A Diffusion Mechanism for Liesegang Rings. I. Spacing Law*

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Jablczynski's equation for spacings between Liesegang rings

$$x_n = ak^n \tag{1}$$

where x_n is the distance of nth ring from the diffusion level, and a and k are constants, may be written as

$$\frac{x_{n-1}}{x_n} = \frac{1}{R} \tag{2}$$

or $$1-\frac{x_{n-1}}{x_n} = \left(1-\frac{1}{R}\right)$$

or $$(x_n - x_{n-1}) = kx_n \tag{3}$$

From statistical consideration, Eq. 3 is more sensitive form of Jablczynski's relation 1. According to the Eq. 3 the plot of $(x_n - x_{n-1})$ against x_n should be straight line curves passing through the origin. In practice the curves are not found to pass through the origin when the distances of the rings are measured from diffusion level for which Eq. 1 stands. The author has advanced a theory and deduced from Fick's diffusion law a few general expressions for the Liesegang phenomenon. The theory reflects light on the mechanism of ring formation, fine structure, influence of various environmental conditions, etc.

Fick's diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{4}$$

may have a solution

$$c = a\,e^{-\alpha x}\cos(\omega t + \beta x + y) \tag{5}$$

given by Riemann[2] for similar type of differential equations. Such a solution would be possible under conditions analogous to those operating in the propagation of sound in air, discharge of a current through a condenser and a resistance, where the motion of the matter is met by an opposing force.

In the phenomenon of Liesegang rings the two electrolytes meet and get precipitated and thus forms a new phase at the boundary of the diffusing salt and the medium. By virtue of the electrical forces at its surface and the fine nature of the particles distributed there, the boundary phase or say 'membrane' will have the tendency in certain cases to oppose the diffusion of salt and so to develop a situation where diffusion may be governed by Eq. 6.

The concentration distribution at a particular instant t_i may be given by

$$c = a\,e^{-\alpha x}\cos(\beta x + \phi) \tag{6}$$

where ϕ is another constant equal to $(\omega t_i + y)$.

During the process of Liesegang ring formation of say silver chromate rings, the diffusion wave front of silver ions moves forward and gives rings one after another. The latter changes in concentration at the preceeding levels when one of the precipitating ions is completely removed cannot influence a ring position. By determining the values of arbitrary constants a and ϕ in Eq. 6 from the known boundary conditions of reacting ions the equations for their concentration distribution can be obtained.

For silver ions, when $x=0$, $C \rightarrow$ maximum. In Eq. 6 C will be maximum, when $\cos(\beta x + \phi)$ is unity or $(\beta x + \phi) = 0$. Since $x=0$, ϕ must be zero to satisfy the above condition. Hence

$$c = a\,e^{-\alpha x}\cos(\beta x) \tag{7}$$

Now, the limiting maximum value of C at $x=0$ is the same as the initial bulk concentration C_0 of silver ions; substituting this value into above equation we have $a = C_0$. Eq. 7 reduces to

$$c = C_0\,e^{-\alpha x}\cos(\beta x) \tag{8}$$

Relation 8 geometrically represents a simple harmonic curve whose amplitude $C_0\,e^{-\alpha x}$ diminishes exponentially to zero with increasing distance. As the chromate ions diffuse in the upward direction their distribution may be represented by the equation

$$C' = C_1\,e^{\alpha' x}\sin(\beta' x) + C_2\,e^{\alpha' x}\cos(\beta' x) \tag{9}$$

where damping coefficient α' has a positive sign. The constants C_1 and C_2 in the above equation can be determined from boundary conditions of chromate ions.

In a thin region of the precipitate the concentration of chromate ions may be taken to be equal to zero because the traces of ions

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1) K. Jablczynski, *Bull. soc. chim., France* (4), 33, 1592 (1923).

2) Riemann, "Particlle Differentialgleichungen", Edit Hattendorff (1938), p. 110.; P. B. Mathur, *Bull. Acad. Polona. Sci.*, 8, 8, 429 (1960).

left there after precipitation get absorbed by the precipitates rendering practically a complete disappearance of the ions. Hence at $x=0$, $C'=0$. Substituting this condition into Eq. 9, we have $C_2=0$, so we have,

$$C'=C_1\,e^{\alpha' x}\sin(\beta' x) \qquad (10)$$

Let us suppose, when $x=x_0$, $C'\rightarrow$ maximum. So, in Eq. 10, C' is maximum when $\sin(\beta' x_0)$ is unity or $\beta' x_0=\pi/2$ or $x_0=\pi/2\,\beta'$ and so

$$C'=C_1\,e^{(\alpha'\pi/2\beta')}$$

Now the limiting maximum value of C' at a distance of x_0 is the same as the initial bulk concentration C_0' of chromate ions. Substituting this value into the above equation we have

$$C_1=C_0'\,e^{-(\alpha'\pi/2\beta')}$$

Eq. 10 thus reduces to the form,

$$C'=(C_0'\,e^{-(\alpha'\pi/2\beta')})\,e^{\alpha' x}\sin(\beta' x) \qquad (11)$$

Eq. 11 represents the distribution of chromate ions where x is measured from zero concentration level.

