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LIESEGANG RINGS

BY

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A

THESIS

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Approved by - Jack Lewis Rivers
Asst. Professor of Physics

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CONTENTS

INTRODUCTION

Although the discovery of the "Liesegang Rings" phenomenon was made sometime before 1855,(8) little was done in the way of study or experimentation until 1896 when R. E. Liesegang discovered that if a crystal or strong solution of silver nitrate is added to a gelatin gel containing dilute potassium chromate, the resulting precipitate of silver chromate is not continuous, as might be expected, but forms a discontinuous periodic pattern. This pattern follows a geometric progression law, $x_n = ak^n$, where x_n is the position of the n<u>th</u> ring, and a and k are constants. K is known as the spacing coeficient. This law may also be written $x_n/x_{n-1} = k$, where the constants are the same. The constant k is also known as the Jablynski constant.

Another useful relationship is one which connects the time of appearance, t_n , of the n<u>th</u> ring and its position. This relationship is $x_n/t_n^{1/2} = k'$, where k' is known as the Morse and Pierce constant.

Since the discovery of this phenomenon there have been many theories proposed in an attempt to explain the mechanism which produces this unusual effect. It is the aim of the writer to clear up one of the major objections to one of the two major theories that are still accepted as possible explanations.

As a great many examples of periodic deposition of matter are found in nature, there have been many suggested correlations with the Liesegang phenomenon. Some of these are the agate and other geologic formations, the banded structure of gallstones and other concretions, the rhythmic swarming of bacilli, tree rings, beet root markings, etc. However, if the constancy of the two ratios mentioned above is taken as the criterion for true Liesegang phenomenon, all but the agate and other geologic formations must be excluded. In regard to these last examples, there is still some interest, although there have been other seemingly more reasonable theories propounded.

One application of the Liesegang phenomenon was propounded by Butcher in 1937.(1) This application makes use of the sensitiveness of the phenomenon to very slight variations in blood composition and quality to analyze blood. Also, Liesegang discussed the production of artificial pearls, and Van Hook has made some pieces of novelty ware by generating patterns in certain media which were then hardened and fixed by tanning.

REVIEW OF LITERATURE

There is a great amount of data available on the Liesegang phenomenon.(12) However, most of this data is qualitative in nature. This is especially true where the amount of precipitate in a given band, or ring, is concerned. Some values of k and k' have been calculated, for instance, by Schleussner.(9)

Four major theories have been proposed to explain the phenomenon. These theories will hereafter be referred to as:

1) The Supersaturation Theory,
2) The Adsorption Theory,
3) The Wave Theory, and
4) The Kinetic Theory.

A short resume of each of these theories follows.

1) The Supersaturation Theory

Proposed by Wilhelm Ostwald,(10a) this theory suggests that, as the incoming ions (A-ions) diffuse through the gel, a solution of the precipitate with a concentration in excess of the normal saturation concentration is formed. Then, when this concentration arrives at a value H, called the "supersolubility", spontaneous crystallization takes place and the concentration reduces to the normal solubility limit. Simultaneous backward diffusion of the A-ions clears the area ahead of the precipitation front. This produces a clearly defined band of precipitation and creates an area without A-ions which must be traversed by the reformed diffusion front before the process can repeat itself.

2) The Adsorption Theory

This theory, as proposed by Bradford,(10a) gives the credit for the periodicity to periodic adsorption of the A-ions by the gel medium, which seems to beg the question.

3) The Wave Theory

This theory, proposed by Christiansen and Wulf,(10a) makes use of the de Broglie wave equation:

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

where: v is the diffusion velocity,

λ is the wavelength (distance between rings),

h is Planck's constant, and

m is the mass of the diffusing particle.

Further application of the Schrödinger wave equation gives approximate formulas for the Liesegang phenomenon.

4) The Kinetic Theory

This theory was used by Van Hook (10b) as an explanation of the action of the Liesegang phenomenon in the presence of seed crystals of the precipitate. The static supersolubility limit proposed by Ostwald could not explain why ring formation could proceed in the presence of crystals of the precipitate. The Kinetic Theory explains this by substituting for the static supersolubility limit the condition that the rate of crystallization, at any point, increases as the concentration builds up by diffusion. This rate may be augmented by the presence of seed crystals of the precipitate. The positions and times of appearance of the bands are found by maximizing the relation for the net concentration which results from the opposing tendencies of diffusion and crystallization.

