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`![Fig. 1](figure)`

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Fig. 1

Figure 1: Fig. 1

Abstract

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MATHEMATICAL PHYSICS

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ON THE QUASIPERIODIC PRECIPITATION OF SEDIMENTS DURING THE MUTUAL DIFFUSION OF TWO SUBSTANCES

(LIESEGANG RINGS)

It is known ([1]) that, during the mutual diffusion of two substances which, upon reacting, give an insoluble precipitate, the latter in a number of cases is distributed discretely in space (Liesegang rings). The most plausible of the existing schemes ([1]) for the formation of Liesegang rings seems to us to be the following. In the process of diffusion the solution becomes supersaturated with the reacting substances A and B. This continues until the product ab of the concentrations of the substances A and B reaches a certain critical value k (the "metastable boundary"). As soon as ab exceeds k, precipitation begins until one of the components of the reaction has completely disappeared at the given point in space. The concentration of this component subsequently remains equal to zero, since the new portions of it arriving by diffusion are bound with the other reacting substance at the boundary of the precipitate. If the rate of expansion of the precipitate region is sufficiently small, then the place where the metastable boundary will be reached and the next precipitate will fall will be located at a certain distance from the place of the initial precipitation. It is precisely from this point of view that the phenomenon of formation of Liesegang rings was considered in ([2]). In the present work an approximate theory of the phenomenon is given in the simplest case of diffusion of substances in a cylindrical tube.

Fig. 1

Let an unlimited reservoir of substance A be placed at the beginning ($x = 0$) of a tube ($x \geqslant 0$) filled with a solution of substance B (Fig. 1). The reservoir is separated from the tube by an impermeable partition, which is removed at the initial instant $t = 0$. The quantities determining the process are: t_0, the characteristic time of the reaction and precipitation of the precipitate; a_0, b_0, the concentrations of substances A and B respectively in the reservoir and in the tube before the start of the process; the diffusion coefficients D_a, D_b; the metastable boundary k; the coordinate x and the time t. From all these quantities one can form only 5 independent dimensionless parameters

$$c = \frac{a_0}{b_0}, \qquad \varkappa = \frac{k}{a_0 b_0}, \qquad \alpha^2 = \frac{D_b}{D_a}, \qquad X = \frac{x}{\sqrt{D_a t_0}}, \qquad T = \frac{t}{t_0}. \quad (1)$$

Considering the process for $x > x_n,\ t_{n+1} > t > t_n$ (x_n, t_n are the place and time of precipitation of the n-th precipitate), one may assert that the dimensionless quantities

$$\mu = \frac{x_{n+1}}{x_n}, \qquad \gamma = \frac{t_{n+1}}{t_n}, \qquad \eta = \frac{\sqrt{D_a t_{n+1}}}{x_{n+1}} \quad (2)$$

depend only on the dimensionless parameters (1), where x and t must be supplied with the index n. Introduce the dimensionless variables $\xi = x/x_n$, $\tau = t/t_n$. Then the $(n+1)$-st precipitate will begin to form at the point $\xi = \mu$ at the time $\tau = \gamma$. The conditions expressing this are, evidently, written in the form:

$$ab = k, \qquad \partial(ab)/\partial\xi = 0 \quad (3)$$

for $\xi = \mu,\ \tau = \gamma$. For sufficiently large n, the quantities μ, γ, η and the distribution of the concentrations a and b in the region $1 < \xi < \infty,\ 1 < \tau < \gamma$ depend only on the first three parameters in (1) and do not depend on n (quasiperiodicity*). In this case there is a relation between the quantities (2),

$$\mu^2 = \gamma. \quad (4)$$

Thus, in order to study only the quasiperiodic regime, it is sufficient to determine the dependence of the distribution of the concentrations a and b in the region $1 < \xi < \infty,\ 1 < \tau < \gamma$ on the parameters $\mu, \gamma, \eta, \alpha, c, \chi$, so that from (3) and (4) the quantities μ, γ, η may be found. Generally speaking, the formation of a precipitate affects the distributions of the concentrations a and b. However, if $k \neq 0$, then, for

$$c \gg 1, \qquad a \gg 1 \quad (5)$$

this influence on the distribution of the concentration a may be neglected.

Since the rate of expansion of the region of precipitate is determined by the smaller of the diffusion rates and by the specific volume of the precipitate, the first of these quantities being small by virtue of (5), then, assuming the second also to be small, the precipitates may be considered concentrated at the points x_n, and the reaction instantaneous in comparison with diffusion.

