THEORY OF HOMOGENEOUS-HETEROGENEOUS RADICAL REACTIONS IN TURBULENT-FLOW CONDITIONS

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V. G. Levich * and A. M. Brodskii

M. V. Lomonosov Moscow State University
and Institute of Electrochemistry, Academy of Sciences, USSR

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In a previous paper [1] a general theory was developed for homogeneous-heterogeneous reactions in moving media. However, in order to obtain more definite results it is necessary to put at the basis of the theory a sufficiently detailed scheme of chemical reactions.

One of the extremely interesting cases of homogeneous-heterogeneous reactions is that of radical-chain reactions in which radicals are generated and/or destroyed on the surfaces of the reaction vessel.† As is well known, in some reactions of this type which are of practical interest the laboratory experiments reveal a significant effect of surface-volume ratio of the reactor, and also a dependence of the overall rate on the nature of the walls. One of the most important examples is the liquid-phase oxidation of hydrocarbons [2]. It is necessary to emphasize that it is not only the value of this ratio which affects the course of such reactions, but also the movement of the liquid [3], which, at sufficiently fast flow rates, determines the rates of supply and removal of radicals at the surface. This circumstance is probably of particular significance in processes carried out on a large technical scale.

We consider here an appropriate process occurring in a uniformly extended (tubular) reactor at very high values of the Peclet number for the mean cross section $\bar{u}R/D_r$, where $\bar{u}$ is the mean liquid velocity, R is the radius of the tube, and D_r is the radical-diffusion constant. The choice of such a system corresponds to the real situation for technological realization of the majority of large-scale processes.

In order to preserve the basic features of the phenomena considered, it is possible not to differentiate in the general discussion between individual radicals, on the grounds that displacement reactions occur very quickly, and to denote the aggregate of radicals by r. A model reaction scheme which includes branching is given in the table.

We confine ourselves to the case of a constant-temperature cross section, and take the diffusion coefficients of all the substances considered to be the same within an order of magnitude. The letters a and b, b' denote the corresponding initial and final products. The substances and their concentrations are denoted by the same letters. On the basis of the previous results [1], the entire interior of the tubular reactor can be divided into a main region and a diffusion boundary layer of thickness δ_r. Homogeneous reactions in the latter can be excluded and an average conservation equation written for the main region (outside the boundary layer) in the form

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

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

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

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*Corresponding Member of the Academy of Sciences of the USSR

†The problem of the effect of diffusion of active centers on reaction rates in flowing media and in laminar-flow conditions has been considered in the work of various authors [4-6], beginning with the first investigations of N. N. Semenov [7].

Model Scheme for Radical Reactions

Reaction	Reaction-rate equation	
	in the volume	on the surface
Generation a → 2r	$k_I a$	$\varkappa_I a_s$
Branching r + a → 3r	$k_{II} a r$	
Primary reaction in the volume r → b + r	$k_{III} r$	
Secondary reaction on the wall r → b' + r	–	$\varkappa_{III} r_s$
Chain termination 2r → a'	$k_{IV} r^2$	$\varkappa_{IV} r_s^2$

The indexes v and s in (1)-(2) signify that the quantities are taken in the main region and at the surface, respectively. The concentrations of radicals and products b' at the surface are determined by the boundary conditions discussed in [1] in the form

$$D_{\mathrm{r}} \frac{r_v - r_s}{\delta_{\mathrm{r}}} = -\varkappa_I a_v + \varkappa_{IV} r_s^2, \qquad D_{\mathrm{b}'} \frac{b'_v - b'_s}{\delta_{\mathrm{b}'}} = \varkappa_{III} r_s, \tag{3}$$

where δ_{r} and $\delta_{\mathrm{b}'}$ are the diffusion-layer thicknesses for radicals and for product b'.