The Adsorption Theory has been largely discounted by many observers as the major mechanism producing the Liesegang phenomenon. For instance, after much experimentation, H. W. Morse (5) arrived at the following conclusion. "These results indicate that any general theory which is to account for periodic precipitation should avoid the introduction of such factors as:- any effect involving the special properties of a gel or other colloid (other than water solution)." The major reason for this statement was the successful use of distilled water as the dispersing medium in the production of a periodic precipitation system. However, it has been demonstrated that adsorption, peptization, and other factors due to the dispersing medium have varying effects on the character of periodic precipitations.(4,7a,7b)

Effectively, the Wave Theory and the Kinetic Theory extend and supplement the Supersaturation Theory. The Wave Theory supplies methods of computing the various constants for a given set of rings. The Kinetic Theory not only offers no particularly valid objections to the Supersaturation Theory, but it also shows how the Liesegang phenomenon can occur with seed crystals of the precipitate present.

In the light of these theories and results, the general consensus of experimenters and theoreticians alike seems to favor a modified Supersaturation theory, where the static supersolubility constant, H, is replaced by a kinetic condition, to explain the gross phenomenon.

An interesting correlation of theoretical and experimental results has been attempted. Carl

Wagner(11) analyzed the theoretical situation using the static supersolubility constant, which he terms K_n. He also assumed that there was no interaction with the medium. The resulting equation follows.

$$(k-1) = (H/\gamma^2)(\ K_n/b_o^{\alpha+\beta})^{1/2\alpha+\beta}$$

This is true if a_o is much greater than b_o and γ^2 is defined by the equation:

$$\exp\ (\gamma^2) = 1/2\ \pi^{-1/2}\ \gamma^{-1}\ (a_o/b_o)$$

k is the Jablynski constant,

H is a constant for a given set of reactants,

K_n is the supersaturation constant,

a_o is the initial concentration of the diffusing, A-ions,

b_o is the initial concentration of the reacting, B-ions,

α and β are the number of atoms of A and B, respectively, in a molecule of the precipitate.

For a given set of reactants and constancy of the ratio a_o/b_o, this equation approximates to:

$$(k-1) = E\ (1/b_o)^{\alpha+\beta/2\alpha+\beta} = F\ (1/a_o)^{\alpha+\beta/2\alpha+\beta}$$

R. Matalon and A. Pacter(4) report the experimental relationship to be:

$$(k-1) = C + D/a_o$$

where C and D are constants for a given set of reactants and gel concentration. However, C will vary with the gel concentration, the set of reactants and b_o, while D depends on the set of reactants and b_o. Matalon and Pacter attempted to show a direct correlation between their results and those of Wagner. If one assumes that Wagner's results had the form:

$$(k-1) = F/a_o$$

as did Matalon and Pacter, and one assumes also that, if the effect of the gel is neglected, C will drop out of the Matalon and Pacter result, the two results will be of exactly the same form. However, this ad hoc modification of Wagner's result hardly seems justified, as the exponent on a_o is seen to be always less than one.

Resume:

Experimental work by Matalon and Pacter concerning the effect of the medium on the Liesegang phenomenon has shown that the composition of the medium has a definite effect on the character of the phenomenon. Also, their experimental results are in fairly close agreement with the results of Wagner which are derived directly from the diffusion equations with the assumption of a static supersolubility constant.

However, any theory based solely on adsorption has been ruled out. Also, the theory based on a static supersolubility constant appears to be overly idealized.

DISCUSSION

Due to the conclusions drawn from the literature, it would appear that a theory based upon a kinetic supersaturation "constant" is most nearly correct. The least complicated theory involving such a constant would be a theory based upon the assumption that the diffusion of A-ions, and thus the formation of product molecules AB, will proceed more rapidly in the direction of advance of the phenomenon than the crystal growth will proceed in the same direction. This condition is also used by Wagner.(11)

In the following discussion of this theory the molecules of AB still in solution will be referred to as the solute, and the molecules of AB which have precipitated out will be referred to as the precipitate.

