STATIONARY STATES OF CHAIN REACTIONS

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Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 3, pp. 73–83, 1966

1. Process involving radicals of one type. The theory of chain reactions [1, 2] deals with the linear diffusion equations, whose solution defines the radical concentration in some restricted volume V.

Consider a simple process involving radicals of one type. Here there are two reactions, the main one being

$$A + R \rightarrow B + (\nu + 1)\,R$$

(a radical R interacts with the initial substance A to give product B and $\nu + 1$ new radicals) and the secondary one being quadratic interaction of chains

$$R + R \rightarrow (\nu' + 2)\,R.$$

Usually $\nu' + 2 = 0$, which leads to chain termination. This chain reaction may occur in a closed volume or in a flow. Boundary conditions are specified for the radical and reactant concentrations at the walls of the vessel. The boundary condition for the radicals is usually zero concentration, which corresponds to chain termination at the wall, but boundary conditions of other types occur if radicals are generated at the wall.

Three conditions are possible: no reaction, explosion, and a steady reaction of finite rate. The last is the only one technically usable, and it must be maintained by continuously supplying reactants and removing products, as by performing the reaction in a flow apparatus. We may speak of a steady state in the absence of a flow of reagents if we consider the walls as semipermeable, letting in reagents and letting out products.

The linear approximation for the steady state is as follows in terms of the dimensionless concentration η of the radicals R in a closed volume:

$$\nabla^2\eta + \lambda\eta = 0. \qquad (1.1)$$

The trivial solution to this is asymptotically stable for $\lambda < \lambda_1$, in which λ_1 is the first eigenvalue of the Laplace operator ∇^2 in region V with given boundary conditions. For $\lambda < \lambda_1$ the reaction either does not occur at all or occurs in a steady state when there is an external source of radicals; for $\lambda > \lambda_1$ we get explosion [1, 2].

The equations of a real chemical process are nonlinear, on account of effects such as heating by the reaction, consumption of initial materials, and quadratic chain interaction. All three sources of nonlinearity occur even in the simplest chain reaction involving a single type of radical. The steady-state process in a closed volume is described by the following system of equations:

$$\nabla^2\eta + \lambda\,[f(\theta)(\zeta + 1)\eta + \mu\eta^2] = 0$$

$$\nabla^2\theta + h\lambda f(\theta)(\zeta + 1)\eta = 0,$$

$$\nabla^2\zeta - g\lambda f(\theta)(\zeta + 1)\eta = 0,$$

$$f(\theta) = \exp\frac{\theta}{1 + RT_0\theta/E} \approx e^{\theta}, \qquad \lambda = \frac{\nu k_0 l^2 c_0}{D},$$

$$h = \frac{qc_0DE}{\gamma\varkappa\nu RT_0^2}, \quad g = \frac{D}{\nu D'}, \quad \mu = \frac{k_0'\nu'}{k_0\nu}. \qquad (1.2)$$

Here $\zeta = (c - c_0)/c_0$ is the dimensionless reactant concentration and $\theta = E(T - T_0)/RT_0^2$ is the dimensionless temperature; c_0 and T_0 are chosen to be such that the boundary conditions for ζ and θ are homogeneous. Also, λ, h, g, and μ are dimensionless parameters, k_0 is the rate constant of the main reaction for $\theta = 0$, E is the activation energy, q is the heat of reaction, R is the gas constant, D and D' are the diffusion coefficients of radicals and molecules, $\varkappa$ is the thermal diffusivity, γ is the thermal capacity of unit volume, and k_0' is the rate constant for the interaction of radicals at $\theta = 0$. In (1.2) we neglect the temperature dependence of the interaction of the radicals, and also the heat produced by this reaction, since these effects are unimportant in the approximation sufficient for our purpose.

System (1.2) resembles (1.1) in always having a trivial solution; moreover, the nonlinearity does not affect the stability of this solution, and the explosion limit is still determined by the first eigenvalue of ∇^2 in volume V with the boundary conditions imposed on η. However, a marked difference in the nonlinear system is that it can have physically meaningful nontrivial solutions, which means that certain conditions give rise to a steady state in which the reaction occurs at a finite rate in the absence of external sources of radicals. A theorem [3] establishes that there are nontrivial solutions to (1.2). Consider the operator equation

$$\eta = \lambda A\eta \qquad (1.3)$$

in which λ is a numerical parameter and A is a completely continuous nonlinear operator having a differential B at the origin θ of the Banach space and satisfying the condition $A\theta = \theta$. Then each characteristic number of odd multiplicity of B is a point of bifurcation of operator A, this point corresponding to the continuous branch of the eigenfunctions of A. By definition, number λ_0 is called the point of bifurcation of operator A if for any $\varepsilon, \delta > 0$ there is a characteristic number λ of operator A such that $|\lambda - \lambda_0| < \varepsilon$, and to number λ there corresponds at least one eigenfunction η with norm $\|\eta\| < \delta$. The presence of a continuous branch of eigenfunctions means that the spectrum of the operator is continuous and that (1.3) has a nontrivial solution for any λ in some interval lying around or to one side of the point of bifurcation λ_0.

