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Liesegang Rings and a Theory of Fast Reaction and Slow Diffusion

Joseph B. Keller

1. INTRODUCTION.

A chemically reacting system usually proceeds monotonically in time toward a state of completed reaction, a state of equilibrium, or a steady state. The ultimate state is generally homogeneous in space, as a consequence of diffusion, even though the initial state may be inhomogeneous. Therefore it is surprising that certain chemical systems do not behave in this way. Instead some of them exhibit temporal oscillations which do not decay in time, but which become temporally periodic. Other systems, or the same systems with different parameter values, perform oscillations which persist but remain chaotic rather than becoming periodic. Still others reach steady states which are not homogeneous in space, but which are spatially periodic or quasi-periodic. There are also systems which continue to oscillate in time and to be quasi-periodic in space.

Examples of such unusual behavior of chemically reacting systems have been known for a long time. One of them was discovered by R. E. Liesegang [1] in 1896 and studied by him for many years thereafter. The spatial pattern which occurs in this system consists of a family of concentric circular rings which are called Liesegang rings in his honor. It is this system and similar ones which we shall examine. In order to analyze them, first we shall have to describe in detail the physical and chemical processes which occur. This we shall do following the ideas of W. Ostwald [2] who, in 1897, outlined...
an explanation involving precipitation and supersaturation. We shall extend that outline to a complete description of the various processes. Then we shall convert this verbal description into a mathematical theory, and formulate an appropriate mathematical problem corresponding to it. All of these considerations, and the subsequent analysis of the problem, are the joint work of S. I. Rubinow and the author, and are presented in greater detail in their paper [3].

In order to treat the mathematical problem we shall make certain appropriate simplifications. The most important of these is a consequence of the fact that the reaction process is fast compared to the diffusion process. This has led us to formulate and develop a general theory of reaction and diffusion processes involving fast reaction and slow diffusion. We shall describe this theory, which should have many other applications, and use it to simplify the present problem. It was worked out by P. S. Hagan and the author, and is contained in their paper [4] together with the related theory of some fast and some slow reactions.

The subsequent analysis of the simplified problem is carried out in [3] employing approximations like those in the related work of C. Wagner [5], S. Prager [6] and Zeldovich, Barenblatt and Salganik [7]. Some predictions of the theory are compared in [3] with certain relevant experimental results. More detailed comparison between theory and experiment will be possible when the equations of the theory are solved numerically. J.-M. Vanden-Broeck and the author [8] are solving them by using the method of finite differences to replace the partial differential equations by a finite set of algebraic equations. These equations, together with the initial, boundary, and jump conditions, are being solved by an appropriate iterative method.

Before turning to the study of Liesegang rings, we shall comment on the periodic or non-monotonic behavior of chemical systems in general. Let us first consider why chemical reactions are expected to proceed monotonically in time. The reason is that the rate of reaction is positive as long as the concentrations of the reactants are positive and the concentration of the reaction products is not too large. Furthermore
there is no mechanism, such as inertia, to cause the reaction to overshoot the equilibrium state or the state of completed reaction. Therefore it is to be expected that a reaction will proceed in one direction at a decreasing rate. However when several reactions occur, there is no longer any justification for this belief. The presence of other processes, such as flow and diffusion, can also lead to destabilization of uniform steady states and the occurrence of temporal or spatial periodicity.

The interest in periodic and non-uniform states of reacting systems has been generated by scientific curiosity, by engineering necessity, and by potential applications in biology. The engineering reason is the need to control and eliminate oscillations which arise in stirred tank and other continuous flow reactors. The biological reasons include the possible explanation of biological clocks and a proposed explanation of morphogenesis. The latter of these, made by A. M. Turing in 1952, is that chemical reaction and diffusion are responsible for the creation of form in biological systems through the development of spatially nonuniform steady states. All of these reasons have led to extensive experimental and theoretical investigations of the non-monotonic and non-uniform behavior of chemical systems.