From the following equation of Nernst(2) it is evident that the rate of growth of crystals is proportional to the concentration of the solute in the bulk solution.

$$dx/dt = B\ A\ (C_2 - C_o)$$

dx/dt is the rate of precipitation of the solute,

A is the surface area of the crystals present,

C_2 is the concentration of the solute in the bulk solution,

C_o is the saturation concentration of the solute in equilibrium with large crystals, and

B is a constant which depends on the rate of diffusion of the solute in the dispersing medium and on the thickness of the layer through which this diffusion takes place.

Within a certain distance from the last zone of precipitation C_2 is essentially equal to C_o. For this distance no new nuclei will be formed and for a short distance further on, where C_2 is only slightly greater than C_o, the rate of growth of the nuclei formed will be quite small. If dx/dt were dependent only on the diffusion gradient (C_2-C_o), the rate of growth of the nuclei formed would keep increasing with no critical value reached as C_2 is a measure of the amount of solute formed. However, dx/dt is also dependent on the size of the crystals present. Thus, when the size of the crystals formed combines with the effect of the diffusion gradient to increase the value of dx/dt to the point where it is equal to the rate of formation of the solute, the advancing diffusion wave is halted until the value of C_2 drops to the value of C_o and the cycle is ready to repeat itself.

The major objection to this theory is that the 'critical' condition is not critical enough. Crystals of appreciable size would be formed on both sides of the main precipitation band and the critical condition would be approached rather slowly. This theory, therefore, would not provide for the narrow bands and the rapid formation of these bands which have been observed experimentally. Thus, a more critical condition is needed.

The above theory is based on the assumption that C_o is a constant. This is not the case. It has been shown experimentally that solubility of a crystal is a function of its size. Theoretical work gives the following formula for this relationship.(3)

$$S_r = S \exp (\alpha/r - \beta/r^4)$$

r is the radius of a crystal which is assumed to be spherical,

S_r is the solubility of a crystal of radius r,

S is the solubility of the solute in equilibrium with large crystals,

α and β are constants for a given dispersing medium and a given product AB

where: $\alpha = 2\sigma M/RT\rho$ and $\beta = q^2 M/8\pi KRT\rho$

σ is the interfacial tension between the solid and its solution,

ρ is the density of the solid,

M is the molecular weight of the AB molecule,

K is the dielectric constant of the medium,

R is the gas constant,

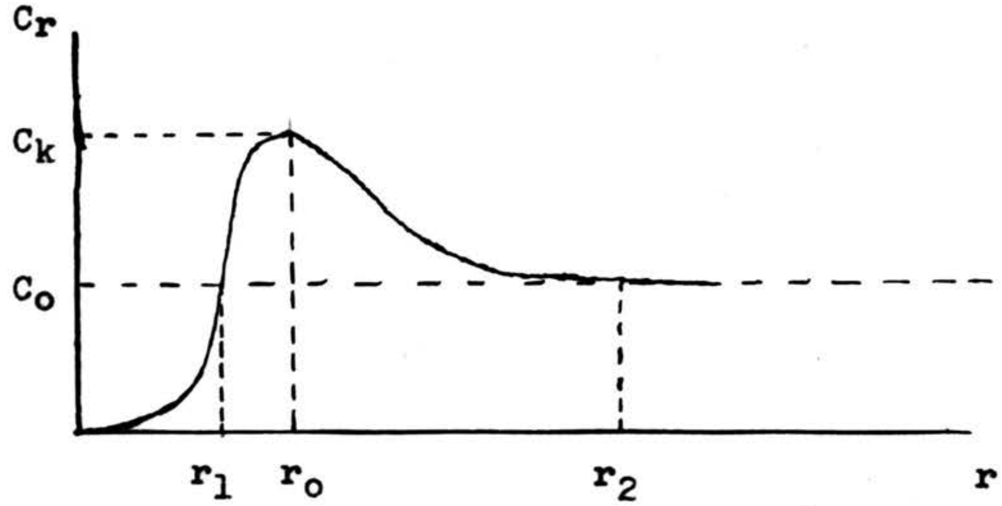
T is the temperature in degrees Kelvin, and

q is the amount of charge on the crystal.

As the saturation concentration is the solubility per unit volume, this equation may be written:

$$C_r = C_o \exp (\alpha/r - \beta/r^4)$$

where C_r is the saturation concentration for a crystal of radius r and C_o is as formerly defined. Figure 1 is a curve showing the relationship between C_r and r and certain critical values of C_r and r are labeled.