We convert (1.2) to a system of nonlinear integral

equations of Hammerstein type,

$$\eta = \lambda \int_V K(x, \xi)\,[f(\theta)(\zeta + 1)\eta + \mu\eta^2]\,d\xi$$
$$\theta = h\lambda \int_V K^\circ(x, \xi)\, f(\theta)(\zeta + 1)\,\eta\, d\xi \equiv \mathbf{A}^\circ(\theta, \zeta, \eta)$$
$$\zeta = -g\lambda \int_V K'(x, \xi)\, f(\theta)(\zeta + 1)\,\eta\, d\xi \equiv \mathbf{A}'(\theta, \zeta, \eta) \quad (1.4)$$

in which the kernels $K(x, \xi)$, $K^\circ(x, \xi)$, $K'(x, \xi)$ are Green's functions of the Laplace operator in volume V with boundary conditions imposed respectively on η, θ, and ζ. Operators $\mathbf{A}^\circ$ and $\mathbf{A}'$ for $\|\eta\|$ sufficiently small satisfy

$$\|\mathbf{A}(\eta, \theta_1, \zeta_1) - \mathbf{A}(\eta, \theta_2, \zeta_2)\| \leqslant \alpha^\circ \|\theta_1 - \theta_2\| + \alpha' \|\zeta_1 - \zeta_2\|,$$

with constants α°, $\alpha' < 1$; the principle of compressed representations [3] implies that there is a unique solution $\theta = \mathbf{R}^\circ\eta$, $\zeta = \mathbf{R}'\eta$, the resolvents $\mathbf{R}^\circ$ and $\mathbf{R}'$ being continuous operators. Hence, for $\|\eta\|$ small, system (1.4) may be reduced to a single integral equation of the form of (1.3) with the nonlinear operator

$$\mathbf{A}\eta \equiv \int_V K(x, \xi)\,[f(\mathbf{R}^\circ\eta)(\mathbf{R}'\eta + 1)\eta + \mu\eta^2]. \quad (1.5)$$

Operator (1.5) is completely continuous, because $K(x, \xi)$ is permissible and the function in brackets is continuous in η; at the origin of the Banach space it has the differential

$$\mathbf{B}\eta \equiv \int_V K(x, \xi)\,\eta\, d\xi. \quad (1.6)$$

The characteristic numbers of operator B coincide with the eigenvalues of ∇^2 and so are all simple. The first point of bifurcation of the operator of (1.5) coincides with the point λ_1 where the trivial solution of (1.2) becomes unstable.

It is insufficient for our purpose to prove that there is a nontrivial solution, since a solution of physical significance must be positive and stable. Operator A allows of the following representation near the point of bifurcation:

$$\mathbf{A}\eta \equiv \mathbf{B}\eta + \mathbf{C}\eta + \mathbf{D}\eta,$$

in which B is a linear operator, namely the differential of (1.6), C is a homogeneous quadratic operator, and D is an operator whose order of smallness is greater than 2. It has been shown [4] that the sign of the nontrivial solution near the point of bifurcation is determined by

$$\operatorname{sign} \xi[\eta(\lambda)] = -\operatorname{sign} \xi(C\varphi_0) \cdot \operatorname{sign}(\lambda - \lambda_0) \quad (1.7)$$

in which φ_0 is the normalized eigenfunction of B corresponding to λ_0 and $\xi(\eta)$ is a linear functional; for the case of a self-conjugate operator,

$$\xi(\eta) = \int_V \eta(x)\,\varphi_0(x)\,dx.$$

Since near the point of bifurcation we have, to terms above the first order of smallness, that

$$\theta = h\lambda_0 \int_V K^\circ(x, \xi)\,\eta\, d\xi, \qquad \zeta = -g\lambda \int_V K'(x, \xi)\,\eta\, d\xi,$$

then

$$\mathbf{C}\eta \equiv \int_V K(x, \xi)\Big[h\lambda_0\eta \int_V K^\circ(\xi, \tau)\,\eta\, d\tau - g\lambda_0\eta \int_V K'(\xi, \tau)\,\eta\, d\tau + \mu\eta^2\Big] d\xi,$$

and the operator of (1.5) has positive eigenvalues in the region $\lambda > \lambda_0$ if

$$F \equiv g\int_V \varphi_0^2(x)\,\psi_0'(x)\,dx - h\int_V \varphi_0^2(x)\,\psi_0^\circ(x)\,dx - \mu\int_V \varphi_0^3(x)\,dx > 0, \quad (1.8)$$

where

$$\psi_0^\circ(x) \equiv \lambda_0 \int_V K^\circ(x, \xi)\,\varphi_0(\xi)\,d\xi,$$
$$\psi_0'(x) \equiv \lambda_0 \int_V K'(x, \xi)\,\varphi_0(\xi)\,d\xi. \quad (1.9)$$

For $F < 0$ the branch of positive eigenfunctions lies in the region $\lambda < \lambda_0$.

