THE LIESEGANG PHENOMENON

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I. INTRODUCTION

When a crystal of silver nitrate is placed on a glass slide covered with a dilute solution of potassium dichromate in gelatin, the resulting precipitate of silver dichromate forms in concentric bands or rings around the crystal. The formation of these rings, named for their discoverer, Raphael E. Liesegang (44, 45), has aroused the curiosity of chemists for more than half a century and has given rise to several often-conflicting theories. In spite of previous extensive study of Liesegang rings, only since 1940 has it been possible to evaluate the conflicting theories on the basis of experimental evidence. Recent work supports the supersaturation theory advanced by Wilhelm Ostwald, who presented the earliest explanation of Liesegang ring formation (55). This paper will not review the more than six hundred publications on this subject, but will present a description of the phenomenon on the basis of diffusion theory. A parallel development, the application of wave-mechanical equations to Liesegang rings, also will be discussed. A brief summary of the factors that influence ring formation will be presented first. Subsequent discussion of diffusion is based on a one-dimensional model in which one reactant is poured into a tube on top of the other reactant. In this case, the rings form perpendicular to the axis of the tube as diffusion of the outer electrolyte proceeds down the tube.

II. DESCRIPTION OF RING FORMATION

A. Generality of the phenomenon

From the variety of reactions which can produce periodic precipitates—i.e., Liesegang rings—it has been postulated that all precipitation reactions can occur rhythmically when subjected to the proper conditions. While this statement hardly is provable, even a cursory examination of the literature reveals that many compounds are capable of producing Liesegang rings. Isemura (36) presents a list of substances from which rings have been prepared in silicic acid gel. It includes lead carbonate, bismuth(III) chromate, cobaltous orthophosphate, cupric iodate, cupric carbonate, silver orthophosphate, silver iodate, cobaltous sulfide, calcium orthophosphate, calcium oxalate, strontium oxalate, lead iodate, and lead orthophosphate. In addition, Isemura lists the following precipitates in gelatin: barium chromate, lead carbonate, cobaltous orthophosphate, silver carbonate, silver iodate, lead iodate, and lead orthophosphate, all of the insoluble mercury salts. Morse (48) has observed periodicity for the following twenty-six substances in aqueous solution: silver(II) cyanide, silver iodate, silver chromate, silver dichromate, silver orthophosphate, lead chloride, lead iodate, lead cyanide, lead hydroxide, lead sulfide, lead oxalate, lead sulfate, manganous hydroxide, manganous carbonate, mercurous chloride, mercurous hydroxide, mercuric carbonate, mercurous carbonate, mercuric oxide, mercuric sulfide, mercuric orthophosphate, cupric sulfide, cupric chromate, cadmium hydroxide, barium sulfate, and barium carbonate. Periodic precipitation also can occur in the vapor phase. For example, the reaction between sulfur trioxide and water vapor produces rings of condensed hydrogen sulfate (22), and rings of ammonium chloride are formed when hydrogen chloride and ammonia are passed into opposite ends of a tube in the absence of water (63).

While this list is not exhaustive, it conveys some idea of the generality of the phenomenon.

B. Formation of periodic structures

Generally, the precipitates formed in tubes are arranged in bands. At the top the precipitate is continuous, but bands soon are produced. They are separated by relatively clear spaces. When formed on a flat slide, the bands are arranged horizontally, often in concentric circles. Frequently, several systems of bands are produced simultaneously or successively. Thus, cadmium sulfide in silica gel forms alternating pink and yellow bands, probably owing to differences in particle size. If lead nitrate is diffused into a gel containing silver chromate bands, lead chromate will form in the clear spaces. The structure of precipitates in Liesegang rings varies from microscopically small to large crystals. Sometimes the usual bands occur in a modified form. Liesegang (47) has reported two-dimensional structures of silver chromate, as distinguished from the usual concentric circles. Dounin and Shemyakin (20) have described periodic precipitations of entirely different orders of magnitude. In addition to the usual bands, which are visible to the naked eye, they describe microsystems that can be seen

only under the microscope. These form either exclusively or between the bands of the macrosystem. The cause of some of these variations is believed to be impurities, temperature changes, and unequal setting of the gel at the walls and center of the tube.

C. Influence of various conditions on ring formation

The influence of the gel, the gel concentration, the electrolyte concentrations, and the temperature on ring formation has been investigated by Isemura (36), who concludes that the kind of gel can alter greatly or prevent ring formation. However, rings also can be formed in aqueous solution without the presence of a gel. Evidence as to the effect of gel concentration is not conclusive. In some cases, the number of bands and the distance between them increase with increasing gel concentration, while in others the number of bands and the distance between them decrease with increasing gel concentration. Generally, bands form only over a narrow concentration of the inner electrolyte. An increase in the concentration of the inner electrolyte hinders the diffusion of the outer electrolyte. The concentration of the outer electrolyte must be higher—preferably by several orders of magnitude—than that of the inner electrolyte. The higher the concentration, the larger are the number of bands and the smaller the intervals between them. If the concentration becomes too high, precipitation is continuous. Generally, either reactant may be made the inner or the outer electrolyte, although altering this relationship may change the appearance of the precipitate.

A change in temperature increases both the diffusion velocity and the solubility of the precipitate; thus, at higher temperatures, fewer bands are formed and the distances between them become greater. There is little doubt that light influences the formation of rhythmic precipitates, but various investigators report contradictory results, and the nature of the influence of light cannot be regarded as known. Küster (42) obtained no bands of silver chromate in the dark, but Davies (12) obtained good bands. Isemura (36) believes that light influences the reaction in cases in which the inner electrolyte reacts with the gel. For example, chromate ion exhibits a tanning action on gels. This tanned gel has less protective action for silver chromate, thus causing the bands to be closer together. Köhn and Mainzhausen (40) found that the rhythmic precipitation of silver chromate was influenced by the presence of chloride ion. In the absence of chloride, bands formed in both the light and the dark. As the chloride-ion concentration is raised from 0.00025 N to 0.001 N, the rhythm disappears in the dark and secondary bands appear in the light. Other studies (41, 64, 65) support the view that the presence of light influences band formation either photochemically—i.e., by producing reactions between ions present—or by promoting a change in the gel, usually under the action of the inner electrolyte.