It can be seen from the Nernst equation that as nuclei are formed ahead of the last precipitation zone they will grow larger as long as the C_r corresponding to their size is less than C_2 at that point, where the Nernst equation now reads:

$$dx/dt = B\ A\ (C_2 - C_r).$$

That is, the nuclei will grow if the diffusion gradient $(C_2 - C_r)$ is greater than zero. The curve in figure 1 shows that as C_2 increases from zero C_r can not be greater than C_2 until C_2 reaches C_k. If the nuclei increase in size to the point where their corresponding C_r is equal to the value of C_2 at that point, the nuclei will cease to grow due to the then zero diffusion gradient. Actually, C_r will be slightly less than C_2 due to the need for a finite diffusion gradient. If C_r lags behind C_2 to any appreciable degree, the value of the diffusion gradient will be correspondingly larger causing accelerated growth of the nuclei which will cause C_r to "catch up" with C_2. Thus, until C_2 reaches the value C_k, the nuclei present will have radii smaller than r_o.

The above discussion is applicable only until C_2, and thus C_r, reach the value C_k. At this point and time any increase in r will cause an increase in A and a decrease in C_r. The decrease in C_r will cause an increase in the diffusion gradient. The combined increase in both the diffusion gradient and A will cause a rapid increase in dx/dt with a corresponding rapid increase in r. This two fold reaction to an increase in r will cause the solute to precipitate out of solution very rapidly until C_2 has decreased to the value C_o.

It can also be shown from the curve in figure 1 that if there are any crystals of radius greater than r_1 and less than r_2 present when C_2 reaches C_o then these crystals will dissolve until they have radius r equal to r_1. Also, if crystals of radius less than r_1 are present, these crystals will grow until their radius equals r_1. This strongly suggests an experiment to test the validity of this theory. According to the theory, after equilibrium has been reached, there should be crystals present of size $r = r_1$ and r greater than r_2 only. This condition can be tested experimentally.

By use of obvious conditions, the values of r_1 and r_o can be found in terms of α and β.

$$r_o = (4\beta/\alpha)^{1/3}$$

$$r_1 = (\beta/\alpha)^{1/3} = r_o/1.6$$

Representative values of σ and q were not available to the writer. However, an independent source$^{(2)}$ gives values of r_o which are on the order of one tenth of a micron to one micron. The crystals of radius less than r_o are therefore less than visible size.

Thus, it is shown that, by taking into account the variance of solubility with particle size, a logical theory can be set up which will provide for both the rapid formation and the narrow width of Liesegang rings. This theory answers the major objections to the theory using a constant solubility.

If the further assumption is made that the amount of solute used to form the nuclei of radius less than r_o is negligible, that is, that it does not materially effect the diffusion of the A-ions and B-ions, Wagner's results will apply with the maximum value of S_r, S_k, substituted for K_n.

To clarify the mechanism proposed above, a description of what would happen at an arbitrary point, y, in advance of the last band of precipitation, will now be given. For simplicity of description, the phenomenon will be assumed to be advancing toward the right.

At point y the initial conditions are a concentration of solute of C_o or less and a preponderance of B-ions which are diffusing in from the right. As the newly formed diffusion wave of A-ions builds up from the left, there is a point at which the varying concentrations of A-ions and B-ions form a maximum value of C_2 for the given time. This maximum value of C_2 will increase and move toward the right as time progresses, assuming that the influx of A-ions is greater than that of B-ions. At some point y_o and time t_o, C_2 will reach the value C_k and a new precipitation band will form. If y is at or near y_o, nuclei will form and increase in radius until $r = r_o$. At this time $C_r = C_k$ and the nuclei will grow rapidly until $C_r = C_2 = C_o$. Those nuclei whose radii do not equal or exceed r_2 will dissolve until $r = r_1$ and those with radii greater than zero but less than r_1 will grow until $r = r_1$. Any excess solute formed in this process will diffuse to crystals of r greater than r_2 and precipitate out.

If y is not near y_o, nuclei will form and grow to the size where r corresponds to the largest value of C_2 reached at this point. As C_2 at this point does not reach C_k, r will not reach r_o. Shortly after t_o, C_2 will decrease to C_o, causing the nuclei at y to increase or decrease to $r = r_1$, with any excess of solute diffusing to the nearer precipitation zone.

The advantages of this theory over that of the static supersolubility constant are as follows. A kinetic explanation for the heretofore unwarranted assumption of a supersolubility limit is given. This new criterion depends to some extent upon the dispersion media.