2. THE MECHANISM OF LIESEGANG RING FORMATION.

Liesegang, while experimenting with photographic materials, prepared a gel containing potassium dichromate. This gel was in the form of a thin layer on a glass plate. He placed a drop of silver nitrate solution on the gel and found, after some time, that concentric circular rings of silver chromate formed in the gel. The process whereby the silver chromate formed into visible solid particles is precipitation, so this phenomenon has sometimes been called "periodic" precipitation. However it is not periodic in either space or time, so that is a misnomer. We prefer to call it recurrent precipitation, since the rings form one after another with increasing spatial and temporal intervals between successive rings.
To explain this phenomenon we suppose that silver ions from the drop go into solution in the gel and diffuse radially outward. Within the gel they encounter chromate ions and react with them to form silver dichromate. As the chromate ions near the drop are consumed by the reaction, more chromate ions diffuse radially inward. Thus the two reactants diffuse toward one another and, upon coming together, continually produce silver dichromate. In this way an expanding circular region of silver dichromate is produced. This is the monotonic behavior to be expected in chemically reacting systems. The question then arises of why only separated rings of silver dichromate are visible at the end of the experiment?

To answer this question we assume that the silver dichromate is not visible until it precipitates out of solution and forms solid particles. Now it is well known that a dissolved substance cannot precipitate until its concentration \( c \) exceeds the saturation concentration \( c^s \). Then the rate of precipitation is proportional to \( c - c^s \), provided that some of the solid is present upon which it can precipitate. However if none of the solid is present the concentration \( c \) may have to reach a higher value \( c^* > c^s \) before precipitation can start. Therefore, following Ostwald, we assume that precipitation starts only when \( c \geq c^* \). After it has started, we assume that it continues as long as \( c \geq c^s \).

In view of these assumptions, precipitation will begin in the gel at the location of the drop of silver nitrate solution, provided that the reactants are present in sufficiently high concentrations to produce silver dichromate with a concentration \( c \geq c^s \). Precipitation will continue within a circle of increasing radius surrounding the drop until \( c \) falls below \( c^* \) at the outer boundary of this circle. Then the precipitation zone will stop growing.

The reason why \( c \) may fall below \( c^* \) is that the chromate ions in the gel are depleted by reaction and by diffusion toward the silver nitrate drop, while the concentration of silver ions is low far from the drop. As time goes on this latter concentration increases everywhere. A time may be reached when this silver ion concentration and that of the
chromate ions is high enough somewhere in the gel to produce silver dichromate with a concentration \( c > c^* \). Then a second zone of precipitation will start to form at that place. After a while this process will be repeated, forming a third zone, and so on. The resulting zones are the Liesegang rings.

Since Liesegang's first experiment, the same phenomenon has been found to occur in many other reactions. Furthermore, it has also been shown to occur in test tubes and capillary tubes, with the formation of planar bands at various positions along the tube instead of rings. It is this one dimensional case which we shall treat.

3. A MATHEMATICAL FORMULATION OF THE THEORY.

To formulate the preceding theory mathematically, we denote by \( a, b, c \) and \( d \) the molar concentrations of the four substances \( A, B, C \) and \( D \). Here \( A \) is analogous to the silver ions, \( B \) to the chromate ions, \( C \) to the dissolved silver dichromate and \( D \) to the solid or precipitated silver dichromate. We assume that \( v_A \) moles of \( A \) can combine with \( v_B \) moles of \( B \) to form \( v_C \) moles of \( C \), and that this reaction is reversible. We also assume that \( C \) can precipitate to form \( D \), but that \( D \) cannot dissolve to form \( C \). In addition we suppose that \( A, B \) and \( C \) can diffuse with diffusion coefficients \( D_A, D_B \) and \( D_C \), but that \( D \) cannot diffuse. Then the four concentrations, which depend upon the time \( t \) and the coordinate \( x \) along the tube, satisfy the following reaction-diffusion-precipitation equations within the tube \( x > 0 \):

\[
\begin{align*}
a_t &= D_A a_{xx} - v_A r, \\
b_t &= D_B b_{xx} - v_B r, \\
c_t &= D_C c_{xx} + v_C r - p(c,d), \\
d_t &= p(c,d).
\end{align*}
\]

Here \( r \) is the reaction rate and \( p \) is the precipitation rate.

We shall assume that \( r \) is given by the law of mass action with rate constant \( k_+ \) for the forward reaction and \( k_- \) for the backward reaction. Thus
The precipitation rate was described in Section 2, and that description leads to the following expression for $p$:

$$p(c,d) = 0, \quad \text{if } c < c^* \text{ and } d = 0,$$

$$= q(c-c^*)_+, \quad \text{if } c > c^* \text{ or } d > 0.$$  \hfill (3.6)

Here $q$ is a rate constant and the subscript $+$ on $c-c^*$ denotes the positive part of $c-c^*$.