From what has been said it follows that the distribution of a is obtained from the relations

$$\frac{\partial a}{\partial \tau} = \eta^2 \frac{\partial^2 a}{\partial \xi^2}, \qquad a\Big|_{\substack{\tau=0 \\ 1<\xi<\infty}} = 0, \qquad a\Big|_{\substack{0<\tau<\infty \\ \xi=0}} = a_0, \tag{6}$$

and is equal to

$$a = a_0 \left[1 - \Phi\left(\frac{\xi}{2\eta\sqrt{\tau}}\right)\right], \qquad \Phi(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-t^2}\, dt, \tag{7}$$

while b is obtained from the conditions

$$\frac{\partial b}{\partial \tau'} = (\alpha\eta)^2 \frac{\partial^2 b}{\partial \xi'^2}; \qquad b\Big|_{\substack{\tau'=-0 \\ 0<\xi'<\infty}} = \psi(\xi'), \qquad b\Big|_{\substack{0<\tau'<\gamma' \\ \xi'=0}} = 0, \tag{8}$$

where $\tau' = \tau - 1$, $\xi' = \xi - 1$, etc.; $\psi(\xi')$ is the unknown distribution of the concentration b beyond the place and by the time of formation of the n-th precipitate. We shall show that, in the approximation adopted, one should take $b(\xi', \gamma' - 0) = \psi(\xi') = b_0$ for $\xi' > 0$.

Evidently,

$$0 < \psi < b_0, \qquad \lim_{\xi' \to \infty} \psi = b_0. \tag{9}$$

From (8) we obtain

$$b(\xi', \gamma') = \int_0^\infty \psi(u)\, G(\xi'_*, u_*)\, du_*, \tag{10}$$

where the notation used is

$$y_* = \frac{y}{2\alpha\eta\sqrt{\gamma'}}, \qquad G(y, z) = \frac{1}{\sqrt{\pi}} \left[e^{-(y-z)^2} - e^{-(y+z)^2}\right]. \tag{11}$$

By the definition of quasiperiodicity, the distribution (10), for $\xi' > \mu'$, as a function of the variable x/x_{n+1}, must coincide with $\psi(\xi')$. Therefore, from (10)

* Quasiperiodicity of precipitate formation has been confirmed experimentally ([1]).

we obtain, replacing ξ' by $\mu\xi' + \mu'$, the integral equation

$$\psi(\xi') = \int_0^\infty \psi(u)\, G(\xi'_{**}, u_*)\, du_*, \tag{12}$$

where the notation used is

$$y_{**} = \mu y_* + \sigma, \qquad \sigma = \mu'/2\alpha\eta\sqrt{\gamma'}. \tag{13}$$

Put

$$\psi(\xi') = b_0[1 - \varphi(\xi')], \tag{14}$$

then from (9) it follows that

$$1 > \varphi(\xi') > 0, \qquad \lim_{\xi' \to \infty} \varphi(\xi') = 0. \tag{15}$$

Substituting (14) into (12), we obtain an equation for determining φ:

$$\varphi(\xi') = \Phi_1(\xi'_{**}) + \int_0^\infty G(\xi'_{**}, u_*)\varphi(u)\, du_*, \qquad \Phi_1 = 1 - \Phi. \tag{16}$$

Applying $N-1$ times to φ the operator standing on the right-hand side of (16), we obtain the distribution $(b - b_0)/b_0$ at the moment $t = t_{n+N}$ for $x > x_{n+N}$

$$\varphi(\xi') = \Phi_1(\xi'_{**}) + \int_0^\infty \sum_0^{N-1} G_j(\xi'_{**}, u_*)\Phi_1(u_{**})\, du_* +$$

$$+ \int_0^\infty G_N(\xi'_{**}, u_*)\varphi(u)\, du_*; \tag{17}$$

$$G_0(\xi'_{**}, u_*) = G(\xi'_{**}, u_*), \qquad G_j(\xi'_{**}, u_*) = \int_0^\infty G_{j-1}(\xi'_{**}, v_*)G(v_{**}, u_*)\, dv_*.$$

The first two terms of (17) give that part of the distribution $(b - b_0)/b_0$ at the $(n + N)$-th stage which would have resulted from the action of sinks switched on in the sections $x = x_{n+j}$ at the moments $t = t_{n+j}$ $(j = 1, 2, \dots, N)$, on the initial distribution $b = b_0$ at the n-th stage. The last term gives a correction for the nonuniformity of the initial distribution at the n-th stage. Discarding this correction and using the fact that $\varphi \geqslant 0$, we obtain a lower estimate for φ. From this estimate there follows, in particular, the convergence of the series of $G_j\Phi_1$ to a function integrable from zero to infinity with respect to u (Beppo