CONCLUSIONS

Due to experimental results found in the literature, it was concluded that some form of kinetic supersolubility limit was needed to explain the mechanism of the Liesegang phenomenon.

The form of the "rate of crystal growth" equation of Nernst suggested that, if a specific type of function were used in place of a constant value for the saturation concentration, just such a kinetic supersolubility limit would be a distinct possibility. When the desired function was found in the literature, it was concluded that this could well be the correct explanation of the mechanism of the Liesegang phenomenon.

SUMMARY

The literature is reviewed to determine the bes form for an explanation of the mechanism which produces the Liesegang phenomenon. It is decided that a theory based on a kinetic supersolubility limit is most nearly correct. A theory based on the rate of precipitation equation of Nernst,

$$dx/dt = B\ A\ (\ C_2 - C_o\ ),$$

is formulated using C_o as a constant, and found to lack a sufficiently critical condition for observed properties of the phenomenon. The actual relationship C_r is then substituted for C_o and a revised theory is formulated, where

$$C_r = C_o \exp\ (\alpha/r - \beta/r^4).$$

This revised theory is found to have the necessary critical condition.

An experiment necessitating the finding of nuclei of single size about a micron in diameter between the rings is proposed to test the validity of this theory.

The advantages of this theory over the existing supersaturation theory are stated.

BIBLIOGRAPHY

(1) Bucher, "Die Diffusion Analyse Blutplasmagel." Basle, Switzerland, 1937. (Cited by Van Hook, 10a)

(2) Buckley, H. E., Crystal growth. N.Y., Wiley, 1951. pp. 26-27 and 149.

(3) Knapp, L. F., The solubility of small particles and the stability of colloids. Trans. Faraday Soc., Vol. 17, pp. 457-459 (1921)

(4) Matalon, R., and Pacter, A., Sol protection and diffusion. J. Colloid Science, Vol. 10, pp. 46-62 (1955)

(5) Morse, H. W., Periodic precipitation in ordinary aqueus solutions. J. Phys. Chem., Vol. 34^2, pp. 1554-1577 (1930)

(6) Neuman, Von K., and Costeanu, V., Quantitative Untersuchungen über rhythmische Fällungen. Koll. Z., Vol. 84, pp. 130-138 (1938)

(7a) Pacter, A., The Liesegang phenomenon III. The structure of the gel medium. J. Colloid Science, Vol. 11, pp. 150-157 (1956)

(7b) Pacter, A., The Liesegang phenomenon II. Addition of protecting agents. Ibid., Vol. 11, pp. 96-106 (1956)

(8) Runge, G., Der Bildungstrieb der Stuffe. 1855 (Cited by Van Hook, 10a)

(9) Schleussner, Von C. A., Diffusionsvorgänge in gelatine, II. Beiträge zur Kenntnis des Liesegang'schen Phänomens. Koll. Z., Vol. 34, pp. 338-341 (1924)

(10a) Van Hook, A., "Liesegang rings." Alexander, Colloid Chemistry, Vol. V. N.Y., Reinhold, 1944. pp. 513-518

(10b) Van Hook, A., Supersaturation and Liesegang ring formation, I and II. J. Phys. Chem., Vol. 42, pp. 1191-1206 (1938)

(10c) Van Hook, A., Supersaturation and Liesegang ring formation V. Ibid., Vol. 45, pp. 879-884 (1941)

(10d) Van Hook, A., The precipitation of silver chromate III. Ibid., Vol. 45, pp. 1194-1203 (1941)

(11) Wagner, C., Mathematical analysis of the formation of periodic precipitations. J. Colloid Science, Vol. 5, pp. 85-97 (1950)

(12) For a more complete list of references prior to 1944, see (10a).

VITA

Robert Edward Young was born June 10, 1933 in Berwyn, Illinois. He was reared in LaGrange, Illinois and attended Cossitt School and Lyons Township High School, graduating from the latter in June 1951.

In September of 1951 he enrolled in Albion College at Albion, Michigan. In June 1955 he graduated from Albion College with an A. B. degree in Physics and Mathematics. He attended Iowa State College, Ames, Iowa during the 1955-1956 school year. In September 1956 he enrolled at Missouri School of Mines, where he has since been attending school as a graduate assistant.