THEORY OF HOMOGENEOUS-HETEROGENEOUS BRANCH CHAIN REACTIONS IN A FLOW

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When investigating branch chain reactions in a flow, we meet with the problems of explaining the dependence of the observed kinetics, and in particular the threshold for the inception of rapid reaction (explosion), on the hydrodynamic characteristics of the flow. An important example of such a problem is that of explaining the connection between the explosion limit and flow speed, pressure, and tube diameter during the transport of such gases as acetylene (pure or in admixture with air) in tubes at whose walls the formation of intense radical sources (metal acetylides) is possible. Another example is the problem of determining the kinetic parameters of a homogeneous-heterogeneous chain reaction from experimental data on the chain explosion limit at various flow speeds.

In the present paper we consider a method for the solution of this problem for the case of flow at large Peclet numbers, using a general approach earlier developed for examining homogeneous-heterogeneous reactions in a flow [1] and the methods for determining the stability limit of branch chain reactions [2].

We shall consider the conditions for the evolution of a branch chain reaction in a liquid or gas flow at large Peclet numbers. The flow can be divided into two regions – the bulk flow, where as a result of intense turbulence the reagent concentrations are constant across a given cross-section and vary only along the flow direction, and the boundary layer where it is permissible to neglect convective mass transfer. We first consider a very simple process which occurs in the bulk liquid or gas and includes the chain propagation reaction

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

and a quadratic chain termination reaction as a result of the interaction of the radicals R. Reaction (1) is branched if the radical stoichiometric coefficient ν is positive. We further consider that at the tube walls there is radical generation with the rate constant $\varkappa$, and quadratic chain termination with rate constant $\varkappa_1$, and that the rate constant for the bulk reactions of propagation and termination of the chain are k and k_1, respectively. Under these conditions the equations and boundary conditions which determine the dimensionless concentration $a(x)$ of the initial substance A (with the scale concentration a_0) and the dimensionless concentration $c(x)$ of the radical R (with the same scale) in the bulk flow and the corresponding dimensionless concentrations $\alpha(y)$ and $\zeta(y)$ in the boundary layer may be written in the form

$$w\frac{da}{dx} = -kac + j_a; \tag{2}$$

$$w\frac{dc}{dx} = \nu kac - k_1c^2 + j_c; \tag{3}$$

$$D\frac{d^2\alpha}{dy^2} - k\alpha\zeta = 0; \tag{4}$$

$$D_1\frac{d^2\zeta}{dy^2} + \nu k\alpha\zeta - k_1\zeta^2 = 0; \tag{5}$$

$$a(0) = 1, \quad c(0) = 0; \tag{6}$$

$$\alpha(\delta) = a, \quad \zeta(\delta) = c; \tag{7}$$

$$\left(\frac{da}{dy}\right)_{y=0} = 0; \tag{8}$$

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$$D_1\left(\frac{d\zeta}{dy}\right)_{y=0} = \varkappa_1\zeta^2(0) - \varkappa; \tag{9}$$

$$j_a = -\frac{D}{R}\left(\frac{da}{dy}\right)_{y=\delta}, \quad j_c = -\frac{D_1}{R}\left(\frac{d\zeta}{dy}\right)_{y=\delta} \tag{10}$$

Here x is a coordinate along the direction of flow, y is a coordinate normal to the boundary layer, δ is the boundary layer thickness, R is the hydraulic radius of the tube, D and D_1 are the molecular diffusion coefficients of the initial substance A and of the radical R, respectively, j_a and j_c are the supply rates of molecules of the initial substance and of the radicals from the boundary layer to the bulk of the turbulent flow. In writing Eqs. (4) and (5) we have neglected boundary layer curvature – which is permissible since $\delta \ll R$ always.

We first consider the Eqs. (2) and (3) for the concentrations in the bulk flow. These equations are first-order; therefore for given j_c, j_a and initial conditions (6) they always have a unique solution. When no radicals are supplied by the boundary layer ($j_c = 0$) the solution of (2), (3), and (6) has the form $a \equiv 1$, $c \equiv 0$, i.e., no reaction occurs. This solution, however, is unstable in the sense that small extraneous radical sources can lead to considerable departure from zero of the radical concentration at sufficiently large distances from the tube entrance. In fact, let us put $j_c = k\varepsilon$, where ε is some small parameter and we consider the radical concentration to be small. Then it follows from (2) that $a \equiv 1$ (to a precision of order ε) and that, neglecting terms of order ε^2, (3) can be written in the form

$$w\frac{dc}{dx} = \nu k c + k\varepsilon, \tag{11}$$

whence

$$c = \frac{\varepsilon}{\nu}\left(e^{\frac{\nu k}{w}x} - 1\right). \tag{12}$$

Clearly the radical concentration remains small only within the length

$$x \ll x^* = \frac{w}{\nu k}\ln\frac{\nu}{\varepsilon} \tag{13}$$

– the "induction length" x^* depending very feebly (logarithmically) on the small parameter ε. The radical concentration can remain small over any distance only if the rate constant for the termination reaction k, is sufficiently large ($k_1 \gg \nu k$), since then with increasing x the radical concentration approximates to the stationary value $c = \nu k/k_1 \ll 1$.