D. Liesegang rings in non-gelatinous media

Most of the work upon Liesegang rings has been done in gels, principally gelatin, agar, and silicic acid. However, there have been two major investigations of non-gelatinous media. Gore has investigated the formation of bands on metal

hydroxides (23, 24, 25, 26), which form lyophilic solutions on peptization with electrolytes. Morse has investigated rhythmic precipitates in aqueous media.

Gore's work on solutions primarily was performed to support the coagulation theory (see Section II,C) and to show that a gelatinous medium was not essential to ring formation.

Various hydroxides—such as those of aluminum, chromium, iron, and zinc—were washed carefully and then peptized by the addition of electrolyte. Coagulation of the resulting solutions was effected by the diffusion of an "outer" electrolyte through the solution. The coagulate was periodic and had all the marks of Liesegang rings. The peptizing and coagulating electrolytes were selected so that they would not react with each other. For example, the following pairs were used in one experiment: potassium iodide and potassium dichromate, potassium iodide and barium chloride, and barium chloride and mercuric chloride. Gore explains this phenomenon in terms of the coagulation theory: the solution and precipitates coexist only long enough to facilitate the adsorption of the solution on the precipitate. Apparently it is important that the peptized solutions be lyophilic, since no ring formation is observed with lyophobic solutions.

Morse studied thirty-six cases of periodic precipitation in aqueous solutions, using some of the salts listed previously and no colloids. His experimental results may be summarized as follows: (*a*) The precipitate is always definitely crystalline. In many cases the rings are separated relatively widely. (*b*) No fine ring structure is observed. The rings usually are visible to the naked eye. (*c*) The substance forming precipitates has a wide range of solubility. (*d*) The "rings" vary from diffuse bands, with crystals scattered through the entire field, to sharply defined rings with no scattered crystals visible. (*e*) With care, rings of nearly the same sharpness as those formed in gels can be formed in water. (*f*) In the cases that have been measured, the distances between rings yield the same quantitative relations as in gels—i.e., the ratio of the distances between successive bands is constant.

There is no evident basis for the classification of these precipitates. Neither crystal form nor valence offers any criterion. The addition of gelatin markedly influences ring and crystal habit.

Any theory proposed as an explanation for Liesegang rings in aqueous solution must take account of the following results:

(*1*) No gel or other colloid is required for precipitation.

(*2*) The precipitates are coarsely crystalline, thus being much larger than those particles which measurably adsorb electrolytes.

(*3*) A majority of the precipitates are not measurably more soluble in the solution formed by the metathesis than they are in pure water.

(*4*) The crystals which make up periodic precipitates are of various habits. They grow like crystals and exhibit no phenomenon analogous to coagulation.

(*5*) The crystals in the precipitates do not start by seeding from crystals already present. They appear at points in the solution distant from any particle of solid phase.

(*6*) The solution very probably is supersaturated with the precipitate at the time the ring appears.

These results indicate that any theory must regard the action of any colloid as distinctly secondary. The colloidal medium is, however, important in influencing the conditions under which precipitation occurs. Not only does the medium provide rigidity so that convection is prevented, but it may influence greatly the solubility and metastable limit of the precipitate.

III. THEORIES OF THE LIESEGANG PHENOMENON[1]

A. The supersaturation theory

In 1897, shortly after the appearance of Liesegang's original paper, Wilhelm Ostwald published an explanation of the phenomenon in his *Lehrbuch der allgemeinen Chemie* (55). Assuming a case where silver nitrate diffuses into gelatin containing potassium dichromate, Ostwald's theory supposes that a precipitate is not formed immediately, but that the silver dichromate remains in supersaturated solution. When it precipitates a short distance behind the diffusion front, the silver dichromate in solution diffuses toward the nuclei, thus forming a clear space through which the silver nitrate must travel before the cycle is repeated. As diffusion proceeds, the silver nitrate becomes more dilute, causing the rings of precipitate to form further and further apart.

The chief opponent of Ostwald's theory was Hatschek (27, 28), who pointed out that Liesegang rings could be obtained even when the gel first had been seeded with crystals of the substance to be precipitated. He even obtained two independent series of bands by first forming silver dichromate bands in the regular way, and then letting potassium dichromate diffuse into the system to react with silver nitrate in the clear spaces. Bands of lead iodide also could be obtained by diffusion of lead nitrate into a gel containing potassium iodide and seed crystals of lead iodide. Hatschek's argument centered on the assumption that supersaturation cannot exist in the presence of a solid phase. Much work has been done to show that the supersaturation theory is compatible with Hatschek's experiment and that there probably exists a definite supersaturation product, H, associated with a metastable limit below which supersaturated solutions may persist for long periods of time.

Notboom also supported a supersaturation theory (54). He believed that Hatschek's contrary results were due to the adsorption of gelatin on the lead iodide crystals. This adsorption, he said, prevents the crystals from acting as nuclei for further crystallization and is not evidence that the solution is not supersaturated. This "encapsulation effect" also has been suggested by Morse (48). His observations in this connection are interesting because they are for water solutions, with the influence of a gel completely eliminated. Morse's observations include the following: (*1*) If the seed crystals are close together, precipitation is completely prevented. (*2*) Each seed grows and exhausts the material from the

[1] The main theories of the Liesegang phenomenon have been discussed briefly by A. Van Hook in J. Alexander's *Colloid Chemistry*, Vol. VI, Reinhold Publishing Corporation, New York (1944). A more extensive review of these theories is presented in this section.

region around it. (*3*) When seeds are widely spaced, precipitation takes place between them. (*4*) Seed crystals grow in the same manner as the crystals in rings near them. (*5*) The principal factor seems to be the low diffusion gradient. This means that the influence of one surface in robbing another of material for growth is slight.