This result may be demonstrated by expanding the solution near the bifurcation point as a series in the small parameter $\varepsilon = \lambda - \lambda_0$. The resulting approximate solution is then examined for stability. The series expansion is performed directly for system (1.2). We seek a solution in the form

$$\eta = \varepsilon\eta^{(1)} + \varepsilon^2\eta^{(2)} + \ldots, \quad \theta = \varepsilon\theta^{(1)} + \ldots, \quad \zeta = \varepsilon\zeta^{(1)} + \ldots. \quad (1.10)$$

Substitution of (1.10) into (1.2) gives

$$\nabla^2\eta^{(1)} + \lambda_0\eta^{(1)} = 0, \quad \nabla^2\theta^{(1)} + h\lambda_0\eta^{(1)} = 0, \quad \nabla^2\zeta^{(1)} - g\lambda_0\eta^{(1)} = 0, \quad (1.11)$$

$$\nabla^2\eta^{(2)} + \lambda_0\eta^{(2)} + \eta^{(1)} + \lambda_0[\eta^{(1)}\theta^{(1)} + \eta^{(1)}\zeta^{(1)} + \mu(\eta^{(1)})^2] = 0. \quad (1.12)$$

From (1.11), with (1.9), we have

$$\eta^{(1)} = \alpha\varphi_0, \qquad \theta^{(1)} = \alpha h\psi_0^\circ, \qquad \zeta^{(1)} = -\alpha g\psi_0', \quad (1.13)$$

where α is a constant as yet undetermined. Substitution of (1.13) into (1.12) shows that this is solvable if

$$\alpha + \lambda_0\alpha^2\Big[h\int_V \varphi_0^2\psi_0^\circ\,dx - g\int_V \varphi_0^2\psi_0'\,dx + \mu\int_V \psi_0^3\,dx\Big] = 0,$$

whence either $\alpha = 0$, which corresponds to the trivial solution, or

$$\alpha = -\Big[\lambda_0\Big(h\int_V \varphi_0^2\psi_0^\circ\,dx - g\int_V \varphi_0^2\psi_0'\,dx + \mu\int_V \varphi_0^3\,dx\Big)\Big]^{-1} = \frac{1}{\lambda_0 F}, \quad (1.14)$$

and so as a first approximation

$$\eta^{(1)} = \frac{(\lambda - \lambda_0)\varphi_0}{\lambda_0 F},$$

with, from (1.7) and (1.8), $\eta > 0$ for $\lambda > \lambda_0$ and $F > 0$ or for $\lambda < \lambda_0$ and $F < 0$. In the latter case $\|\eta\|$ increases from the continuous branch as λ decreases, which is a physically inapplicable solution; also, the existence of an infinite set of nontrivial solutions corresponding to an infinite set of eigenvalues of ∇^2 is equally unacceptable. Further examination shows that all these inapplicable solutions are unstable.

Let $\eta^* = \eta - \eta^\circ$, $\theta^* = \theta - \theta^\circ$, $\zeta^* = \zeta - \zeta^\circ$ be the deviations of $\eta(x, t)$, $\theta(x, t)$, $\zeta(x, t)$ from their steady-state values $\eta^\circ(x)$, $\theta^\circ(x)$, $\zeta^\circ(x)$ as defined by (1.2). The steady-state solution is asymptotically stable if there is a $\delta > 0$ such that from $\|\eta^*\| < \delta$, $\|\theta^*\| < \delta$, $\|\zeta^*\| < \delta$ it follows that $\eta^* \to 0$, $\theta^* \to 0$, $\zeta^* \to 0$ for $t \to \infty$. Near the steady state the time dependence of η^*, ζ^*, and θ^* is defined by the linear system

$$\begin{aligned}
\frac{\partial \eta^*}{\partial \tau} &= \nabla^2 \eta^* + \lambda\left[f(\theta^\circ)(\zeta^\circ + 1)\eta^* + 2\mu\eta^\circ\eta^* + \right.\\
&\left. + \left(\frac{\partial f}{\partial \theta}\right)_{\theta=\theta^\circ}\eta^\circ(\zeta^\circ + 1)\theta^* + f(\theta^\circ)\eta^\circ\zeta^*\right],\\
\beta^\circ\frac{\partial \theta^*}{\partial \tau} &= \nabla^2\theta^* + h\lambda\left[f(\theta^\circ)(\zeta^\circ + 1)\eta^* + \right.\\
&\left. + \left(\frac{df}{d\theta}\right)_{\theta=\theta^\circ}\eta^\circ(\zeta^\circ + 1)\theta^* + f(\theta^\circ)\eta^\circ\zeta^*\right],\\
\beta'\frac{\partial \zeta^*}{\partial \tau} &= \nabla^2\zeta^* - g\lambda\left[f(\theta^\circ)(\zeta^\circ + 1)\eta^* + \right.\\
&\left. + \left(\frac{df}{d\theta}\right)_{\theta=\theta^\circ}\eta^\circ(\zeta^\circ + 1)\theta^* + f(\theta^\circ)\eta^\circ\zeta^*\right.,
\end{aligned} \tag{1.15}$$