For the case* of turbulent flow in the tube one can write for δ_i [3]

$$\delta_i \sim \mathrm{Pr}^{3/4} D_i / \sqrt{k_f} \;\; \overline{u} \text{ — smooth surface,} \tag{4}$$

$$\delta_i \sim \frac{(\nu_i D_i)^{1/4} h^{1/2}}{\sqrt[4]{k_{\text{mep}}}\, \overline{u}^{1/2}} \lesssim h \text{ — rough surface with scale h.} \tag{4a}$$

For laminar flow, but at large values of the Peclet numbers,

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

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

For radical reactions, because of their high reactivities, the quantity $\partial r_v / \partial x$ in Eq. (2) can in many cases be put approximately equal to zero (quasistationary-state method). Thus we arrive at the system of Eqs. (1), (1'), and (2), equivalent to the equation for a reactor of ideal displacement with a particular law for the formation of the final products b and b', dependent on the hydrodynamics of the reactor. Omitting the derivative in (2) and substituting the value of r_s from the first of equations (3), we obtain an equation for radical balance:

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

Such simple but cumbersome formulas can be simplified in certain specific cases. We consider first the relationship between recombination in the volume and on the surface. From (6) it is clear that surface-recombination reactions always can be ignored if the radius R of the tube satisfies the condition

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

This condition is fulfilled if the inequality

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*The discussion relates to a tube of such large diameter that curvature can be ignored. However, the formulas relating to concretization of δ_i preserve their forms for the extended reactor of arbitrary form.

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

is satisfied.

Inequality (8) has an obvious meaning: the ratio of the mean time for diffusion through the distance R to the mean time for generation of radicals in the volume must be large. In order to fulfill the inequality which is the reverse of (7), the recombination of radicals in the volume can be ignored.

Similarly, generation and branching in the volume can be ignored only if

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

On the other hand, when the reverse inequality is fulfilled the generation of radicals on the wall can be ignored.

As an example we consider the limiting case when radicals are not formed on the wall ($\varkappa_I = 0$) and at the same time the rate constant for removal of radicals on the wall $\varkappa_{IV}$ is very high. In this case we find from (3)

$$r_s \cong -\left(\frac{D_r}{2\varkappa_{IV}\delta_r}\right)\left[-1 + \sqrt{1 - \frac{4\varkappa_{IV} - \delta_r r_v}{D_r}}\right] \simeq \left(\frac{D\, r_v}{\varkappa_{IV}\delta_r}\right)^{1/2} \ll r_v. \tag{10}$$

In addition it is assumed that R is sufficiently large and

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

In the case under discussion, formula (6) gives, with the additional assumption of strong branching (the second component on the right side of Eq. (6) is much larger than the first),

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

In addition, from (1), (1'), and (3) we have (cf. also [1])

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

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

Since a_V is connected with b_V and b'_V by stoichiometric relationships, the rate of consumption of a_V is expressed through the rate of formation of b_V and b'_V. Dividing (12) by (13) and taking (11) into account, we find for our limiting case a relationship between the rates of formation of b_V and b'_V

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

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

We will not consider here other individual cases where Eq. (6) allows simplification. The appropriate calculations do not present any difficulty. We shall only stress that from the general relationships the following conclusions can be reached.

The relationship between the main and side products, the relationship between abstraction (generation) in the volume of the reactor and on the walls, and consequently the total rate of conversion of the initial material, depend not only on the rate constants but also on hydrodynamic factors, the nature of the wall and especially its roughness (in terms of the thickness of the diffusion boundary layer δ), and the geometry of the vessel (in terms of the radius R). With a change in scale the most diverse interrelationship can be realized between volume and surface reactions, dimensions of the reactor, and flow rate. This makes it especially necessary to carry out the following measurements whenever the wall is observed to affect a radical reaction: 1) the reaction rate as a function of liquid-flow rate; 2) the reaction rate as a function of tube radius for a given value of the transfer parameters.

Knowledge of the necessary combinations of chemical constants obtained in this way makes it possible to carry out a quantitative calculation for flow reactors and guarantees the correct scale-change operations. These considerations probably apply generally to heterogeneous flows: reactions in mixing streams, during bubbling, etc.

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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.**