Evidence for supersaturation includes (*1*) rapidity of ring formation and (*2*) rapidity of crystal growth from the time the rings first appear. The quantitative studies on supersaturation will be discussed in Section IV.

B. The adsorption theory of Bradford (9)

Bradford's theory explains the clear spaces between rings as due to the adsorption of the inner electrolyte by the precipitate; hence the primary condition for ring formation is the degree of dispersion of the precipitate, which determines its adsorbing capacity. The reaction medium affects particle size. If the particles are large, adsorption is small and no ring formation can be expected. If the particles are very small, diffusion is hindered, causing the rings not to form. Periodic structures form under intermediary conditions.

Bradford's original explanation obviously is unsatisfactory. Hatschek (29) and Morse (48) have shown that rings with large crystals can be grown, and Dhar (16) pointed out that silver dichromate adsorbed little potassium dichromate.

Nevertheless, it can be shown that adsorption of the inner electrolyte by the precipitate is an important factor in ring formation. For instance, if lead nitrate is allowed to diffuse into agar containing potassium chromate, a nearly colorless zone appears near the ring, showing that the chromate ion has been removed. There is no precipitation in that zone. Moreover, ring formation in many cases seems to depend on crystal size. The most familiar of these cases is that of silver chromate, which forms fine crystals and rings in gelatin, but large crystals and no rings in agar.

Investigation of crystal size in gels shows that solubility and supersaturation can be influenced by the presence of various ions. The variation in crystal size can be related to the equation of von Weimarn:

$$N = K\frac{P}{L}$$

N is a dispersion coefficient which is related to the mean magnitude of the single crystals in gram-molecules by the expression

$$Gm \times N = \text{constant}$$

L is the solubility, P is the supersaturation, and K is a function of the solvent viscosity as well as of the size and structure of the ions in solution.

Both P and K are functions of the medium. To produce a fine precipitate of silver chromate in agar, N must be made large. Bands can be produced if the solubility L is diminished by addition of alcohol, but high values of P can be obtained by the addition of highly charged anions. For example, adding varying

amounts of citrate can be used to produce any desired surface area; indeed, a series of silver chromate rings of varying particle size has been prepared in agar in this manner.

Hedges has pointed out, however, that the assumption of adsorption is unnecessary. The inner electrolyte must diffuse against the incoming solution (and hence the precipitate) because of the concentration gradient, and this alone accounts for dilution under the band. Adsorption can, of course, accelerate the diffusion process, but alone it acts only over short distances.

Thus, while adsorption undoubtedly occurs, it alone cannot account for all the observed phenomena. Moreover, it cannot be isolated from simultaneous processes which produce the same effect.

It also has been proposed that the clear spaces between rings result from Coulomb repulsion between the diffusing ions adsorbed on the precipitate and the same ions which are still free (7). In this model, precipitation can occur only when the distance between the last ring and the ions diffusing past it has become great enough for repulsion to be negligible. This view is consistent with some of the quantitative relations of the Liesegang phenomenon (37, 60, 72). However, while such Coulomb repulsion undoubtedly exists (assuming that ions of the same sign are actually adsorbed on the precipitate), the primary cause for the diffusion process is the concentration gradient of the ions concerned.

C. The coagulation theory (17, 18, 19, 61)

The main feature of the coagulation theory is that the substance to be precipitated is produced first as a colloidal dispersion—not as a supersaturated solution. The precipitate forms because the colloid is coagulated by an excess of diffusing electrolyte. Indeed, it can be shown that many precipitates can coagulate and adsorb their own solutions, and that adsorption of its own solution by a precipitate occurs to a greater extent than adsorption of the electrolyte.

Dhar and coworkers also pointed out the following pertinent facts: (*a*) In the presence of gelatin the following substances can be peptized and also form rings: silver chloride, silver iodide, silver bromide, silver iodate, silver thiocyanate, silver orthophosphate, lead iodide, lead chloride, lead sulfate, cupric hydroxide, cobaltous hydroxide, silver sulfide, mercuric sulfide, cupric sulfide. The sulfates of barium, strontium, and calcium cannot be peptized, and they form no rings. (*b*) When the concentration of silver chromate in gelatin is low, the layers between rings are almost clear. With higher concentrations they contain peptized particles. This means that the peptized silver chromate originally present diffuses or is attracted by the precipitates, leaving clear spaces.

Liesegang ring formation, then, is due to the coagulation of a peptized solution. The influence of the medium partially determines the extent of peptization or coagulation.

Consider a tube containing gelatin and potassium chromate. If silver nitrate is added, the silver chromate which is formed tends to disperse colloidally because of the peptizing influence of the gel. However, since the potassium nitrate concentration is high, the solution coagulates and precipitation occurs. Just

under the precipitate the silver nitrate concentration is less, and a layer of peptized solution is formed. Further diffusion of silver nitrate and potassium nitrate tends to make this solution unstable. Also, the precipitate tries to adsorb the solution. Both factors combine to cause precipitation of the peptized solution on the precipitate. This leaves an area under the precipitate free of potassium chromate. The silver nitrate must diffuse through this area before the process can be repeated.

