutions in capillary spaces, but the writer finds it generally applicable to the results obtained from the crystallization of a salt from aqueous solution as well. In one case, it is metathesis which brings about the rapid change in concentration; in the other, it is rapid evaporation, or rapid cooling, or both,

which causes the supersaturation to increase so rapidly that it is periodically relieved by the formation of new crystal groups.

Morse's theory fits the results of this research better than any other. There seems to be no necessity for considering the possibility of adsorption and coagulation in the formation of bands of lead iodide. Supersaturation is accepted to be the sine qua non of the phenomenon.

As for Hedges' theory (32) advanced to explain the periodic crystallization of substances from the melt or from solution, the writer's comment is: There is nothing opposed to Morse's theory in the idea that bands are formed by the variations in the thickness of the film due to surface tension. It seems that this is simply the mechanism by which the rapid changes in concentration are brought about. Probably the phenomenon depends upon the heaping up of material, as Hedges suggests. Microscopic examination revealed two levels in the potassium dichromate crystallized under the conditions described at length under the discussion of experimental work. The crests probably grew higher than the other layer because the solid crystals held the super-saturated solution

to them by surface tension until the concentration was lowered to such a point that crystal growth was relatively slow and the crystals formed were thin. Meanwhile evaporation was raising the concentration in the solution just beyond that in which the thin crystals were slowly growing. There new crystal nuclei formed and grew into thick crystals until the concentration was again lowered by their rapid growth. It is generally believed that the growth of dendritic crystals of substances usually non-dendritic in general crystal habit is due to the fact that only the end of the crystal is bathed in a supersaturated solution. This idea is supported by the fact that ~~in~~ the thick area and the dendrites pointing in the direction of the withdrawal of the solution boundary terminate at the same place.

The experimental results do not support several of Hedges' statements. He found that the periodic structure did not form at high or low rates of crystallization. This research has shown that whole microscope slides crystallize in a flash, and there may be periodicity throughout the solid mass. Hedges claimed that the thinnest liquid films did not crystallize rhythmically, but the writer has observed constant periodicity in films so thin that very careful adjustment of the light in the microscope was

necessary in order to see that there was any matter there at all, even though the substance was colored. These minor discrepancies, however, do not invalidate the theory as a whole, since the process whereby the ridges form probably takes place with extreme rapidity and in thin films when the periods are very small.

B. Summary

1. A study of the literature dealing with periodic crystal structures had been made. This reveals that the interest in the subject has been wide-spread, and the work already accomplished is extensive.

2. The theories on the formation of rhythmic crystal structures have been reviewed, and evaluated in the light of experimental results.

3. The relation between the nature and condition of the surface and the crystallization upon that surface has been studied. The conclusion has been reached that periodic crystallization is independent of surface variations.

4. The spacing of rhythmic bands of lead iodide has been shown to vary from 42 to 1 period per millimeter, when eight solutions of different concentrations of lead nitrate were allowed to diffuse into films of solutions of potassium iodide of one concentration. The more dilute the lead nitrate, the greater the spaces between bands. Contrary to the practice of other workers, the more dilute solution has, in many cases, been placed on the outside successfully.

5. Morse's statement concerning the sensitivity of silver bromide precipitate to slight shock has been confirmed in the production of a banded structure due to accidental jarring. No evidence of true banding of the precipitate was found when the slide was undisturbed.

6. Several methods for producing rhythmic crystallization of potassium dichromate have been devised, and optimum conditions for their use have been determined.

7. An investigation of the effect of impurities upon the rhythmic crystallization of potassium dichromate has been made and the conclusion drawn that this salt is not sensitive to the presence of a number of impurities.

8. Sodium dichromate and ammonium dichromate have been discovered to crystallize periodically from thin films of hot aqueous solutions.

9. Supersaturation in capillary spaces seems to be one of the chief factors in causing periodicity in crystal structures.

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