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Abstract

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THEORY OF HOMOGENEOUS-HETEROGENEOUS RADICAL REACTIONS IN A TURBULENT FLOW

In the paper (^1) a general theory of homogeneous-heterogeneous reactions in moving media was developed. However, in order to obtain more concrete results, it is necessary to base the theory on a sufficiently detailed scheme of chemical transformations.

One very interesting case of homogeneous-heterogeneous reactions is that of radical-chain reactions with initiation and/or destruction of radicals on the surfaces of the reaction vessel.* As is known, in some reactions of this type that are of practical interest, laboratory experiments have revealed a substantial influence of the surface-to-volume ratio of the reactor, as well as a dependence of the total rate on the nature of the wall. As one of the most important examples one may cite reactions of liquid-phase oxidation of hydrocarbons (^2). It must be emphasized that in reality the course of such reactions should be affected not only by the value of the indicated ratio, but also by the motion of the liquid (^3), which, for sufficiently rapid flows, determines the rate at which radicals are supplied to and removed from the surface. This circumstance should be especially important in the transition to carrying out processes on larger technical scales.

Table 1

Model scheme of radical reactions

Reaction	Rate law of the reactionin the volume	Rate law of the reactionon the surface
Initiation $a \to 2r$	$k_I a$	$\chi_I a_s$
Branching $r + a \to 3r$	$k_{\mathrm{II}} a r$	–
Main reaction in the volume $r \to b + r$	$k_{\mathrm{III}} r$	–

Reaction	Rate law of the reactionin the volume	Rate law of the reactionon the surface
Side reaction on the wall $r \to b' + r$	–	$\chi_{\mathrm{III}} r_s$
Chain termination $2r \to a'$	$k_{\mathrm{IV}} r^2$	$\chi_{\mathrm{IV}} r_s^2$

We shall consider here the corresponding process under the conditions of a one-dimensional extended (tubular) reactor at very large values of the mean cross-sectional Peclet number $\bar{u}R/D_r$, where $\bar{u}$ is the mean velocity of the liquid, R is the tube radius, and D_r is the diffusion coefficient of the radicals. The choice of such a system corresponds to the real situation in the technical implementation of most large-scale processes.

To preserve the principal features of the phenomena under consideration, in this case it is possible, in a general discussion, not to distinguish individual radicals, assuming that substitution reactions proceed sufficiently rapidly, and to denote the co–

the aggregate of radicals via r. A model reaction scheme including branching may accordingly be taken in the form presented in Table 1.

In this case one may restrict oneself to the case of a temperature constant over the cross section and regard the diffusion coefficients of all the substances considered as being of the same order of magnitude. The letters a and b, b' denote, respectively, the initial and final products. The substances and their concentrations are denoted by the same letters. On the basis of the results of [1], the entire interior of the tubular reactor can be divided into the main region and a diffusion boundary layer of thickness δ_r. In the latter, volume reactions may be neglected, and the averaged conservation equation for the main region (outside the boundary layer) may be written in the form

$$\bar{u}\frac{\partial b_v}{\partial x} = k_{\mathrm{III}} r_v, \tag{1}$$

$$\bar{u}\frac{\partial b'_v}{\partial x} = \frac{1}{R} j'_{b'}, \tag{1'}$$

$$\bar{u}\frac{\partial r_v}{\partial x} = 2k_{\mathrm{I}} a_v + 2k_{\mathrm{II}} a_v r_v - k_{\mathrm{IV}} r_v^2 - \frac{1}{R} D_r \frac{r_v - r_s}{\delta_r}. \tag{2}$$

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* The problem of the influence of diffusion of active centers on the rate of a reaction in a quiescent medium and in laminar flow was considered in works by a number of authors (^{4}-6), beginning with the first studies of N. N. Semenov (^7).