If adsorption is not complete, or if the electrolyte concentration is not sufficient to make the solution unstable, alternate layers of precipitated and peptized solution are formed. On this basis, Liesegang rings may be classified into two types: (*a*) substances which can adsorb their own solutions, causing a layer of precipitate to be followed by a clear region, and (*b*) substances which do not adsorb their own solutions and therefore give an alternation of coagulated and peptized layers. Case (*b*) may be considered from a different point of view—i.e., that the soluble electrolyte formed in the reaction is adsorbed on the precipitate. This lowers its concentration behind the precipitate and permits the stable peptized solution to exist.

The work of Gore provides some support for this theory. It also shows that the gelatin is not an essential component in the process.

The chief difficulty with the coagulation theory is that colloidal silver chromate cannot diffuse through any appreciable distance. Thus, it would be difficult to visualize any feasible mechanism which would allow particles of peptized solution to travel any distance to a layer of precipitate. If, on the other hand, it should be claimed that the solution is highly dispersed, the similarity to the diffusion of a crystalloid would be so great that there would be little basis for choosing between the coagulation theory and the supersaturation theory.

D. The diffusion wave theory (56)

The chief difference between the diffusion wave theory and the preceding theories is the importance placed on the soluble product formed in the reaction.

Wolfgang Ostwald bases his argument on these two ideas:

(*1*) In all reactions giving rise to rings, three main diffusion waves form and interfere with one another. The first two arise from the diffusion of the original reactants toward one another, while the third forms at their point of contact and runs in both directions simultaneously. Consider, for example, the reaction

$$MgCl_2 + 2NH_4OH \rightleftharpoons Mg(OH)_2 + 2NH_4Cl$$

The outer electrolyte (ammonium hydroxide) diffuses into the gel containing magnesium chloride. The diffusion of these two toward each other sets up two waves. A precipitate of magnesium hydroxide forms while the ammonium chloride sets up the third wave (figure 1a).

(*2*) Many periodic reactions are reversible in the sense of the law of mass action: i.e., the electrolyte which is formed can inhibit further reaction.

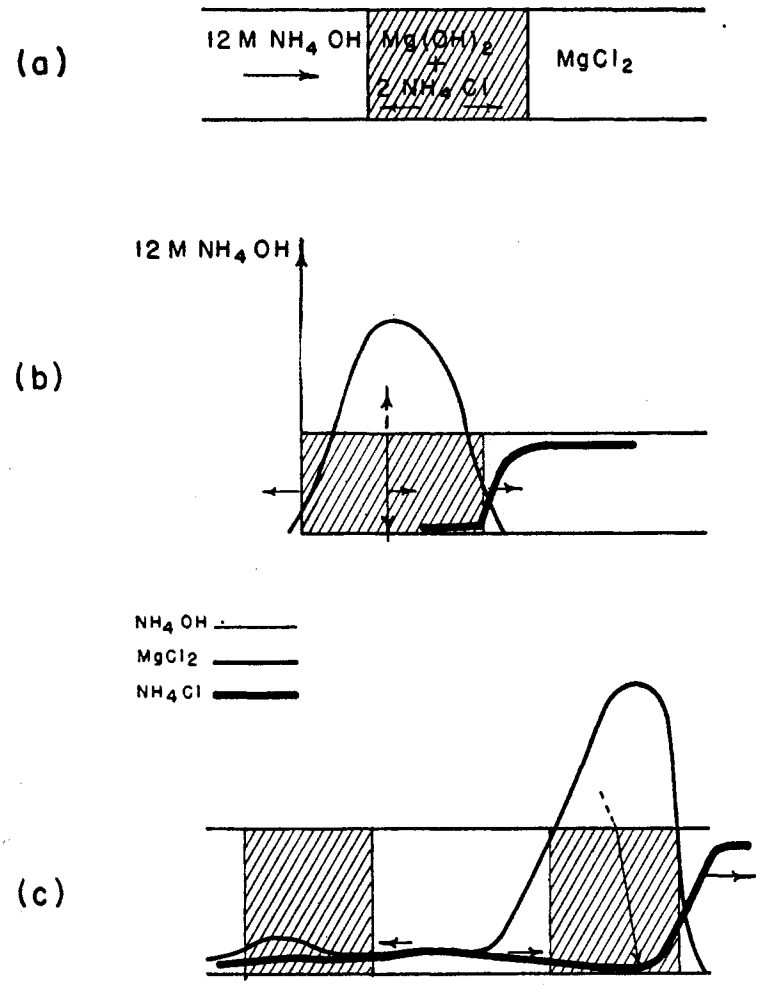

FIG. 1. Concentration changes during formation of Liesegang rings according to the diffusion wave theory. (a): Diffusion of ammonium hydroxide into a gel containing magnesium chloride. (b) and (c): Illustration of the two principles of Ostwald's diffusion wave theory.

From the point of view of the theory, it is important that a precipitation reaction be self-inhibiting.

The two principles of Ostwald's theory are illustrated in figures 1b and 1c, which show the initial stages. The first ammonium hydroxide is removed by precipitation of magnesium hydroxide; hence, its diffusion wave is disturbed. By thus fixing the hydroxide ion chemically, the concentration of ammonium hydroxide is decreased and its diffusion wave is held back. At the same time, the diffusion wave of ammonium chloride increases. Thus the ammonium chloride wave at first will run ahead of the ammonium hydroxide wave.

According to the theory, continuous precipitation stops when the magnesium

chloride concentration is so small and that of ammonium chloride so great that precipitation is prevented.

