THE FUNDAMENTAL LAWS OF HOMOGENEOUS-HETEROGENEOUS NONBRANCHED RADICAL REACTIONS

A. M. Brodskii, Yu. Ya. Gurevich,
and V. G. Levich†

UDC 541.12.038.3

One of the most important tasks of chemical technology in the calculation of continuous reactors is to find a connection between the yield of the final products, on the one hand, and the rates of the corresponding elementary reactions, the dynamic flow parameters, and the geometry of the reactor, on the other hand. For homogeneous-heterogeneous reactions with high rates of flow, an approach to the solution of this problem based on the use of the approximations of boundary layer theory has been formulated in a number of papers [1-3].

It is known that, in spite of the very low relative volume of the boundary layer region, its role in the processes taking place may be extremely important or even decisive. Such a situation must, in particular, be realized according to a number of mechanisms proposed in the literature for the cracking of hydrocarbons [4] at not too high temperatures. According to these mechanisms, an accelerated generation of the radicals responsible for the cracking reaction takes place at the walls (especially if the wall temperature is higher than the temperature of the flowing medium or if oxygen is chemosorbed on it).

In this paper we shall establish a relation determining, under various conditions, the relative role of the bulk reaction and the surface-layer reaction or, which is the same thing, the dependence of the rate of the reaction averaged over the cross-section of the reactor on the surface-volume ratio. The relations mentioned, which are particularly important for transfer from the laboratory to the industrial scale, give, in particular, an understanding of why in the case of nonbranched chain reactions the dependence of the observed rate of the reaction on the volume: surface ratio is most pronounced in the liquid phase.

Let the formation of the desired product A→B take place over the whole volume of the reactor while for this over-all reaction to take place the presence of free radicals R playing the role of active centers and generated only at the wall is required. From the walls, the radicals diffuse into the bulk where their recombination R+R→M also takes place. The product M so formed is not an active center with respect to the main reaction A→B. We shall denote the volume concentration of radicals R by c, and then in the region of the boundary layer their distribution is described by the equation

$$D\, d^2c\,/\,dz^2 - kc^2 = 0, \tag{1}$$

where D is the diffusion coefficient of the radicals; k is the rate constant of the recombination reaction; and z is a coordinate reckoned along the normal to the wall of the reactor, the curvature of the surface being neglected since the thickness of the boundary layer δ is much smaller than the radius of curvature R.

If the establishment of a stationary concentration of radicals at the surface and the establishment of the bulk-wall equilibrium take place fairly rapidly, the magnitude c closely adjacent to the wall can be regarded as equal to c_0, where the concentration c_0 depends on the concentration of the main reactants and the temperature. The second limiting condition for Equation (1) will be established at the boundary between the boundary layer and the turbulent core of the flowing medium: $c(\delta) = c^*$, where c^* is the concentration of radicals in the bulk volume of the reactor. The magnitude c^* is unknown a priori, but it can be determined after the solution of Equation (1) on the basis of the following considerations. The constant value of the concentration of radicals in the bulk is determined by the competition of two factors: the flow of radicals from the walls into the bulk and their recombination, which takes place

---

†Corresponding Member of the Academy of Sciences of the USSR.

Institute of Electrochemistry, Academy of Sciences of the USSR; M. V. Lomonosov Moscow State University. Translated from Doklady Akademii Nauk SSSR, Vol. 183, No. 5, pp. 1143-1146, December, 1968. Original article submitted July 22, 1968.

in the bulk. Under stationary conditions, these factors balance out one another and we therefore find that the following relation must hold:†

$$j|_\delta = k(c^*)^2\Delta. \tag{2}$$

Here $j|_\delta$ is the flow of radicals at the boundary between the boundary layer and the bulk volume and Δ is the volume-surface ratio of the reactor; if the cross section of the reactor is a circle of radius R, then $\Delta = R/2$. After the solution of Equation (1), the magnitude $j|_\delta$ can be expressed in terms of c_0 and c^*.

Passing to the dimensionless magnitudes $y = c/c_0$ and $\rho = z/\delta$, we obtain the boundary value problem

$$y'' - \varepsilon y^2 = 0, \quad y(0) = 1, \quad y(1) = \eta, \tag{3}$$

where $\varepsilon = k\delta^2 c_0/D$ and $\eta = c^*/c_0$.

The dimensionless parameter ε depends on the rate of recombination of the radicals, their surface concentration, and the diffusion coefficient and also (through δ^2) on the hydrodynamic characteristics of the flow. Numerical estimates show that ε can vary within wide limits while if one considers the processes in the gas phase it is possible to realize the condition $\varepsilon \leq 1$ and in the liquid phase $\varepsilon \geq 1$.

The solution of Equation (3) is written in the form

$$\rho = \int_y^1 [{}^2/_3\varepsilon(\xi^3 + \lambda^3)]^{-{}^1/_2} d\xi, \tag{4}$$

where λ is the integration constant, which is determined from the condition $y|_{\rho=1} = \eta$. The integral $\rho(y)$ can be expressed in general form in terms of elliptic functions [5]; however, in the most interesting limiting cases the calculations can be completed with the aid of elementary functions.