Fig. 2

Figure 2: Fig. 2

Levi theorem ([3])), and from (15) it follows that the influence of the correction as $N \to \infty$ vanishes. Thus, for φ one obtains the formula

$$\varphi(\xi') = \Phi_1(\xi'_{**}) + \int_0^\infty \sum_{j=0}^\infty G_j(\xi'_{**}, u_*)\Phi_1(u_{**})\, du_*, \tag{18}$$

and it can be shown that conditions (15) are satisfied for this function. It is important that the right-hand side of (18) tends to zero not only as $\xi' \to \infty$, but also as $\sigma \to \infty$, since $\xi'_{**} = \mu\xi'_* + \sigma$. Therefore $\varphi(\xi') \to 0$ as $a \to 0$. Indeed, if in (14) one sets $\varphi(\xi') = 0$ and increases k so that the precipitate still forms at $\tau = \gamma$, then the point $\xi = \mu_1$ of precipitate formation will be located to the left of the point $\xi = \mu$, so that the corresponding $\eta = \eta_1$ will increase and, consequently, $\sigma = \sigma_1$ will decrease. The solution (7) is then written in the form

$$b = b_0\Phi\left(\frac{\xi'}{2\alpha\eta_1\sqrt{\tau'}}\right). \tag{19}$$

From (3), (7), (19) we find

$$\Phi(\sigma_1)e^{\sigma_1^2}\alpha\sqrt{\frac{\gamma-1}{\gamma}} = \Phi_1(s_1)e^{s_1^2}, \qquad a_0\Phi_1(s_1) \geq k_1/b_0. \tag{20}$$

Here $s_1 = \mu_1/2\eta_1\sqrt{\gamma}$. From (20) it is seen that $\sigma_1 \to \infty$ as $\alpha \to 0$, whence it also follows from the preceding that $\sigma \to \infty$ as $\alpha \to 0$.

Thus, for sufficiently small α one may neglect the nonuniformity of the distribution of the concentration of substance B to the right of the place where the next precipitate appears at the moment of its appearance, i.e., take $b(\xi', \gamma' - 0) \equiv \psi(\xi') = b_0$ for $\xi' > 0$. Therefore the distribution b is given by formula (19), in which η_1 is replaced by η. From this formula, and also from (3), (4), (7), we obtain equations for determining the unknown parameters μ and η

$$\exp\left\{\frac{\mu-1}{\mu+1} - \frac{1}{2\alpha^2\eta^2}\right\}\alpha^2\frac{\mu^2-1}{\mu^2} =$$

$$= \Phi_1^2\left(\frac{1}{2\eta}\right)\exp\left(\frac{1}{2\eta^2}\right), \qquad \Phi_1\left(\frac{1}{2\eta}\right) = \chi. \tag{21}$$

Fig. 2

The criterion for the smallness of α is the closeness to unity of the quantity

$$\Phi\left(\frac{\mu-1}{2\alpha\eta\sqrt{\mu^2-1}}\right).$$

In Fig. 2 the graphs $\mu(\alpha)$ for various χ, constructed from formulas (21), are shown. There also, for estimating the range of applicability of these graphs, the corresponding graphs of

$$\Phi\left(\frac{\mu-1}{2\alpha\eta\sqrt{\mu^2-1}}\right)$$

are presented.

Thus, for example, it is seen from Fig. 2 that if the difference of Φ from 1 is neglected within 0.02, then formulas (21), for $\chi = 0.05;\ 0.2;\ 0.5$, may be used up to the values $\alpha = 0.5;\ 0.3;\ 0.15$, respectively.

The results obtained may be used for the experimental determination of the metastable boundary k. For this it is necessary to know from experiment a_0, b_0, μ, and α. From μ and α, using (21), one can find η and χ, and from χ and the known a_0, b_0, using (1), find k. If measurement of the diffusion coefficient of the internal component (B) is for some reason difficult, then, by measuring μ, D_a, and t_n, one can determine η from (1) and then, from μ and η using (21), find χ and α, i.e., k and D_b. The determination of μ is best carried out not from neighboring precipitates, but from precipitates separated by several intermediate ones, according to the formula $\mu^N = x_{n+N}/x_n$, where, owing to quasiperiodicity, knowledge of the number n is not required.

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