According to the law of mass action

$$[Mg(OH)_2] = \frac{K[MgCl_2][NH_4OH]^2}{[NH_4Cl]^2}$$

In order for precipitation to start, the right-hand side of the equation must not drop below a certain value, which depends not only on the temperature but also on any hydrogen and hydroxide ions present. The self-inhibition is due not only to an increase of ammonium chloride but also to the low concentration of magnesium chloride in the precipitation zone. All three quantities change so that the product drops below the minimal value necessary for precipitation. Owing to the high concentration of ammonium hydroxide, this situation can be only temporary. The ammonium hydroxide wave catches up with and eventually overtakes the ammonium chloride wave, so that the critical concentration is again exceeded. Simultaneously, the ammonium hydroxide meets higher concentrations of magnesium chloride and a new precipitate forms. In these periodic changes of ammonium chloride and ammonium hydroxide waves, the concentration product changes and produces bands.

Ostwald believes that the following experimental evidence supports his theory: (*1*) All ring systems which have been investigated are destroyed by adding later an excess of the electrolyte formed in the reaction. Thus, in the case just considered, addition of ammonium chloride will destroy the rings of magnesium hydroxide. (*2*) Previous addition of that electrolyte (ammonium chloride above) to the gel changes not only the width and separation of the rings but will also produce rings out of continuous precipitates.

The chief objections to the theory rest on the ring systems which do not contain a third electrolyte. Thus, ring systems of gold are formed by the action of sulfur dioxide on gold salts and the reduction of silver salts to silver by ferrous sulfate (46), as well as by the reduction of cupric sulfate to cuprous oxide (33) by alkaline glucose. Ring systems also can be produced by first carrying out the reaction and then diffusing an excess of one of the reagents into the system (31). In this case there can be no third wave. Thus, while the electrolytes which are present in the system undoubtedly affect the solubility of the precipitate, they cannot be proved essential to its rhythmic formation.

E. Hedges' comprehensive theory (32)

Hedges has analyzed the four theories which were discussed previously, in an attempt to establish a common ground between them. He observes that each theory fails because some experiments can be cited in which bands occur, although a necessary condition of the theory is not fulfilled. All theories postulate a critical condition as an essential factor in ring formation. Ostwald considers the metastable limit as the point at which the supersaturated solution precipitates. In Bradford's theory there is a critical concentration of the inner electrolyte, which occurs some distance after the medium has been impoverished of the elec-

trolyte by adsorption by the precipitate. The outer electrolyte must diffuse until this critical concentration is reached before further precipitation takes place. In the coagulation theory a critical concentration of electrolyte is required for coagulation of the colloidal product. Wolfgang Ostwald's theory also specifies a critical concentration necessary for precipitation.

The other necessary factor contained in each theory provides for the mobilization of material. Both of the Ostwalds consider this factor to be diffusion; Dhar and Bradford believe it to be adsorption. Adsorption, however, can act only over short distances, while diffusion is the only feasible mechanism over longer distances. Mobilization occurs when the critical condition is being approached, with the material moving from the zones which become clear spaces to those which become rings. Coagulation banding can be explained if the solution—or at least part of it—is mobile. This mobility results partly from the solvent action of the soluble electrolyte.

The spacing of the bands will depend on the difference in the rate of penetration of the diffusing agent and the rate of mobilization of internal reagents and products. The medium influences the threshold value of the critical condition and the speed of mobilization, and also provides a stable medium for the ring structure.

IV. SUPERSATURATION AND THE METASTABLE LIMIT[2]

The most serious objection to the supersaturation theory as an explanation for the formation of Liesegang rings is the fact that the rings will form even in the presence of seed crystals. To overcome this objection, it must be shown (*1*) that supersaturated solutions can exist even in the presence of solid phase and (*2*) that the velocity of diffusion of the outer electrolyte is greater than the rate of crystal growth.

Wilhelm Ostwald (55), in the absence of experimental evidence, postulated that precipitation occurred when the solution became highly supersaturated. The corresponding concentration at which crystals formed even in the absence of solid phase was regarded as the metastable limit. The ion product at that concentration was called the supersaturation product (49, 55). Much experimental evidence supporting this hypothesis has accumulated. The following section deals with this evidence.

A. Supersaturation

Solutions of silver chromate in water are stable when supersaturated to the extent of two or three times their solubility of 1×10^{-4} (66). However, these solutions equilibrate to saturation within several days if seeds are present. Solutions supersaturated to the extent of five or six times the solubility are more unstable. In 3 per cent gelatin solution, silver-ion concentrations of 18×10^{-4} were obtained, showing the effect of the colloid in enhancing supersaturation.

[2] In this section and the one following a quantitative description of factors relevant to ring formation is presented. A choice between the theories discussed in Section III can be made on the basis of this evidence.

Both E.M.F. and conductance measurements show that the silver-ion concentration is much greater in solutions of silver chromate containing gelatin than in ordinary aqueous solutions (8). Both silver and chromate ions have been shown to interact with gelatin (7, 69). For example, the activity of silver ion is less in gelatin than in an aqueous solution of silver nitrate at the same concentration. It is probable also that gelatin is adsorbed on the nuclei of silver sulfate and thereby inhibits their further growth by the adsorption of ions. That these phenomena do not depend upon the particular system used is shown by similar results obtained with lead iodide in agar (5, 6). Thus, it appears fairly certain that supersaturated solutions are fairly stable and that this stability is enhanced by the addition of colloidal material. More direct evidence that supersaturation actually occurs during periodic precipitation is shown by direct analysis. Slabs of 5 per cent gelatin about to have silver chromate deposited in them were found to be supersaturated (69). It has been shown previously (48) that periodic precipitation can occur in the presence of seed crystals, but that a definite, fairly high seed concentration is required to prevent ring formation. The relationship between seed density and the extent of ring formation has been derived by Van Hook (67) on the basis of an inexhaustible reservoir of silver nitrate and negligible counter-diffusion of chromate ions. The derivation is based essentially on Fick's law. The quantity dw diffusing across 1 sq. cm. in time dt when the concentration gradient of silver nitrate is $-dc/dx$ is

$$dw = -D\frac{dc}{dx}\,dt$$

where the diffusion coefficient D is assumed to be constant. The amount of silver nitrate diffusing into a volume dx at a distance x from the origin is $D\,dc/dx$ and the amount leaving is

$$D\frac{dc}{dx} - D\frac{\partial\frac{dc}{dx}}{\partial x}\,dx$$

The amount accumulating is

$$D\left[\frac{dc}{dx} - \left(\frac{dc}{dx} - \frac{\partial\frac{dc}{dx}}{\partial x}\right)\right]dx = D\frac{d^2c}{dx^2}\,dx \tag{1}$$