in which $\tau = tD/l^2$ is the dimensionless time and $\beta^\circ = D/\varkappa$, $\beta' = D/D'$. We seek the solution to (1.15) in the form

$$\eta^* = e^{\mu\tau}u(x), \qquad \theta^* = e^{\mu\tau}v(x), \qquad \zeta^* = e^{\mu\tau}w(x).$$

Near the point of bifurcation we have, to terms above the first order of smallness in $\varepsilon = \lambda - \lambda_0$, that

$$\begin{aligned}
&\nabla^2 u + (\lambda_0 - \mu)u + \varepsilon\left(1 + \frac{h\psi_0^\circ}{F} - \frac{g\psi_0'}{F} + \right.\\
&\left. + \frac{2\mu\varphi_0}{F}\right)u + \varepsilon\frac{\varphi_0}{F}(v + w) = 0,\\
&\nabla^2 v + h\lambda_0 u - \beta^\circ\mu v + \varepsilon h\left(1 + \frac{h\psi_0^\circ}{F} - \right.\\
&\left. - \frac{g\psi_0'}{F}\right)u + \varepsilon h\frac{\varphi_0}{F}(v + w) = 0,\\
&\nabla^2 w - g\lambda_0 u - \beta'\mu w - \varepsilon g\left(1 + \frac{h\psi_0^\circ}{F} - \right.\\
&\left. - \frac{g\psi_0'}{F}\right)u - \varepsilon g\frac{\varphi_0}{F}(v + w) = 0.
\end{aligned} \tag{1.16}$$

This steady-state solution is asymptotically stable if (1.16) has nontrivial solutions only for $\mu < 0$. We seek the solution in the form

$$\mu = \mu^{(0)} + \varepsilon\mu^{(1)} + \ldots, \quad u = u^{(0)} + \varepsilon u^{(1)} + \ldots,$$
$$v = v^{(0)} + \ldots, w = w^{(0)} + \ldots.$$

Then

$$\begin{aligned}
&\nabla^2 u^{(0)} + (\lambda_0 - \mu^{(0)})u^{(0)} = 0,\\
&\nabla^2 v^{(0)} + h\lambda_0 u^{(0)} - \beta^\circ\mu^{(0)}v^{(0)} = 0,\\
&\nabla^2 w^{(0)} - g\lambda_0 u^{(0)} - \beta'\mu^{(0)}w^{(0)} = 0,\\
&\nabla^2 u^{(1)} + (\lambda_0 - \mu^{(0)})u^{(1)} - \mu^{(1)}u^{(0)} + \left(1 + \frac{h\psi_0^\circ}{F} - \right.\\
&\left. - \frac{g\psi_0'}{F} + \frac{2\mu\varphi_0}{F}\right)u^{(0)} + \frac{\varphi_0}{F}(v^{(0)} + w^{(0)}) = 0.
\end{aligned} \tag{1.17}$$

From (1.17) we see that, if λ_0 coincides with any eigenvalue of ∇^2 except the first, there are numbers $\mu^{(0)} > 0$ such that $u^{(0)} \not\equiv 0$, so, for $|\varepsilon|$ sufficiently small, system (1.16) has nontrivial solutions for $\mu > 0$. Hence the nontrivial stationary solutions are unstable for branches corresponding to all points of bifurcation, $\lambda_0 = \lambda_1$, the largest $\mu^{(0)} = 0$, and (1.17) gives

$$u^{(0)} = \varphi_0(x), \qquad v^{(0)} = h\psi_0^\circ(x), \qquad w^{(0)} = -g\psi_0'(x),$$

(the arbitrary constant is omitted as being unimportant). Transferring to the equation for the first approximation, we find that this is soluble for $\mu^{(1)} = -1$, so, for $|\varepsilon|$ sufficiently small, the largest value of μ has the same sign as $\lambda_1 - \lambda$. Hence, stable positive steady-state solutions (ones belonging to the continuous branch from the first point of bifurcation) exist only for $\lambda > \lambda_1$. The sole stable solution to (1.2) for $\lambda < \lambda_1$ is trivial (no reaction); there are no stable solutions for $\lambda > \lambda_1$ if (1.8) is not obeyed for the values of the parameters corresponding to $\lambda = \lambda_1$ ($F < 0$), and explosion occurs; but if $F > 0$, then for $\lambda > \lambda_1$ there exists a single stable nontrivial steady-state solution, i. e., the chain reaction occurs in a steady state with a finite rate in the absence of external sources, the steady-state radical concentration being inversely related to $|F|$.

