

# THE CHAIN THERMAL-EXPLOSION LIMIT

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L. M. Pis'men and V. G. Levich\*

Institute of Electrochemistry, Academy of Sciences, USSR

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In this paper, a study is made of the effect of slow nonradical reactions on the conditions for the existence of a stable steady state in the chain process. We shall consider a process participated in by a single type of radical, including three reactions—of first, second, and third order in the concentration of the radicals.

The dimensionless concentrations,  $\eta$ , of radicals, and  $\zeta$  of molecules of the initial substance, and the dimensionless temperature  $\theta$  in the reaction zone  $V$  are given by the system of nonlinear equations:

$$\begin{aligned} L\eta + \lambda[f(\zeta, \theta)\eta + \mu\eta^2 + \varepsilon] &= 0, \\ L'\zeta - g\lambda f(\zeta, \theta)\eta &= 0, \\ L^0\theta + h\lambda f(\zeta, \theta)\eta &= 0, \end{aligned} \quad (1)$$

where  $L$ ,  $L'$ , and  $L^0$  are second-order differential operators. In the absence of convection  $L = \nabla^2$  and in a steady-flow reactor,  $L = \nabla^2 - P\omega(x)\nabla$ , where  $\omega(x)$  is the dimensionless flow rate (with the scale  $w_0$ ) at the point  $x$ ,  $P = w_0 l/D$  is the Péclet number,  $l$  is the linear scale, and  $D$  is the diffusion coefficient of the radicals. The operators  $L'$  and  $L^0$  are of the same form, but with the Péclet numbers  $P' = w_0 l/D'$  and  $P^0 = w_0 l/\kappa$ , where  $\kappa$  is the thermal diffusivity coefficient, and  $D'$  is the diffusion coefficient of the molecules.

We shall assume that the temperature dependence of the reaction rate is given by the Arrhenius equation, and that all three reactions go by double collisions. The dimensionless variables  $\zeta$  and  $\theta$  are chosen in such a way that the boundary conditions for the system (1) are homogeneous:  $\zeta = (c - c_0)/c_0$ ,  $\theta = E(T - T_0)/RT_0^2$ . Then:

$$f(\zeta, \theta) = (\zeta + 1) \exp \frac{\theta}{1 + \frac{RT_0}{E}\theta} \approx (\zeta + 1) e^\theta,$$

$$h = \frac{1}{\nu} \frac{D}{\kappa} \frac{E}{RT_0} \frac{qc_0}{\gamma T_0}, \quad \lambda = \frac{\nu k_0 c_0 l^2}{D}, \quad g = \frac{D}{D'\nu}, \quad \mu = \frac{k_0^{(2)} \nu^{(2)}}{k_0 \nu}, \quad \varepsilon = \frac{\nu^{(0)} k_0^{(0)} c_0}{k_0 \nu},$$

where  $c$  is the concentration,  $T$  is the temperature,  $k$  is rate constant of the reaction; the subscript zero denotes the value at the boundary (taken as the scale),  $\nu$  is the stoichiometric coefficient of the radicals, and the upper index in parentheses shows that the quantity in question refers to reaction of second or zero order in the concentration of radicals, while for the fundamental reaction (first order) this index is omitted.  $\gamma$  is the specific heat of unit volume of the reacting system,  $R$  is the gas content,  $E$  is the activation energy of the main reaction, and  $q$  is the heat effect. The temperature dependence and the heat effect of the remaining two reactions, as well as the effect that they have on the burnout of the original material and the back effect of the latter on the rate of the reactions are not considered in Eqs. (1), so that not all the effects show up in this approximation, although it is sufficient for our purposes.

Since reactions involving only stable molecules go much more slowly than radical reactions, the quantity  $\varepsilon$  may be regarded as a small parameter. The unperturbed nonlinear system found from (1) for  $\varepsilon = 0$ , has been investigated previously in [1]. This system always has a trivial solution which is stable for  $\lambda < \lambda_0$ , where  $\lambda_0$  is the smallest eigenvalue for the operator  $L$  in the region  $V$  with the boundary conditions imposed on  $\eta$ .

\* Corresponding Member of the Academy of Sciences, USSR.

For  $\lambda > \lambda_0$  there is a stable positive solution of the unperturbed system if the following inequality is satisfied:

$$a = h \int_V \varphi_0^*(x) \varphi_0(x) \psi_0^0(x) dx - g \int_V \varphi_0^*(x) \varphi_0(x) \psi_0'(x) dx + \mu \int_V \varphi_0^*(x) \varphi_0^2(x) dx < 0, \quad (2)$$

where  $\varphi_0(x)$ ,  $\varphi_0^*(x)$  are the normalized eigenfunctions of the operator  $L$  and the conjugate operator  $L^*$  corresponding to eigenvalue  $\lambda_0$ , and:

$$\psi_0^0(x) = \lambda_0 \int_V K^0(x, \xi) \varphi_0(\xi) d\xi, \quad \psi_0'(x) = \lambda_0 \int_V K'(x, \xi) \varphi_0(\xi) d\xi, \quad (3)$$

where  $K^0(x, \xi)$  and  $K'(x, \xi)$  are the Green's functions of the operators  $L^0$  and  $L'$  in the region  $V$  with the boundary conditions for  $\theta$  and  $\zeta$  respectively. If the inequality (2) is not satisfied, a positive solution exists for  $\lambda < \lambda_0$  and is unstable, while for  $\lambda > \lambda_0$  there are no stable steady-state solutions (explosion region).