The indices v and s in (1)–(2) indicate that the quantities are taken, respectively, in the main region and at the surface. The concentrations of radicals and of the reaction product b' at the surface are determined by boundary conditions of the type considered in [1]:

$$D_r \frac{r_v - r_s}{\delta_r} = -\chi_{\mathrm{I}} a_v + \chi_{\mathrm{IV}} r_s^2,$$

$$D_{b'} \frac{b'_v - b'_s}{\delta_{b'}} = \chi_{\mathrm{III}} r_s, \tag{3}$$

where δ_r and $\delta_{b'}$ are the thicknesses of the diffusion layers of radicals and of the product b'.

In the case* of a turbulent flow regime in a tube, for δ_i one may write [3]

$$\delta_i \sim \mathrm{Pr}^{3/4} D_i / \sqrt{\bar{k}_f}\, \bar{u} \quad \text{—smooth surface,} \tag{4}$$

$$\delta_i \sim \frac{(\nu_{iD} i)^{1/4} h^{1/2}}{\sqrt[4]{k_{\mathrm{fr}}}\, \bar{u}^{1/2}} \lesssim h \quad \text{—rough surface with scale } h. \tag{4a}$$

In laminar flow, but at large Peclet numbers, respectively,

$$\delta_i \sim \frac{1}{(\mathrm{Re}\,\mathrm{Pr})^{1/3}} \sqrt{R^2 x} \quad \text{for } x > \mathrm{Re}\,\mathrm{Pr}\, R, \tag{5}$$

$$\delta_i \sim \frac{1}{(\mathrm{Pr})^{1/2}} \sqrt{\frac{\nu_i x}{u}} \quad \text{—entrance section, } x < \mathrm{Re}\,\mathrm{Pr}\, R. \tag{5'}$$

For radical reactions, in view of their high reactivity, in many cases the quantity $\partial r_v / \partial x$ in equation (2) may be set approximately equal to zero (the method of quasistationary concentrations of intermediate products). Thus we arrive at a system of equations (1), (1′), and (2), equivalent to the equation of an ideal plug-flow reactor with a definite law of formation of the final products b and b', depending on the hydrodynamics of the reactor. Omitting in (2) the derivative and substituting the value of r_s from the first of equations (3), we find the radical-balance equation:

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* All arguments are carried out for a tube of such large diameter that curvature may be neglected. However, in essence, up to the specification of δ_i, the formulas retain their form for an extended reactor of arbitrary shape.

$$2k_I a_v + 4k_{\mathrm{II}} a_{vr} v + \frac{1}{R}\varkappa_I a_v = k_{\mathrm{IV}} r_v^2 + \frac{1}{R}\varkappa_{\mathrm{IV}}\left[-\frac{D_r}{2\delta_r\varkappa_{\mathrm{IV}}} + \sqrt{\left(\frac{D_r}{2\delta_r\varkappa_{\mathrm{IV}}}\right)^2 + \frac{\varkappa_I a_v}{\varkappa_{\mathrm{IV}}} + \frac{D_{rr} v}{\delta_r \varkappa_{\mathrm{IV}}}}\right]^2. \tag{6}$$

The resulting simple, but somewhat cumbersome, formulas can be simplified in various limiting cases. Let us first consider the relation between recombination in the volume and on the surface. From (6) it is clear that the surface-recombination reaction can always be neglected if the tube radius R satisfies the condition

$$R \gg \frac{\varkappa_{\mathrm{IV}}\left[-D_r/2\delta_r\varkappa_{\mathrm{IV}} + \sqrt{(D_r/2\delta_r\varkappa_{\mathrm{IV}})^2 + \varkappa_I a_v/\varkappa_{\mathrm{IV}} + D_{rr} v/\delta_r\varkappa_{\mathrm{IV}}}\right]^2}{k_{\mathrm{IV}} r_v^2}. \tag{7}$$

This condition is satisfied if the inequality

$$\frac{R\delta_r}{D_r} \gg \frac{1}{k_I a_v / r + k_{\mathrm{II}} a_v}. \tag{8}$$

is satisfied.

Inequality (8) has an obvious meaning: the ratio of the mean time for diffusive traversal of the distance R to the mean time of radical generation in the volume must be large. When the inequality opposite to (7) is satisfied, recombination of radicals in the volume can be neglected.