This is potentially

$$\frac{D\frac{d^2c}{dx^2}}{2}\,dx \text{ moles}$$

of silver chromate if the chromate-ion concentration is sufficient. If crystal seeds are dispersed uniformly throughout the medium, each will grow at the rate of

$$\frac{dw}{dt} = ks[f(C - C_0)] \tag{2}$$

where $(C - C_0)$ is the supersaturation of silver chromate. The total growth will be $nks[f(C - C_0)]$, where n is the seed density. The concentration of silver chromate, C, refers to a non-stable equilibrium and therefore can be interpreted in terms of an equivalent concentration of silver nitrate—i.e., potential silver chromate—generated by incoming silver nitrate. The limit of band formation corresponds to the condition that the rate of crystal growth equals the rate of diffusion of silver nitrate into the section. Hence

$$nks[f(C - C_0)] = \frac{D\dfrac{d^2c}{dx^2}}{2}\,dx$$

or

$$\frac{d^2c}{dx^2} = \frac{2nks}{D} f(C - C_0) \tag{3}$$

Van Hook assumes $f(C - C_0) = (C - C_0)^\alpha$ empirically and solves equation 3, using as boundary conditions that $dy/dx = 0$ when $C = C_0$ and C is a constant, B, at $x = 0$. His solution is

$$\frac{1}{(C - C)^\alpha} - \frac{1}{(B - C)^{(\alpha-1)/2}} = \frac{\alpha - 1}{2}\sqrt{\frac{1}{\alpha + 1}\left(\frac{2nks}{D}\right)}\,x \tag{4}$$

When everything except n is held constant, the extent of band formation is given by equation 5.

$$nx_2 = \text{constant} \tag{5}$$

It should be pointed out, however, that equation 5 is independent of the form of $(C - C_0)$ but follows directly from equation 3. Hence equation 5 is valid regardless of the dependence of the velocity of crystal growth on supersaturation. Experimental work shows that equation 5 represents the data for a wide range of concentration and values of n. Some deviations were found at the high and low concentrations. For a large n this may be attributed to ignoring the counter-diffusion of chromate ions, and for small n to the initially rapid growth of nuclei.

B. Crystal growth

There has been considerable work done on the rates of crystallization of both soluble and insoluble solutes from solution (4, 5, 6, 14, 15, 39, 68, 75); in most of these cases the precipitating material is formed without excess of one forming ion over another. The velocity of precipitation can be represented as some function of the supersaturation, and the curve usually consists of a relatively flat induction period, followed by a rapidly decreasing portion. These two parts may be associated with the formation and growth, respectively, of crystal nuclei. Silver chromate is entirely normal in this respect. The progressive addition of seeds, at a definite supersaturation product H^0, continuously diminishes the length of the induction period and also accelerates the growth velocity. The

induction period (J) is some function of the ion product. For silver chromate equation 6

$$J(H^0)^n = \text{constant} \tag{6}$$

has been proposed (39). This type of equation agrees with the idea that non-equivalent amounts of precipitating agents discourage new centers of crystallization (43). The equations for velocity of crystal growth have been solved by Van Hook (68) under certain assumptions. The data are best represented by a first-order reaction for nuclei formation, followed by a second-order growth for each of these nuclei. The concentration is interpreted in terms of a supersaturation $S = C - C_0$.

Then

$$\frac{dS}{dt} = -\left(\frac{dS_1}{dt} + \frac{dS_2}{dt}\right) = K_1S + K_2nS^2 \tag{7}$$

where n is the seed density. For the induction period

$$\frac{dS_1}{dt} = K_1S \tag{8}$$

The solution of equation 8 is

$$\ln \frac{S_0}{S_J} = K_1J \tag{9}$$

and, since S does not change materially during the induction period,

$$S_0J = (H^0 - K_{sp})J = \text{constant} \tag{10}$$

When varying amounts of seeds are added at a given beginning concentration,

$$\int_A^{N_S} dn = K\int_0^J S dt \tag{11}$$

Since n_J is constant during the induction period,

$$N_J - A = kS_0J \tag{12}$$

a result confirmed by experiment. The growth curve is represented by

$$-\frac{dS_2}{dt} = k_2nS^2 \tag{13}$$

If the seed density is constant and large, integration of equation 13 gives

$$\frac{1}{t}\left(\frac{1}{S} - \frac{1}{S_0}\right) = K_2A \tag{14}$$

When A is small or zero, the effect of seed generation cannot be neglected. In that case n can be expressed as

$$n = A + kSt \tag{15}$$

An approximate solution of equation 13 under these conditions is

$$\frac{1}{t}\left(\frac{1}{S} - \frac{1}{S_0}\right) = k_2\left(A + \frac{k'S^0t}{2}\right)$$

Qualitatively this correction improves the constancy of the velocity constants in the latter part of the reactions, especially when A is small. For precipitation from non-equivalent solutions, the velocity expressions are valid only over a narrow range. The deviations become more serious with a greater excess of either reactant. In a gelatin medium the above equations are valid over a much greater range of concentration. However, the reaction rate constants observed in gelatin are within one-tenth of the values in water medium, suggesting an identical mechanism for both cases (71).