Since we have assumed that the reactions occur in the tube occupying the region $x > 0$, we must specify the initial conditions within the tube and boundary conditions at the end $x = 0$. To correspond with Liesegang's experiment, we assume that only $B$ is present initially. Thus we require that

$$a = c = d = 0, \quad b = b_0 \text{ at } t = 0, \quad x > 0.$$

At the endpoint $x = 0$ we assume that $A$ is kept at the concentration $a_0$ while $B$ and $C$ cannot leave the tube there. Thus

$$a = a_0, \quad b_x = c_x = 0 \text{ at } x = 0, \quad t > 0.$$  \hfill (3.8)

In addition to these conditions, we require that $a$, $b$, $c$ and their $x$ derivatives be continuous throughout the tube for $t > 0$:

$$a, b, c, a_x, b_x, c_x \text{ continuous for } x > 0, \quad t > 0.$$  \hfill (3.9)

The preceding equations constitute our mathematical formulation of the theory of Liesegang band formation. The bands are the regions within which $d(x,t)$ is positive after a sufficiently long time. Thus the bands are defined by

$$d(x,t) > 0.$$  \hfill (3.10)

This formulation is complete in the sense that the equations seem to have a unique solution. This solution determines exactly where the bands will be, the thickness of each band, the time when each band starts to form, the concentrations between the bands, etc. The solution will also show whether or not bands do form, and it will yield the sets of
parameter values for which they form. The solution can be calculated numerically, but we have not calculated it. Instead we have first simplified the equations and then analyzed the resulting problem.

4. REDUCTION TO A SIMPLER PROBLEM.

In order to simplify the theory presented in Section 3, we shall proceed heuristically, making assumptions based upon intuitive chemical considerations. Later on we shall indicate how the same simplified theory results from a systematic application of the theory of fast reactions and slow diffusion. Our first assumption is that the reaction term \( v_A \) in (3.1) is negligible compared to the other terms in that equation. This assumption is valid when the concentration of \( B \) is sufficiently small. It yields

\[
a_t = D_A a_{xx} \tag{4.1}
\]

Next we add \( v_B \) times (3.3) to \( v_C \) times (3.1) to eliminate \( r \) and obtain

\[
v_{c_{xx}} + v_{B_{xx}} = v_C D_B b_{xx} + v_B D_C c_{xx} - v_B p(c,d) \tag{4.2}
\]

Then we assume that the reaction proceeds so rapidly that it is in equilibrium, which yields

\[
r(a,b,c) = 0 \tag{4.3}
\]

We shall use (4.2) and (4.3) instead of (3.2) and (3.3). But then we must replace the two boundary conditions \( b_x = c_x = 0 \) by the single condition that \( B, \) both free and contained in \( C, \) cannot escape through the boundary:

\[
v_{c_B x} + v_{B c_x} = 0 \text{ at } x = 0, \ t > 0 \tag{4.4}
\]

With these modifications the problem can be dealt with by first solving (4.1) for \( a(x,t) \) with \( a(x,0) = 0 \) and \( a(0,t) = a_0. \) The solution is

\[
a(x,t) = a_0 \text{ erfc}[x/(4D_A t)^{1/2}] \tag{4.5}
\]

Then (4.3) can be solved for \( b \) in terms of \( a \) and \( c \) and the result can be used to eliminate \( b \) from (4.2) and (4.4). In this way (4.2) becomes an equation for \( c \) in which \( d \) seems to occur.
However both in the region where $p = 0$ and in the region where $p > 0$, $d$ does not occur in the equation for $c$. Thus the entire problem can be reduced to one of determining $c$ in each of these regions. The boundary between the two regions consists of the curve on which $c = c^*$ together with the upper halves of the tangents to this curve where it becomes vertical. Once $c$ is found, $d$ can be calculated from (3.4).

The reduction just described is carried out in detail in the work of Keller and Rubinow [3], where the resulting equations are analyzed and solved approximately. Therefore we shall not describe that analysis and its results. Instead we shall present the theory of fast reaction and slow diffusion, and show how it can be used to derive the reduced problem in a systematic way.