Similarly, initiation and branching in the volume can be neglected only if

$$R < \varkappa_I / (k_I + k_{\mathrm{II}} r_v). \tag{9}$$

If the opposite inequality is satisfied, one can, conversely, neglect initiation of radicals at the wall.

As an example, let us consider the limiting case in which radicals are not formed at the wall ($\varkappa_I = 0$) and at the same time the rate constant for radical destruction at the wall $\varkappa_{\mathrm{IV}}$ is very large. From (3) we then find in this case

$$r_s \simeq -\left(\frac{D_r}{2\varkappa_{\mathrm{IV}}\delta_r}\right)\left[-1 + \sqrt{1 - \frac{4\varkappa_{\mathrm{IV}}\delta_{rr} v}{D_r}}\right] \simeq \left(\frac{D_{rr} v}{\varkappa_{\mathrm{IV}}\delta_r}\right)^{1/2} \ll r_v. \tag{10}$$

It is assumed here that R is sufficiently large and

$$r_v > D_r / \delta_r \varkappa_{\mathrm{IV}}.$$

Formula (6), in the case under consideration and with the additional assumption of strong branching (the second term on the right-hand side of (6) is much larger than the first), gives

$$r_v = \left(2k_{\mathrm{II}}a_v - \frac{1}{R}\frac{D_r}{\delta_r}\right) \Big/ k_{\mathrm{IV}}. \tag{11}$$

At the same time, from (1), (1′), and (3) we have (see also (1))

$$-\bar{u}\frac{\partial b_v}{\partial x} = 2k_{\mathrm{III}}\left(k_{\mathrm{II}}a_v - \frac{1}{2R}\frac{D_r}{\delta_r}\right) \Big/ k_{\mathrm{IV}}, \tag{12}$$

$$-\bar{u}\frac{\partial b'_v}{\partial x} = \frac{1}{R}\varkappa_{\mathrm{III}}\left(\frac{D_{rr}v}{\varkappa_{\mathrm{IV}}\delta_r}\right)^{1/2}. \tag{13}$$

Since a_v is related to b_v and b'_v by stoichiometric ratios, the consumption rate of a_v is expressed through the rate of formation of b_v and b'_v. Raz-

dividing (12) by (13), with allowance for (11), we find for our limiting case the relation between the rates of formation b_v and b'_v

$$\frac{\partial b_v}{\partial b'_v} = \frac{R}{2}\frac{k_{\mathrm{III}}}{\chi_{\mathrm{III}}}\left(\frac{\delta_r\chi_{\mathrm{IV}}}{D_r}\right)^{1/2}\left[\sqrt{\left(2k_{\mathrm{II}}a_v - \frac{1}{R}\frac{D_r}{\delta_r}\right)/k_{\mathrm{IV}}}\right]. \tag{14}$$

The limiting case indicated above is evidently very close to that realized in sufficiently large apparatuses during oxidation.

We shall not consider here other particular cases in which the general formula (6) admits simplifications. The corresponding calculations present no difficulty. We shall merely emphasize that the following conclusions can be drawn from the general relations.

The ratio between the main and side products, the ratio between termination (initiation) in the reactor volume and on the walls, and, consequently, the total rate of conversion of the initial substance depend substantially not only on the reaction constants but also on the factors of hydrodynamic similarity, on the nature of the wall, in particular its roughness (through the thickness of the diffusion boundary layer δ), and on the geometry of the vessel (through the radius R). In scale-up, the most varied interrelations may be realized between bulk and surface reactions, the size of the reactor, and the flow rate. This circumstance makes it especially necessary, in each case in which an influence of the walls on the radical reaction is observed, to carry out the following measurements: 1) reaction rates as a function of the liquid-flow velocity; 2) reaction rates as a function of the tube radius at a specified value of the transport parameters.

Knowledge of the necessary combinations of chemical constants thereby obtained will make it possible to carry out quantitative calculations of flow reactors and will ensure correct scale-up. The above treatment should be generalized to the case of nonuniform flows: reactions in mixing jets, during bubbling, etc.

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Note: Figure translations are in progress. See original paper for figures.