V. THE DIFFUSION EQUATION

Shortly after the discovery of Liesegang rings, it was learned that, since they were formed by diffusion, it would be possible to calculate the ion concentrations at the place and time of precipitation. Morse and Pierce carried out such a calculation (49) to determine the supersaturation product H. Their model assumes an inexhaustible reservoir of silver ion and a diffusion process undisturbed by ring formation. Fick's second law for silver and chromate ions, respectively, is

$$D_1 \frac{\partial^2 u}{\partial x^2} = \frac{\partial u}{\partial t} \tag{17}$$

and

$$D_2 \frac{\partial^2 v}{\partial x^2} = \frac{\partial v}{\partial t} \tag{18}$$

where u and v are the ion concentrations. Taking as initial conditions that $u = U_0$ for $x = 0$ and all values of t, and $v = V_0$ for all positive values of x, and $v = 0$ for all negative values at $t = 0$, the solutions obtained are

$$u = \frac{2U_0}{\sqrt{\pi}} \int_{x/2\sqrt{D_1 t}}^{\infty} e - \beta^2 \, d\beta \tag{19}$$

and

$$v = \frac{V_0}{\sqrt{\pi}} \int_{x/2\sqrt{D_2 t}}^{\infty} e - \beta^2 \, d\beta \tag{20}$$

where β is a variable of integration. For silver chromate the supersaturation product is then

$$H = u^2 v = \frac{4U_0^2 V_0}{\pi^{3/2}} \left[\int_{x/2\sqrt{D_1 t}}^{\infty} e - \beta^2 \, d\beta\right]^2 \left[\int_{x/2\sqrt{D_2 t}}^{\infty} e - \beta^2 \, d\beta\right] \tag{21}$$

From equation 21 it follows that if H is constant and D_1 and D_2 are constant, then $x/\sqrt{t}$ must be constant also, independent of U_0 and V_0. Experiments con-

firm this conclusion. Several authors have attempted refinements of the derivation developed by Morse and Pierce (1, 2, 33, 34, 50).

Other equations have been given as criteria for the occurrence of Liesegang rings (37, 60, 72), all of which can be derived (62) from the condition

$$\frac{x}{\sqrt{t}} = \text{constant} \tag{22}$$

or directly from the diffusion equations (59). Equation 22 also has been derived by Van Hook (70) without assuming the existence of a supersaturation product. More recently, the conditions for periodic precipitation have been analyzed by Wagner (74). He takes into account the disturbance in the diffusion of the outer electrolyte resulting from the precipitate formed. His initial conditions are the same as those of Morse and Pierce, except that D_1 and D_2 are equal. He shows that equation 22 is a necessary consequence of the diffusion equations and that it holds true in the case of continuous precipitation; hence the periodic interruptions can be regarded as small perturbations of general diffusion processes. He also recognizes that the end of a precipitation zone results from the discrepancy between the linear growth rate of a crystal and the diffusion rate, and from the necessity for considerable supersaturation in order to have a noticeable rate of formation of new nuclei. Wagner derives an equation for the distance between successive rings which agrees in general with experimental facts and also is consistent with other equations which are known to apply (37, 60, 72). No attempt will be made here to reproduce Wagner's mathematical derivation, but his qualitative description of the process is given because it most closely follows our present knowledge of the subject. Figure 2 shows the concentrations of the reactants as functions of the distance x from the boundary of the original solutions.

This initial state, involving a quasi-continuous precipitation zone, can be obtained by introducing a sufficient number of nuclei capable of growing into the

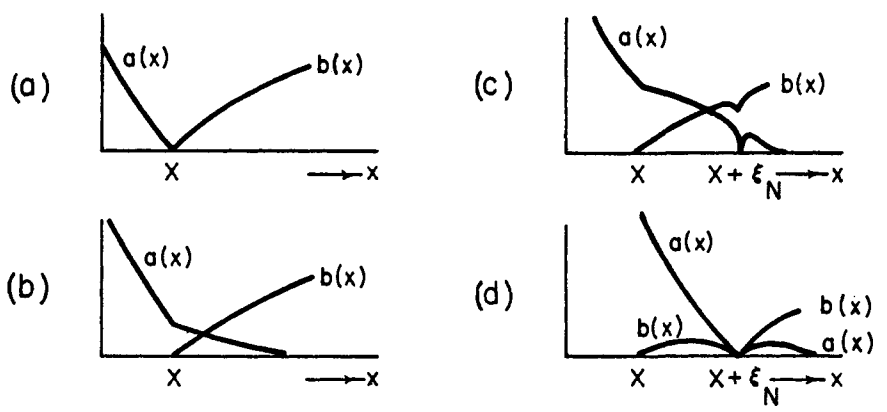

FIG. 2. Concentrations a and b as functions of the distance $\xi = x - X$ at different times after formation of a quasi-continuous precipitation zone.

space $x < X$ at $t < 0$. As shown above, we have $u = v = 0$ at the end of the precipitation zone at $x = X$ (figure 2a), and the diffusion rate of ions A in the positive direction of the x-axis equals that of ions B in the negative direction. If nuclei are missing in the region $x > X$, the precipitation no longer can advance for reasons indicated above. Since the curve $a(x)$ is concave upward, the concentration (x) increases in the course of time; conversely, the curve $b(x)$ is concave downward, and accordingly the concentration (x) decreases. Thus, more ions A than ions B arrive at $x = X$, and, consequently, ions A enter the region $x = X$ as shown in figure 2b. According to the continuing precipitation and consumption of ions A at $x = X$, there is a discontinuity of the slope of the curve $a(x)$ at $x = X$.