If all the variables are subject to the same boundary conditions (e. g., zero ones), (1.8) takes the simple form

$$F = g - h - \mu > 0. \tag{1.18}$$

If we neglect chain interaction (the effect should not be decisive), condition (1.18) may be put as

$$\frac{E}{RT_0}\frac{qc_0}{\gamma T_0}\frac{D'}{\varkappa} < 1. \tag{1.19}$$

This shows that the conditions for a nontrivial solution are set up by lowering the reactant concentration and raising the wall temperature.

2. Process involving radicals of different types. This is the general case of a process in a flow system involving an arbitrary number of reactions. This introduces vector functions and differential operators that are not self-conjugate, but it is found that the conditions for existence of a stable stationary solution do not change essentially in form.

We envisage a process involving different radical types and including all possible uni-, bi-, and trimolecular reactions between these and with the stable molecules. We introduce dimensionless variables of two types. Let the components η_i of vector η be the dimensionless concentrations (scale c_0) of the radicals or of intermediates that decompose to radicals, while

the components ζ_i of vector ζ are the dimensionless concentrations (scale c_0 and initial levels c_{i0}, chosen such that the boundary conditions for the ζ_i are homogeneous) of the initial reactants, reaction products, or intermediates whose reactions do not give rise to radicals; vector ζ also includes the dimensionless temperature $(T-T_0)/T_0$. The equations describing the steady state in the general case have the form

$$\mathbf{L}\eta + f(\eta, \zeta) = 0, \qquad \mathbf{L}'\zeta + f'(\eta, \zeta) = 0. \qquad (2.1)$$

Here L and L' are second-order differential operators in the space of vector functions. The usual form for L is*

$$\mathbf{L} = I\nabla^2 - \mathbf{P}\omega(x)\nabla$$

where I is unit matrix and P is a diagonal matric composed of the numbers $P_i = lw_0/D_i$, in which l is the linear scale and D_i is the effective diffusion coefficient of radical i; $\omega(x)$ is the dimensionless flow speed at point x (scale w_0).

Operator L' has the same structure with a matrix P'; $f(\eta, \zeta)$ and $f'(\eta, \zeta)$ are nonlinear vector functions whose components are $l^2\sigma_i/D_ic_0$, $l^2\sigma_i'/D_ic^0$, in which σ_i and σ_i' are the rates of formation of the corresponding radical or substance per unit reaction volume. The component of f' corresponding to the dimensionless temperature has the form $l^2\sigma^\circ/\gamma\varkappa T_0$, in which σ° is the rate of heat release. We assume that only reactions involving radicals have appreciable rates, so f_i and f_i', and also $\partial f_i/\partial\zeta_j$, $\partial f_i'/\partial\zeta_j$, are exactly zero for $\eta = 0$.

Equations (2.1) are defined in some closed region V with homogeneous boundary conditions.

System (2.1) always has a trivial solution whose stability region coincides with the stability region of the linear system

$$\mathbf{L}\eta + A\eta = 0, \qquad A = \left(\frac{\partial f}{\partial \eta}\right)_{\eta=\zeta=0}, \qquad (2.2)$$

in which A is the Jacobi matrix of the vector function $f(\eta, \zeta)$.

We examine the linear system on the assumption that the P_i are the same for all radicals, i.e., that

$$\mathbf{L} = IL, \qquad L = \nabla^2 - P\omega(x)\nabla,$$

and that the same boundary conditions (e.g., zero ones) are imposed on the concentrations of all radicals.

Let U and U^{-1} be matrices composed respectively of the column-vectors and line-vectors of matrix A,

$$AU = U\Lambda, \quad U^{-1}A = \Lambda U^{-1},$$

where Λ is the normal form of matrix A. We introduce a new variable: a vector y whose components are y_i,

$$\eta = Uy, \qquad \eta_i = \sum_j u_{ij}y_j. \qquad (2.3)$$

We multiply (1.2) from the left by U^{-1} to convert it to

$$Ly + \Lambda y = 0. \qquad (2.4)$$

*We assume that the flow is incompressible, so that $\nabla\omega(x) = 0$.