5. FAST REACTION AND SLOW DIFFUSION.

In many chemical systems, such as those considered in the preceding sections, both chemical reactions and diffusion occur, but at quite different rates. Often the reactions proceed much more rapidly than the diffusion. In such cases it is possible to simplify the analysis of the process by taking advantage of this difference in rates. One way of doing so is to assume that the reactions have reached equilibrium or completion at each point of space. Then the state at each point is constrained to satisfy the condition that the reaction rates vanish there. When this constraint is adjoined to the reaction-diffusion equations governing the system, an overdetermined set of equations results. Chemical and physical reasoning can then be used to delete some of the equations and thereby make the system determined.

Instead of using this intuitive procedure, it is possible to proceed in a systematic mathematical manner which we shall now describe. The basic idea is to introduce into the equations a small parameter $\epsilon$ which is the ratio of the time scale for reaction to the time scale for diffusion. Then the asymptotic expansion of the solution is sought for $\epsilon$ near zero. This expansion can be constructed either by the "two time" method or by the method of matched asymptotic expansions.
Both of these methods are utilized in [4]. Here we shall indicate how to obtain the desired results via the latter method.

Let us begin by considering the following system of reaction-diffusion equations:

\[ u_t(x,t,c) = f(u,x,t,ct,c) + \epsilon D u, \quad (5.1) \]

\[ u(x,0,c) = g(x). \quad (5.2) \]

Here \( u(x,t,c) \) is a vector of concentrations, temperature and possibly other dependent variables, \( f(u,x,t,ct,c) \) is a vector of reaction rates, heat production rate, etc. and \( D \) is the diffusion coefficient matrix. The essential feature of (5.1) is that the diffusion term contains the factor \( c \), which is small. We have also permitted \( f \) to depend upon all the variables, and even to have a slow time dependence via the argument \( ct \). In the initial condition (5.2) the function \( g(x) \) is given.

To obtain the asymptotic expansion of \( u \) for \( \epsilon \) small, we assume first that it is of the form

\[ u(x,t,c) = u^0(x,t) + \epsilon u^{(1)}(x,t) + \cdots. \quad (5.3) \]

We shall call this the initial layer expansion of \( u \). We now substitute (5.3) into (5.1) and (5.2) and set \( \epsilon = 0 \) to obtain

\[ u^0_t(x,t) = f(u^0,x,t,0,0), \quad (5.4) \]

\[ u^0(x,0) = g(x). \quad (5.5) \]

These equations describe the evolution in time of \( u^0 \) at the point \( x \). Further terms in (5.3) can be found by considering the coefficients of higher powers of \( \epsilon \) in (5.1) and (5.2), but we shall not examine them. Instead we shall consider the behavior of \( u^0(x,t) \) as \( t \to \infty \).

To this end, we assume that \( f(u^0,x,t,0,0) \) has a limit as \( t \to \infty \), and then we may expect \( u^0(x,t) \) to have a limit also. Let us denote it by \( u^0(x,\infty) \). Thus we assume that

\[ \lim_{t \to \infty} u^0(x,t) = u^0(x,\infty). \quad (5.6) \]
Then \( u^0(x,\varepsilon) \) must satisfy the following equilibrium condition, which results from (5.4):

\[
f[u^0(x,\varepsilon), x, \varepsilon, 0, 0] = 0. \tag{5.7}
\]

In general \( u^0(x,\varepsilon) \) is not uniquely determined by (5.7), but it is determined by the initial condition (5.5) and the reaction equation (5.4). It is this limit \( u^0(x,\varepsilon) \) of \( u^0(x,t) \) which will be needed to determine the outer expansion of \( u \), which we consider next.

The initial layer expansion (5.3) is presumably valid for fixed values of \( \varepsilon \) as \( \varepsilon \to 0 \). In order to find the behavior of \( u \) for long times of order \( \varepsilon^{-1} \), we must construct another expansion, called the outer expansion of \( u \). In order to construct it, we first introduce the new time variable \( \tau = \varepsilon t \) and consider \( u \) to be a function of \( \tau \):

\[
u(x,t,\varepsilon) = v(x,\tau,\varepsilon), \quad \tau = \varepsilon t. \tag{5.8}
\]

Then (5.1) becomes the following equation for \( v \):

\[
cv_x(x,\tau,\varepsilon) = f(v, x, \varepsilon^{-1}, \tau, \varepsilon) + \varepsilon D_\varepsilon v. \tag{5.9}
\]

Next we assume that \( v \) has the expansion

\[
v(x,t,\varepsilon) = v^0(x,\tau) + \varepsilon v^{(1)}(x,\tau) + \cdots. \tag{5.10}
\]

This is the outer expansion of \( u \).