Let us now suppose that $(n-1)$ rings have already formed and nth ring is in the process of formation. So the concentration of chromate ions at $(n-1)$th level has fallen to zero. Let C_n and C_n' be the concentrations of silver and chromate ions respectively at nth rings, and x_n and x_{n-1}, the distances of nth and $(n-1)$th levels respectively from the initial diffusion level. The reference line for chromate ions corresponding to the nth ring is $(n-1)$th ring level, while for silver ions it is the initial diffusion level. In order that the two equations could be combined, the line of reference for the two ions must be the same. Substituting $x=(x_n-x_{n-1})$ into Eq. 11 for chromate ions and $x=x_n$ in Eq. 8 for silver ions and corresponding concentrations in the two equations, we get the following equations for silver and chromate ions respectively,

$$C_n=C_0\,e^{-\alpha x_n}\cos(\beta x_n) \qquad (12)$$

$$C_n'=C_0'\,e^{-(\alpha'\pi/2\beta')}\,e^{\alpha'(x_n-x_{n-1})}\times\sin[\beta'(x_n-x_{n-1})] \qquad (13)$$

The distribution of the concentration product of silver and chromate ions can be obtained by combining Eqs. 12 and 13

$$C_nC_n'=C_0C_0'\,e^{-(\alpha'\pi/2\beta')}\,e^{-\alpha x_n}\,e^{\alpha'(x_n-x_{n-1})}\times\sin[\beta'(x_n-x_{n-1})]\cos(\beta x_n) \qquad (14)$$

The above equation represents the curve shown in Fig. 1. The periodic terms cos. and sin. alternate between the limits ±1, and the concentration curve shows two types of periodicities one by broad wave PQRS and the other by narrow waves. By putting $\cos(\beta x_n)=1$, we get the curve PQRS which is the locus of the points of maxima of narrow curves, and by putting $\sin(\beta'(x_n-x_{n-1}))=1$, the remaining equation represents only the finer structures of a half wave PQ.

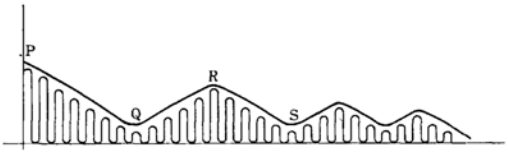

Fig. 1

The condition for the precipitation at the place is that the ionic product should exceed or be equal to the solubility product of the sparingly soluble salt at the level

$$C_nC_n'\geqq S$$

In critical case $C_nC_n'=S$; so substituting the condition into Eq. 14, we have

$$S=[C_0C_0'\,e^{-(\alpha'\pi/2\beta')}\,e^{-\alpha x_n}\,e^{\alpha'(x_n-x_{n-1})}]\times\sin[\beta'(x_n-x_{n-1})]\cos(\beta x_n) \qquad (15)$$

The above equation represents the phenomenon of Liesegang Rings in general form. The graphical representation of the equation is made in Fig. 2. The dotted liness in Fig. 2 indicates the solubility product of sparingly soluble salt. The spaces where the ionic product curve falls below SS′ level indicates void regions while those places where the curve crosses the line SS′ indicates the precipitate regions. Void spaces and precipitate regions have been represented in the figure by clear and dark areas respectively. The broader band structure of Liesegang systems will be given by

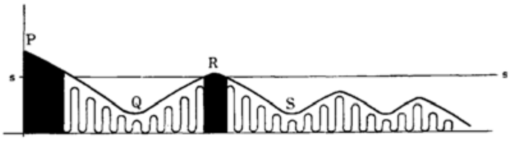

Fig. 2

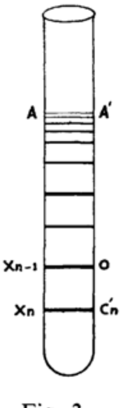

Fig. 3

$$S=[C_0C_0'\,\mathrm{e}^{-(\alpha'\pi/2\beta')}\,\mathrm{e}^{-\alpha x_n}\,\mathrm{e}^{\alpha'(x_n-x_{n-1})}]$$
$$\times\sin\{\beta'(x_n-x_{n-1})\} \qquad (16)$$

In case where the modulus of decay α and frequency factor β' of the wave profile of chromate ions are sufficiently small, Eq. 16 can be simplified further by putting $\mathrm{e}^{\alpha'(x_n-x_{n-1})}$ =unity, and

$$\sin[\beta'(x_n-x_{n-1})]=\beta'(x_n-x_{n-1})$$

So, we get

$$S=(C_0C_0'\,\mathrm{e}^{-(\alpha'\pi/2\beta')})\mathrm{e}^{-\alpha x_n}\,\beta'(x_n-x_{n-1}) \qquad (17)$$

or $$(x_n-x_{n-1})=\left(\frac{S\,\mathrm{e}^{(\alpha'\pi/2\beta')}}{C_0C_0'}\right)\mathrm{e}^{\alpha x_n} \qquad (18)$$

or $$(x_n-x_{n-1})=\left[P\left(\frac{S}{C_0C_0'}\right)\right]\mathrm{e}^{\alpha x_n} \qquad (19)$$

P is a constant.