This conversion corresponds to transition to an orthogonal net of reactions in the formal theory of unimolecular isothermal reactions [5], but the present system differs in that matrix A in the general case cannot be reduced to a symmetric one by similarity transformations and also in that matrix Λ is not obliged to be diagonal. The property of A of importance to us is that all its nondiagonal elements are nonnegative. We can state a number c such that all the elements of matrix $A^+ = A + cI$ are nonnegative, whereupon all the eigenvalues of matrix A^+ exceed the corresponding ones of A by c, while the eigenvectors of the two matrices coincide. A theorem due to Frobenius [6] indicates that the eigenvalue of A^+ largest in modulus is real, positive, and simple, while the components of the corresponding column and row vectors are all positive. All of these properties, except the obligatory positiveness of the largest eigenvalue, apply also to matrix A, which has nonnegative nondiagonal elements.

Operator L has analogous properties. The integral operator corresponding to L,

$$\mathbf{B}\varphi = \int_V K(x, \xi)\varphi d\xi$$

(on which $K(x, \xi)$ is the Green's function) is positive (i.e., transforms any nonnegative function into a nonnegative one); a theorem [6] indicates that its eigenvalue largest in modulus (to which corresponds a positive eigenfunction φ) is real, positive, and simple. The characteristic numbers of B coincide with the eigenvalues λ of L, so the first (least) eigenvalue λ_0 of L is real, positive, and simple.

Let λ_1 be the largest eigenvalue of A. The trivial solution to (2.2) or (2.4) is unstable for $\lambda_1 > \lambda_0$, and $\lambda_1 = \lambda_0$ defines the explosion limit or the first point of bifurcation of (2.1).

It is of interest to compare the explosion limits of a flow system and of a system having no reagent flow. Operator L has a conjugate operator $L^* = \nabla^2 + P\omega(x)\nabla$ and allows of separation into real and imaginary parts,

$$L = R + iS, \qquad R = (L + L^*)/2 = \nabla^2,$$

$$S = (L - L^*)/2i = iP\omega(x)\nabla$$

in which R and S are self-conjugate operators. If φ_0 and φ_0^* are normalized eigenfunctions of L and L^* corresponding to λ_0, then

$$\mathrm{Re}\int_V \varphi_0^*(L - \lambda_0)\varphi\, dx = \int_V \varphi_0^* R\varphi_0\, dx - \lambda_0 = 0. \qquad (2.5)$$

But

$$\int_V \varphi_0^* R\varphi_0\, dx \geqslant \lambda_0^{(R)},$$

where $\lambda_0^{(R)}$ is the least eigenvalue of $R = \nabla^2$, so (2.5) can be obeyed only for $\lambda_0 > \lambda_0^{(R)}$, so the least eigenvalue of L exceeds the least eigenvalue of the Laplace operator in the same region V, i.e., the presence of a directional flow stabilizes the chain process and displaces the explosion limit λ_0 upwards. The following are two simple examples:

1) One-dimensional flow along the x axis at a constant speed w_0,

$$L = \frac{d^2}{dx^2} - P\frac{d}{dx}.$$

If the reaction occurs in section $0 \leq x \leq 1$ and the radicals are removed

at the ends, then

$$\lambda_0 = \pi^2 + P^2/4.$$

2) A cylinder $0 \le x \le 1$, $0 \le r \le R$; flow with a constant speed w_0 along the x axis, zero boundary conditions. Then

$$L = \frac{\partial^2}{\partial x^2} - P\frac{\partial}{\partial x} + \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}, \qquad \lambda_0 = \pi^2 + \frac{\rho^2}{R^2} + \frac{P^2}{4},$$

where ρ is the first zero of the Bessel function $J_0(r)$. In both cases the explosion limit exceeds the limit in the absence of the flow by $P^2/4$.

If in these examples we neglect the diffusion transport along the flow direction, as is usually done in hydrodynamic problems, we conclude that the trivial solution is always stable, that there are no points of bifurcation, and that explosion is impossible. For the general case this corresponds to replacing L by the first-order differential operator $P\omega(x)\nabla$, which obviously has no eigenfunctions that become zero at the boundary of the closed region. In fact, we cannot neglect the diffusion term if fast reactions are involved, because these set up large concentration gradients along the flow direction.

Consider now the nonlinear problem, which may be examined by the method used above for the one-dimensional case. To examine the sign and stability of the trivial solution near the bifurcation point it is sufficient to write the equation for ζ in the linear approximation and that for η in the quadratic one. We have

$$L'\zeta + A'\eta = 0, \tag{2.6}$$

$$L\eta + A\eta + \eta B\eta + \eta B'\zeta = 0, \tag{2.7}$$

where A' is a rectangular matrix with the elements

$$a'_{ij} = \left(\frac{\partial f'_i}{\partial \eta_j}\right)_{\eta=\zeta=0}$$

and B and B' are third-rank matrices with the elements

$$b_{ijk} = \frac{1}{2}\left(\frac{\partial^2 f_i}{\partial \eta_j \partial \eta_k}\right)_{\eta=\zeta=0}, \qquad b'_{ijk} = \left(\frac{\partial^2 f_i}{\partial \eta_j \partial \zeta_k}\right)_{\eta=\zeta=0}.$$