In the region $x > X$ a new precipitation zone is formed only if the supersaturation product is reached. The position of the beginning of the new precipitation zone can be obtained by calculating the position of the spatial maximum of the product of the concentrations as a function of time and then determining the position $X + \xi_n$ at which the maximum of the concentration product equals the supersaturation product. Immediately after the formation of new nuclei, ions B are prevalent and thus the concentration of ions A decreases practically to zero, as indicated in figure 2c. Later on, the diffusion rate of ions A arriving at X increases and, conversely, that of ions B decreases until the diffusion rates of ions A and B are equivalent. Thus conditions similar to the initial conditions are reached, as indicated in figure 2d. In this manner a larger number of distinctly separate precipitation zones can be formed. In contrast to figure 2a, figure 2d shows a small concentration of ions A in the region beyond the new precipitation zone at $x > X + \xi_n$, but this difference may be disregarded.

VI. THE WAVE THEORY OF THE LIESEGANG PHENOMENON

In 1924 de Broglie (10) suggested that moving particles have wave properties, just as light waves have corpuscular properties. The fundamental equation is the well-known relation

$$\lambda = \frac{h}{mv}$$

where λ is the wave length of a particle of mass m moving with velocity v, and h is Planck's constant. The periodicity of both waves and Liesegang rings has suggested to some workers that the rings perhaps can be interpreted in terms of waves. This visual analogy is strengthened by observations which indicate that Liesegang rings may exhibit optical phenomena analogous to those usually associated with waves. Thus, the wave front of a ring system is refracted in an optical sense when passing the boundary between gels of different concentrations (51). Supersaturation and interference patterns can be produced, with respect to both intensity and geometry, which result from the superposition of two wave trains, when their wave length, direction, and amplitude are individually or collectively different (57, 58). The explanation for the similarity of two such diverse phenomena may rest in the formal similarity which exists between the

classical diffusion equations and those of wave mechanics (21). In the absence of an external field the diffusion and wave equations are, respectively,

$$\frac{\partial u}{\partial t} = D\nabla u \tag{1}$$

$$\frac{\partial \psi}{\partial t} = \xi \cdot \nabla \psi \tag{2}$$

where $\xi = ih/4\pi m$. It should be remembered that the "diffusion coefficient" is imaginary. Under the same initial and boundary conditions the solutions of equations 1 and 2 are identical. From this formal analogy some workers have proceeded to consider the Liesegang phenomenon as wave-mechanical. Christiansen and Wulff (11) have solved the Schroedinger equation, assuming that Fick's diffusion law and the Morse and Pierce equations are valid. The latter is the form x^2/t = constant. Differentiation gives the diffusion velocity:

$$\frac{dx}{dt} = \frac{x}{2t}$$

Substitution of this equation into the de Broglie relation gives:

$$\frac{x^2}{t} = \frac{2x}{\lambda} \cdot \frac{h}{M}$$

The number of waves is given by the expression

$$N = 1/\lambda = \frac{M}{n} \cdot \frac{x}{2t}$$

The substitution for N is made in the one-dimensional form of the Schroedinger equation:

$$\frac{\partial^2 \psi}{\partial x^2} + 4\pi^2 N^2 \psi = 0$$

The solution produces a "quantum number" m which determines the number of rings which can be produced. The calculated values of m do not always agree with experiment. Moreover, the calculation of m is not always unambiguous, various theoretical values of m being used (38). However, the relation λv = constant has been confirmed experimentally (73). The value of λv depends on the concentration of the outer electrolyte but not on that of the inner. At low gel concentration λv approaches the limit hN/M, where N is Avogadro's number and M the mass of the diffusing particle. λv will be constant only if $\Delta v/v$ = a constant, which is not usually the case.

Substitution of values for h and m into the de Broglie equation gives $\lambda = 40 \times 10^{-6}/v$ for a particle of molecular weight 100. Hence, when v is in the range 10^{-3} to 10^{-5} cm./sec., λ becomes microscopically observable. Moreover, since $v \approx \sqrt{D/t}$, where D is the diffusion constant and t the time after the beginning of diffusion, it follows that waves (or rings) should be visible after several minutes, if $D \approx 10^{-5}$. This is in accord with some experimental observations.

The temperature dependence of the constant λv has been studied for rings produced by the reaction (52, 53):

$$Pb(NO_3)_2 + 2KI \rightarrow PbI_2 + 2KNO_3$$

The product increases up to the limit hN/M according to the expression

$$\lambda v = \lambda_0 v_0 e^{Bt}$$

where λ_0 and v_0 refer to the values at 0°C. and B is a constant.

VII. CONCLUSIONS

From an examination of the various theories proposed to account for the formation of Liesegang rings, it appears that the application of the ordinary diffusion laws is quite adequate. Up to now, no completely rigorous solution of the diffusion equations under proper boundary conditions (instead of simplified assumptions) has been carried out. This is due principally to the mathematical difficulties involved. While the qualitative and semiquantiative agreement between theory and experiment is quite satisfactory, no rigorous comparison between the two—e.g., ring distances and times of formation observed experimentally and derived theoretically—has been carried out.

The wave-mechanical model is not so well developed. Its justification appears to rest primarily on the mathematical similarities between the wave and the diffusion equations and on the visual analogies between rings and waves. The treatment is valid to the extent that every phenomenon involving the motion of matter may be described in terms of waves. However, it may be questioned whether it gives us any better understanding than the conventional diffusion model. Thus, it appears, on the basis of present evidence, that the supersaturation theory of Wilhelm Ostwald is adequate for the description of the gross features of the Liesegang phenomenon. The laws of diffusion and crystal growth should be entirely adequate for the explanation of the qualitative and the quantitative aspects of ring formation, without the introduction of any special assumptions.

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