Since $\beta'=2\pi/\lambda'$, λ' being the wave length of chromate ions wave, Eq. 18 can be written as

$$(x_n-x_{n-1})=\left(\frac{S\lambda'\,\mathrm{e}^{\alpha'\lambda'/4}}{2\pi C_0C_0'}\right)\mathrm{e}^{\alpha x_n} \qquad (20)$$

or $$(x_n-x_{n-1})=\psi\,\mathrm{e}^{\alpha x_n} \qquad (21)$$

Taking the logarithm, we have

$$\log(x_n-x_{n-1})=A+\alpha x_n \qquad (22)$$

where A is another constant.

It may be noted here that the nature of Eq. 22 is not affected by changing the line of reference in the measurement of the rings. If d is the distance of n' order ring from a new reference level, then

$$x_n=(x_{n'}-d)$$

or $$\log(x_{n'}-x_{n'-1})=A+\alpha(x_n-d)$$

or $$\log(x_{n'}-x_{n'-1})=A'+\alpha' x_{n'} \qquad (23)$$

Two Eqs. 22 and 23 differ only in constants.

In a Liesegang ring system αx_n may be considered as a small quantity for first few rings and so $\mathrm{e}^{\alpha x_n}$ can be expanded and higher terms may be neglected. Eq. 21 thus reduces to

$$(x_{n'}-x_{n'-1})=\beta'+\alpha' x_{n'} \qquad (24)$$

Eq. 24 differs from Eq. 3 in the constant β. The derivations here thus lead to an equation which is a corrected form of Jablczynski's empirical relation 1 or 3 which has already been studied by several workers. It may be noted that even Eq. 24 is a special case of more general expressions (15, 19, 20 and 23) for the phenomenon of Liesegang rings.

Discussion

Eq. 15 has graphically been represented in Fig. 1. The figure predicts the presence of fine structure between precipitate bands. Such structures have already been reported by Riegel and Reinhands[4], Hedges[5] and Friend[6] for the silver chromate system in gelatin gel. The author also made studies on the growth of rings. Liesegang rings of silver chromate were obtained by diffusing 2.5, 5, 7.5 and 10% silver nitrate solutions through test tubes containing 2, 4, 6 and 8% gelatin gels impregnated with 0.01 M chromate. The temperature was maintained befow 16°CF during the experiment. Distinct fringes of bright yellow color closely packed rings were seen when gelatin was dilute. The rings obtained were watched continuously for 12 hr. and it was found that even precipitate rings developed not as one single ring but as an aggregate of two or more closely packed fine rings which grew thicker and thicker with time and finally small gaps in between them gradually disappeared and thick layers of precipitates were formed. The observation proves the validity of Eqs. 14 and 15. For close study of the phenomenon, it is always useful to carry out experiments at low temperature and with low concentrations of gel.

Eq. 19 indicates that the rings would get more and more packed as the initial concentrations of ions increase and solubility product decreases. The effect of solubility on silver chromate rings has been studied by Varma and Ghosh[7] and influence of ionic concentration by several other workers[8]. Their results are in conformity with the conclusions drawn above.

The theory indicates that the nature of diffusion is mainly responsible for rhythmic phenomenon; a proper type of membrane[9] however becomes a necessary condition for the occurance of the process. Several factors such as colloidal formation super-saturation, etc., may help or hinder the formation of a proper type of membrane, but they themselves cannot be considered as the cause for Liesegang rings. The phenomenon may occur even in the absence of any of these conditions.

The experimental support of various expressions obtained above for Liesegang rings justifies the use of Raimann solution for Fick's diffusion equation. The theory thus indirectly throws light on the mechanism of diffusion.

In subsequent communications other aspects

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4) E. R. Riegel and M. C. Reinhard, *J. Phys. Chem.*, **31**, 713 (1927).

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7) K. K. Varma and S. Ghosh, *Kolloid-Z.*, **133**, 1, 32 (1953).

8) R. Metalon and A. Packter, *Loc. Cit.* A. Packter, *Kolloid-Z.*, **142**, 109 (1955).

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of Liesegang ring phenomenon will be treated quantitatively.

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