The solution to (2.1) or to (2.6) and (2.7) near the bifurcation point is sought as a series in $\varepsilon = \lambda_1 - \lambda_0$,

$$\eta_i = \varepsilon\eta_i^{(1)} + \varepsilon^2\eta_i^{(2)} + \ldots, \quad y_i = \varepsilon y_i^{(1)} + \varepsilon^2 y_i^{(2)} + \ldots,$$
$$\zeta_i = \varepsilon\zeta_i^{(1)} + \ldots. \tag{2.8}$$

The equations for the functions of the first approximation coincide with (2.4) and (2.6); the solution gives

$$y_1^{(1)} = \alpha\varphi_0(x), \qquad y_i^{(1)} \equiv 0 \quad (i \neq 1)$$
$$\eta_i^{(1)} = a u_{i1}\varphi_0(x)$$
$$\zeta_i^{(1)} = \alpha\sum_j a'_{ij}u_{j1}\int_V K_i'(x,\xi)\varphi_0(\xi)\,d\xi \equiv \alpha\psi_i(x). \tag{2.9}$$

Here $\varphi_0(x)$ is the normalized eigenfunction of L in region V corresponding to eigenvalue λ, subject to the boundary conditions for η, while $K_i'(x,\xi)$ is the Green's function of L_i' in the region V subject to the boundary conditions on ζ_i. Constant α is deduced from the condition for solubility of the equations for the functions in the second approximation. We have seen above that all $u_{i1} > 0$, so the solution to this system is positive for $\alpha > 0$. We transform (2.7) in accordance with (2.3); using (2.8) and (2.9), we get the equation for $y_1^{(2)}$ as

$$Ly_1^{(2)} + \lambda_0 y_1^{(2)} + \alpha\varphi_0 + \alpha^2(\mu\varphi_0^2 + \varphi_0\sum_i g_i\psi_i) = 0,$$
$$\mu = \sum_{i,j,k} u_{1i}^{-1}b_{ijk}u_{j1}u_{k1}, \qquad g_k = \sum_{i,j} u_{1i}^{-1}b'_{ijk}u_{j1}. \tag{2.10}$$

Equation (2.10) is soluble either for $\alpha = 0$, which corresponds to the trivial solution, or if

$$\alpha = -\left[\mu\int_V \varphi_0^*\varphi_0^2\,dx + \sum_i g_i\int_V \varphi_0^*\psi_i\varphi_0\,dx\right]^{-1}, \tag{2.11}$$

where φ_0^* is the normalized eigenfunction of the conjugate operator L* in region V for eigenvalue λ_0 subject to the boundary conditions for η. If (2.10) is soluble, the equations for the other functions of the second approximation are also soluble.

Hence (2.1) has positive solutions in the region $\lambda_1 > \lambda_0$ if

$$-F \equiv \mu\int_V \varphi_0^*\varphi_0^2\,dx + \sum g_i\int_V \varphi_0^*\psi_i\varphi_0\,dx < 0, \tag{2.12}$$

or in the region $\lambda_1 < \lambda_0$ in the converse case. The proof of the asymptotic stability of the solution for $\lambda_1 > \lambda_0$ is derived exactly as for the one-dimensional case and will not be given. Hence (2.12), as tested with the values of the parameters corresponding to $\lambda_1 = \lambda_0$, is the condition for there to be a stable stationary state for $\lambda_1 > \lambda_0$ such that the process occurs at a finite rate in the absence of external sources of radicals.

We may examine the conditions for the existence of nontrivial solutions to (2.1) also in the most general case, where the linear system of (2.2) does not reduce to the form of (2.4). Let (2.2) have a nontrivial solution for some value A_0 of A; then A_0 will be a bifurcation value of A, so there must be nontrivial solutions to (2.1) of small norm for the vector function f of (2.1) with a Jacobi matrix A close to A_0. We may assert that the nontrivial solutions from the branch corresponding to $A = A_0$ can be stable only if the nonstationary equation corresponding to (2.2) does not have solutions at $A = A_0$ that increase with time without bound. The matrix A_0 with this property is the analog of the least eigenvalue of an operator in the space of scalar functions.