Both the inner expansion (5.5) and the outer expansion (5.10) represent \( u \). If there is a common region of validity of the two expansions, as we assume, then in it they must be asymptotic to one another. Thus we have in this region

\[
\begin{align*}
&u^0(x,t) + \varepsilon v^{(1)}(x,t) + \cdots = v^0(x,\varepsilon t) + \varepsilon v^{(1)}(x,\varepsilon t) + \cdots.
\end{align*}
\]

Suppose that (5.11) holds for \( \varepsilon = \varepsilon^{-1/2} \). Then by choosing this value for \( \varepsilon \) and letting \( \varepsilon \to 0 \) in (5.11) we obtain

\[
u^0(x,\varepsilon) = v^0(x,0). \tag{5.12}
\]

This procedure for deriving (5.12) is called "matching" the initial layer expansion and the outer expansion. The result (5.12) yields the initial value of \( v^0 \) terms of the "final" value of \( u^0 \).
We next substitute (5.1) into (5.9) and set \( \epsilon = 0 \) to get
\[
 f[v^0(x, \tau), x, \tau, 0] = 0. \quad (5.13)
\]
This equation shows that \( v^0 \) must lie on the equilibrium surface (or manifold) defined by \( f = 0 \), but it does not determine where \( v^0 \) is on this surface unless the surface is a single point. From (5.12) we know that at \( \tau = 0 \), \( v^0 \) starts at the point \( u^0(x, \omega) \). To find how it evolves as \( \tau \) increases, we consider the terms of order \( \epsilon \) in (5.9), which yield the following linear equation for \( v^{(1)} \):
\[
 f(v^0(x, \tau), x, \omega, \tau, 0) = v^0 - Dv^0 - f_e. \quad (5.14)
\]
The gradient matrix \( f_v \) in (5.14), which is the coefficient of \( v^{(1)} \), will generally be a singular matrix. Let us suppose that it has \( k \) left null-vectors \( \xi_1, \ldots, \xi_k \). Then (5.14) is solvable for \( v^{(1)} \) only if the right side satisfies \( k \) solvability conditions. They can be obtained by scalar multiplication of (5.14) on the left by each left null-vector. This yields the \( k \) conditions
\[
 f(v^0(x, \tau), x, \omega, \tau, 0) = 0, \quad j = 1, \ldots, k. \quad (5.15)
\]
This is a system of \( k \) equations that determine how \( v^0(x, \tau) \) diffuses on the equilibrium surface upon which it is constrained to lie by (5.13). The initial value of \( v^0 \) is given by (5.12). Thus (5.12), (5.13) and (5.15) determine the slow diffusion of \( v^0(x, \tau) \), the leading term in the outer expansion of \( u(x, \epsilon^{-1} \tau, \epsilon) \). The fast reaction is governed by (5.4) and (5.5), which determine \( u^0(x, \tau) \), the leading term in the initial layer expansion of \( u(x, t, \epsilon) \).

The system of equations (5.13) and (5.15), together with the initial condition (5.12), are the results of our analysis. We shall not examine them further here, nor shall we obtain more terms in the outer expansion. These and other matters are considered in [4].
6. APPLICATION TO THE THEORY OF LIESEGANG BANDS.

We shall now apply the theory of Section 5 to the equations of Section 3, which constitute our formulation of the theory of Liesegang bands. To do so we first rewrite these equations, introducing explicitly the small parameter $\varepsilon$ to indicate the relative size of each term. In (3.1) for example, the diffusion term is small of order $\varepsilon$, say, but the reaction term is supposed to be smaller. Therefore we shall assume it to be of order $\varepsilon^2$. Thus we write (3.1) in the form

$$a_t = \varepsilon D_A a_{xx} - \varepsilon^2 \nu_A x. \quad (6.1)$$

Similarly we write (3.2) and (3.3) in the form

$$b_t = \varepsilon D_B b_{xx} - \nu_B x, \quad (6.2)$$

$$c_t = \varepsilon D_C c_{xx} + \nu_C x - \varepsilon \rho. \quad (6.3)$$

The system (6.1)-(6.3) is of the form (5.1) with the following identifications:

$$u = \begin{bmatrix} a \\ b \\ c \end{bmatrix}, \quad f = \begin{bmatrix} -\varepsilon^2 \nu_A x \\ -\nu_B x \\ \nu_C x - \varepsilon \rho \end{bmatrix},$$

$$D = \begin{bmatrix} D_A & 0 & 0 \\ 0 & D_B & 0 \\ 0 & 0 & D_C \end{bmatrix}. \quad (6.4)$$