Starting with the solution of the unperturbed system, it is possible to calculate the solution of the system (1) in the form of a series in the small parameter  $\varepsilon$ . The expansion coefficients are found with the aid of the corresponding equations in variations, and if the latter are solvable, the solution (1) obviously differs from the solution of the unperturbed system by a quantity of first order of smallness in  $\varepsilon$ , and maintains its stability. In the vicinity of the bifurcation point  $\lambda = \lambda_0$ , however, this path does not lead to the goal, since the dependence of the solution of the system (1) on the parameter  $\varepsilon$  ceases to be analytic. In this case, a solution may be found by means of an expansion in  $\sqrt{\varepsilon}$ .

In the vicinity of the bifurcation point, the second and third equations of the system (1) always have a unique solution [1],  $\zeta = R^1 \eta$ ,  $\theta = R^0 \eta$ , where  $R^1$  and  $R^0$  are resolvents, with, to a first approximation:

$$\zeta = -g \lambda_0 \int_V K(x, \xi) \eta d\xi, \quad \theta = h \lambda_0 \int_V K^0(x, \xi) \eta d\xi.$$

Accordingly, the system (1), for  $\lambda$  nearly equal to  $\lambda_0$ , may be reduced to the single equation:

$$L\eta + \lambda [f(R^1 \eta, R^0 \eta) \eta + \mu \eta^2 + \varepsilon] = 0. \quad (4)$$

Assuming  $\lambda = \lambda_0(1 + \delta \sqrt{\varepsilon})$ ,  $\eta = \sqrt{\varepsilon} \eta^{(1)} + \varepsilon \eta^{(2)} + \dots$  and expanding  $f(R^1 \eta, R^0 \eta)$  in Taylor's series, we have, to a first approximation:

$$L\eta^{(1)} + \lambda_0 \eta^{(1)} = 0, \quad (5)$$

from which  $\eta^{(1)} = \alpha \varphi_0$ ,  $R^1 \eta^{(1)} = -\alpha g \psi_0^0$ ,  $R^0 \eta^{(1)} = \alpha h \psi_0^0$ . The constant  $\alpha$  is found from the solvability condition for the second-approximation equation:

$$L\eta^{(2)} + \lambda_0 \eta^{(2)} + \lambda_0 [\eta^{(1)} R^1 \eta^{(1)} + \eta^{(1)} R^0 \eta^{(1)} + \mu (\eta^{(1)})^2 + \delta \eta^{(1)} + 1] = 0. \quad (6)$$

We find

$$\alpha = -\frac{\delta}{2a} \left( 1 \pm \sqrt{1 - \frac{4ab}{\delta^2}} \right), \quad (7)$$

where the quantity  $a$  is given by (2) and  $b = \int_V \varphi_0^*(x) dx$ . It may be seen from (7) that for  $a > 0$  and  $\delta < -2\sqrt{ab}$  there are two positive solutions—one decreasing and one increasing with increase in  $\delta$ . For  $a > 0$  and  $\delta > -2\sqrt{ab}$ , there are no positive solutions. For  $a < 0$ , the two solutions have different signs, and change sign at the point  $\delta = 0$  (i.e.,  $\lambda = \lambda_0$ ), while the positive branch of the function  $\alpha(\delta)$  is a smooth curve. It is easy here to see the qualitative agreement with the solution of the unperturbed system.

The number  $\lambda^*$  is a branch point [2] of the nonlinear Eq. (4), if the linear equation

$$Ly + \lambda^* \left[ \eta \frac{d}{d\eta} f(R'\eta, R^0\eta) + f(R'\eta, R^0\eta) + 2\mu\eta \right] y = 0 \quad (8)$$

has a nontrivial solution. Using the approximate solution  $\eta \cong \sqrt{\varepsilon\eta^{(1)}}$  obtained above, we find, to a first approximation

$$\lambda^* = \lambda_0(1 - 2\sqrt{ab\varepsilon}). \quad (9)$$

There are no branch points for  $a < 0$ . If  $a > 0$ , the branch point defined by (9) is the explosive limit, above which ( $\lambda > \lambda^*$ ) no steady-state process is possible. The corresponding limiting radical concentration is given (to a first approximation) by

$$\eta^* = \sqrt{\frac{b\varepsilon}{a}} \varphi_0(x). \quad (10)$$

We shall consider a simple example. Let  $L = d^2/dx^2$  and  $\eta = \zeta = \theta = 0$  for  $x = 0$  and  $x = 1$  (plane vessel with no convection). Then  $\lambda_0 = \pi^2$ ,

$$\varphi_0 = \varphi_0^* = \psi_0' = \psi_0^0 = \sqrt{2} \sin \pi x, \quad b = \frac{2\sqrt{2}}{\pi}, \quad a = \frac{8\sqrt{2}}{3\pi} (h - g + \mu),$$

and Eqs. (9) and (10) give:

$$\lambda^* = \pi^2(1 - 2.08\sqrt{\varepsilon(h - g + \mu)}), \quad \eta^* = \sqrt{\frac{1.50\varepsilon}{h - g + \mu}} \sin \pi x.$$

The results obtained may easily be generalized to the case of a complex process involving different types of radicals and stable substances. The over-all governing principle is as follows. The conditions for the existence of a stable steady-state process are most altered when slow nonradical reactions come into the picture. If an explosive region exists in the unperturbed system, and there are slow reactions going at a rate of order  $\varepsilon$  under conditions such that there is a bifurcation point in the unperturbed system, the effect is to shift the explosive limit by an amount of order  $\sqrt{\varepsilon}$ . The limiting radical concentrations before explosion are of the same order. All these quantities may be calculated from formulas similar to (9) and (10), but with another set of values for the constants  $a$  and  $b$ .

The results just presented are also immediately applicable to autocatalytic reactions that are most chain-like in nature.

#### LITERATURE CITED

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2. M. A. Krasnosel'skii, Topological methods in the theory of nonlinear integral equations [in Russian] (1956).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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