Let φ_0 and φ_0^* be normalized vector eigenfunctions of L and L* in region V with given boundary conditions; then

$$L\varphi_0 + A_0\varphi_0 = 0, \quad L^*\varphi_0^* + A_0^*\varphi_0^* = 0, \quad \langle\varphi, \varphi^*\rangle = 1,$$

where A_0^* is the transposed matrix A_0 and <> denotes integration over the whole of V and summation with respect to the components of the vector function. We put $A = A_0 + \varepsilon A_1$ and seek a solution to (2.1) in the form of the series of (2.8) with respect to the small parameter $\varepsilon > 0$. The equations for the first approximation coincide with (2.2) and (2.6); solution of them, by analogy with (2.9), gives

$$\eta^{(1)} = \alpha\varphi_0(x), \quad \zeta^{(1)} = \alpha\int_V \mathbf{K}'(x,\xi)A'\varphi_0(\xi)\,d\xi \equiv \alpha\psi_0(x), \tag{2.13}$$

where $K'(x, \xi)$ is the matrix Green's function of L' in region V subject to the boundary conditions on ξ. The equation for the second approximation for η becomes

$$L\eta^{(2)} + A_0\eta^{(2)} + \alpha A_1\varphi_0 + \alpha^2\varphi_0 B\varphi_0 + \alpha^2\varphi_0 B'\psi_0 = 0. \quad (2.14)$$

This is soluble either for $\alpha = 0$, which corresponds to the trivial solution, or for

$$\alpha = -\frac{\langle\varphi_0^*, A_1\varphi_0\rangle}{\langle\varphi_0^*, \varphi_0 B\varphi_0\rangle + \langle\varphi_0^*, \varphi_0, B'\psi_0\rangle} \equiv \frac{\delta}{F}. \quad (2.15)$$

Consider the stability of the nontrivial solution. Let the vector functions $\eta^* = \eta - \eta^\circ$, $\zeta^* = \zeta - \zeta^\circ$ be the deviations of the vector functions $\eta(x, t)$, $\zeta(x, t)$ from their stationary values $\eta^\circ(x)$, $\zeta^\circ(x)$ as defined by (2.1). The time variation of η^* and ζ^* near the steady state is described by a system of linear equations with coefficients dependent on the coordinates. We use (2.13) and (2.15) to write the equation for η^* up to terms of above the first order in ε, and for ζ^* up to terms of above the zeroth order,

$$\beta\frac{\partial\eta^*}{\partial\tau} = L\eta^* + (A_0 + \varepsilon A_1)\eta^* + \frac{\varepsilon\delta}{F}(2\varphi_0 B\eta^* + \eta^* B'\psi_0 + \varphi_0 B'\zeta^*) \quad \beta'\frac{\partial\zeta^*}{\partial\tau} = L'\zeta^* + A'\eta^*, \quad (2.16)$$

where $\tau = t/t_0$ is the dimensionless time and β and β' are diagonal matrices with the elements $l^2 t_0/D_i$, $l^2 t_0/D_i$ respectively. We seek the solution to (2.16) in the form

$$\eta^* = e^{\mu\tau}u(x), \qquad \zeta^* = e^{\mu\tau}v(x).$$

Then

$$Lu + (A_0 + \varepsilon A_1 - \mu\beta)u + \varepsilon\delta F^{-1}(2\varphi_0 Bu + uB'\psi_0 + \varphi_0 B'v) = 0, \quad L'v + A'u - \mu\beta' v = 0. \quad (2.17)$$

This stationary solution is asymptotically stable if (2.17) does not have nontrivial solutions for $\mu \geq 0$. We put

$$\mu = \mu^{(0)} + \varepsilon\mu^{(1)} + \ldots, \qquad u = u^{(0)} + \varepsilon u^{(1)} + \ldots, \qquad v = v^{(0)} + \ldots.$$

In the zeroth approximation

$$Lu^{(0)} + (A_0 - \mu^{(0)}\beta)u^{(0)} = 0, \quad L'v^{(0)} + A'u^{(0)} - \mu^{(0)}\beta v^{(0)} = 0. \quad (2.18)$$

The above-mentioned property of matrix A_0 means that the largest $\mu^{(0)}$ for which (2.18) has a nontrivial solution is zero; then $u^{(0)} = \varphi_0$, $v^{(0)} = \psi_0$ (the arbitrary constant is omitted as unimportant). The equation of the first approximation for u is written as

$$Lu^{(1)} + A_0 u^{(1)} + A_1\varphi_0 - \mu^{(1)}\beta\varphi_0 = 0. \quad (2.19)$$

This equation is solvable if

$$\mu^{(1)} = \frac{\langle\varphi_0^*, A_1\varphi_0\rangle}{\langle\varphi_0^*, \beta\varphi_0\rangle}.$$

But $\langle\varphi_0^*, \beta\varphi_0\rangle$ is positive, so this stationary solution is positive and stable ($L > 0$, $\mu < 0$) for

$$\langle\varphi_0^*, A_1\varphi_0\rangle = \delta < 0, \qquad \langle\varphi_0^*, \varphi_0 B\varphi_0\rangle + \langle\varphi_0^*, \varphi_0 B'\psi_0\rangle = -F < 0. \quad (2.20)$$

The process then occurs in a stationary fashion at a finite rate in the absence of external sources of radicals. Conditions (2.12) and $\lambda_1 > \lambda_0$ given above are particular cases of (2.20).

I am indebted to V. G. Levich for interest in this work and for useful discussions.

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8 April 1965 Moscow