Thus the leading term of the initial layer expansion, $u^0 = (a^0, b^0, c^0)$, satisfies (5.4) which becomes

$$a_t^0 = 0, \quad (6.5)$$

$$b_t^0 = -\nu_B x (a^0, b^0, c^0), \quad (6.6)$$

$$c_t^0 = \nu_C x (a^0, b^0, c^0). \quad (6.7)$$

From (3.7) the corresponding initial conditions are

$$a^0(x,0) = c^0(x,0) = 0, \quad b^0(x,0) = b_0, \quad x > 0. \quad (6.8)$$
With these initial conditions and \( r \) given by (3.5), the solution of (6.5)-(6.7) is

\[
a^0(x,t) = c^0(x,t) = 0, \quad b^0(x,t) = b_0, \quad x > 0.
\]

(6.9)

Thus nothing changes in the initial layer, to this order.

To treat the outer expansion we shall write

\[
u(x,t,\varepsilon) = \nu(x,t,\varepsilon) = \begin{pmatrix} \alpha(x,t,\varepsilon) \\ \beta(x,t,\varepsilon) \\ \gamma(x,t,\varepsilon) \end{pmatrix}
\]

(6.10)

Then by using (6.4) for \( f \) in (5.13) we get the single equation

\[
r[a^0(x,t),\beta^0(x,t),\gamma^0(x,t)] = 0.
\]

(6.11)

Thus the leading term in the outer expansion satisfies (4.3), as we assumed in Section 4.

Next from (6.4) we compute \( f_v \) at \( \varepsilon = 0 \), and obtain

\[
f_v = (f_a, f_b, f_c) = \begin{pmatrix} 0 & 0 & 0 \\ -\nu_{B^0} a & -\nu_{B^0} b & -\nu_{B^0} c \\ \nu_{C^0} a & \nu_{C^0} b & \nu_{C^0} c \end{pmatrix}
\]

(6.12)

This matrix has two linearly independent left null-vectors

\[
\mathbf{\varepsilon}_1 = (1, 0, 0), \quad \mathbf{\varepsilon}_2 = (0, \nu_C, \nu_B).
\]

(6.13)

We also compute \( f_c \) at \( \varepsilon = 0 \), which is given by

\[
f_c = \begin{pmatrix} 0 \\ 0 \\ -\varepsilon_c \end{pmatrix}
\]

(6.14)

We can now use each of the vectors \( \mathbf{\varepsilon}_1 \) and \( \mathbf{\varepsilon}_2 \) given by (6.13) in (5.15), together with \( f_c \) given by (6.14) and \( D \) given by (6.4). By using \( \mathbf{\varepsilon}_1 \) in (5.15), we obtain

\[
a^0 = D_a^n x^n.
\]

(6.15)

This is just (4.1) of Section 4, with \( a \) replaced by \( a^0 \) and \( t \) replaced by \( \tau \). Then by using \( \mathbf{\varepsilon}_2 \) in (5.15) we get

\[
\nu_{C^0} \tau + \nu_{B^0} \tau = \nu_{C^0} B^n x^n + \nu_{B^0} C^n x^n - p(y, d).
\]

(6.16)
This is exactly (4.2) with $b$, $c$ and $t$ replaced by $\beta^0$, $\gamma^0$ and $t_0$ respectively.

We have now shown how the simplified equations of Section 4 follow from the equations for the outer asymptotic expansion derived in Section 5. The corresponding initial conditions are obtained by using (6.9) in (5.12), and they are just those used in Section 4. An extension of the theory of Section 5 is needed to derive the boundary conditions (4.4) and $a_0(0,\tau) = a_o$, but we shall not present it here.

This completes the application of the theory of fast reaction and slow diffusion to the equations of Section 3, when they are written in the form (6.1)-(6.3). Of course that way of writing the equations depends upon the parameters in the problem. They must be such that the terms in these equations have the indicated relative magnitudes.

REFERENCES

3. J. B. Keller and S. I. Rubinow, Recurrent precipitation and Liesegang rings, to be published.

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