Since radicals formed at the tube walls reach the bulk flow from the boundary layer it is now necessary to study the character of the solutions of Eqs. (4) and (5) describing the process in the boundary layer. When $\varkappa = 0$, these equations always have the trivial solution $\alpha \equiv a \equiv 1$, $\zeta \equiv 0$. This solution is stable if all eigenvalues μ of the linearized equation

$$D_1\frac{d^2\zeta}{dy^2} + \nu k\zeta = \mu\zeta \tag{14}$$

with the boundary condition $\zeta(0) = \zeta(\delta) = 0$ are negative. This condition is satisfied if

$$\frac{\nu k\delta^2}{D_1} < \pi^2. \tag{15}$$

It can be shown [2] that when inequality (15) is not satisfied then for $\varkappa = 0$ there exists a stable, non-trivial solution of the problem (4), (5) which has a finite radical concentration in the boundary layer and, correspondingly, a finite current of radicals from the boundary layer into the bulk flow; the latter (when the bulk chain termination rate is not too large) leads to rapid growth of the radical concentration in the bulk flow along the length of the tube, i.e., to explosion. Hence the validity of condition (15) is a necessary condition for the stability of the system.

If inequality (15) is satisfied, then at small $\varkappa$ the radical concentration in the boundary layer is small and the reaction in the boundary layer can be neglected because of the smallness of its relative volume. In this case we may assume

$$j_a = 0, \; j_c = \varkappa/R. \tag{16}$$

Correspondingly, $\varepsilon = \varkappa/kR$ and the "induction length" is given by

$$x^* = \frac{w}{\nu k} \ln \frac{\nu k R}{\varkappa}. \tag{17}$$

Clearly, inequality (15) can be violated at a reduced flow rate and a correspondingly increased thickness δ of the boundary layer. A reduction in the velocity, according to (17), leads at the same time to a reduced "induction length" x^*. Thus, increasing the linear flow rate always results in the stabilization of the system.

The boundary layer plays a rather different role when, owing to a considerable radical recombination rate at the walls, there emerges the possibility of a quasi-stationary development of the reaction at low radical concentrations in the flow (cool flames). Assuming that the radical concentration is small and that the conditions for a quasi-stationary regime are satisfied we may write the equations determining the radical concentration in the flow in the form

$$\nu k a c + j_c = 0. \tag{18}$$

The progress of chains in the boundary layer may be neglected owing to its small volume. Thus, the radical concentration in the boundary layer is given by the equation

$$\zeta = \zeta(0) + \frac{R j_c}{D_1} y \tag{19}$$

and it follows from boundary condition (9) that

$$\zeta(0) = \sqrt{(R j_c + \varkappa) / \varkappa_1}. \tag{20}$$

The boundary condition $\zeta(\delta) = c$ may now be written in the form

$$c = \sqrt{(R j_c + \varkappa) / \varkappa_1} + \delta R j_c / D_1. \tag{21}$$

The solution of the system (19), (21) gives

$$j_c = -\frac{\varkappa_1 / R}{2(p+q)^2}\left(\sqrt{1 + 4\frac{\varkappa}{\varkappa_1}(p+q)^2} - 1\right), \tag{22}$$

$$c = \frac{p}{2(p+q)^2}\left(\sqrt{1 + 4\frac{\varkappa}{\varkappa_1}(p+q)^2} - 1\right), \tag{23}$$

where $p = \varkappa_1/\nu k R$, $q = \varkappa_1 \delta / D_1$. It should be remembered that these formulas are only valid for values of the various parameters such that $c \ll 1$ and when inequality (15) is satisfied. From (21) and (22) it is seen that by diminishing the linear flow rate and, correspondingly, the constants δ and q the quasistationary concentration and chain reaction rate is reduced; subsequent reduction of the flow rate may, however, lead to explosion owing to the violation of the boundary layer stability condition (15). With increasing flow rate, a limiting quasistationary concentration

$$c = \sqrt{\frac{\varkappa}{\varkappa_1} + \frac{1}{4p^2}} - \frac{1}{2p} \tag{24}$$

is achieved, which depends only on the kinetic characteristics of the process.

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