Let us first consider the case $\eta \ll \lambda \ll 1$; the physical meaning of these conditions will be determined below. From (4) by the substitution $\xi = t\lambda$ we obtain

$$\sqrt{{}^2/_3\varepsilon\lambda} = \int_{-1/\lambda}^{-\eta/\lambda} \frac{dt}{\sqrt{1-t^3}} \approx \int_{-\infty}^{0} \frac{dt}{\sqrt{1-t^3}} = \beta, \text{ whence } \lambda = \frac{3\beta^2}{2\varepsilon}. \tag{5}$$

Calculation gives $\beta = 2.8$; from which it follows that the inequality $\lambda \ll 1$ in fact means $\varepsilon \gg 1$, which corresponds physically to the case of a fairly rapid recombination of the radicals.

Let us now determine the magnitude η. According to (4),

$$j|_\delta = -D\left.\frac{dc}{dz}\right|_{z=\delta} = \frac{Dc_0}{\delta}\sqrt{{}^2/_3\varepsilon(\eta^3+\lambda^3)} \approx \frac{Dc_0}{\delta}\sqrt{{}^2/_3\varepsilon\lambda^3} = \frac{Dc_0}{\delta}\beta\lambda, \tag{6}$$

whence, substituting (6) in (2) we find $\frac{Dc_0}{\delta}\beta\lambda = kc_0^2\eta^2\Delta$, i.e., taking (5) into account,

$$\eta = \lambda\sqrt{\frac{2}{3\beta}\frac{\delta}{\Delta}}. \tag{7}$$

Since $\delta/\Delta \ll 1$, then, as follows from (7), with the condition $\lambda \ll 1$ (i.e., $\varepsilon \gg 1$) the assumption $\eta \ll \lambda$ made previously is automatically satisfied for the mean concentration over the region of the boundary layer c we obtain

$$\bar{c} = \frac{c_0}{\sqrt{{}^2/_3\varepsilon}} \int_0^1 \frac{y\,dy}{\sqrt{y^3+\lambda^3}} \approx \frac{2c_0}{\sqrt{{}^2/_3\varepsilon}}. \tag{8}$$

---

† Where radicals are generated independently in the bulk, an appropriate member must be introduced into Equation (2).

Now let $\lambda >> 1$. By determining the magnitude λ from (4), we obtain

$$\lambda^{3/2} = \int\limits_{\eta}^{1} \frac{dy}{\sqrt{2/3\,\varepsilon}} = \sqrt{\frac{3}{2\varepsilon}}\,(1-\eta),$$

i.e., the condition $\lambda \ll 1$ corresponds to $\varepsilon \ll 1$ – the case of a slow radical recombination reaction. For the flow of radicals from the wall into the bulk of the turbulent core, we find (since $\lambda \gg 1$, $\lambda \gg \eta$)

$$j\,|_{\delta} = \frac{Dc_0}{\delta}\sqrt{2/3\,\varepsilon\lambda^3} = \frac{Dc_0}{\delta}(1-\eta). \tag{10}$$

We may note that Expression (10) for $j\,|_{\delta}$ coincides accurately with that obtained in the theory of the boundary layer in the absence of a bulk chemical reaction [7]. For the mean value of the concentration we have

$$\bar{c} = \frac{c_0}{\sqrt{2/3\,\varepsilon}} \int\limits_{\eta}^{1} \lambda^{-3/2}\, y\, dy = c_0 \frac{1-\eta^2}{2(1-\eta)} = c_0 \frac{1+\eta}{2}, \tag{11}$$

i.e., the same result as in the theory [7] where the assumption is made of a linear distribution of concentration from $z = 0$ to $z = \delta$.

For the magnitude η, from (2) taking (10) into account we find

$$\eta^2 = \frac{\delta}{\varepsilon\Delta}(1-\eta). \tag{12}$$

Now we can calculate the effective rate w_{eff} of formation of the product B, which forms the basis of the materials balance equation

$$\frac{d}{dx}(ub) = \dot{w}_{\text{eff}}(x) \tag{13}$$

(here u is the rate of flow averaged over the cross section, b is the concentration of substance B, and the coordinate x is calculated along the axis of the reactor). Let $Q = Q_{\delta} + Q_V$ be the yield of the reaction in unit length of the reactor, which is composed of the amount of desired product formed in the region of the boundary layer Q_{δ} and in the region of turbulent flow Q_V. Since in the region of turbulent flow the concentrations of all the substances are constant, $Q_V = S\varkappa c^* a_V$, where S is the cross-sectional area of the reactor, $\varkappa$ is the rate of the chemical reaction $A + R \rightarrow B$, and a_V is the bulk concentration of substance A. The magnitude w_{eff} is expressed in a simple manner in terms of Q:

$$w_{\text{eff}} = \frac{Q}{S} = \frac{Q_v}{S}\left(1 + \frac{Q_{\delta}}{Q_v}\right) = \varkappa a_v c_0 \eta \left(1 + \frac{Q_{\delta}}{Q_v}\right). \tag{14}$$

Taking into account the fact that $Q_{\delta}/Q_V = c\delta/c^*\Delta$, for the dimensionless effective rate $\omega = \omega_{\text{eff}}/\varkappa a_V c_0$ we obtain

ε	$\varepsilon \ll \delta/\Delta$	$\delta/\Delta \ll \varepsilon \ll 1$	$1 \ll \varepsilon \ll \Delta/\delta$	$\Delta/\delta \ll \varepsilon$
ω	1	$\sqrt{\frac{\delta}{\varepsilon\Delta}}$	$\frac{\delta}{\Delta}\sqrt{\frac{6}{\varepsilon}}$	$\frac{1}{\varepsilon}\sqrt{\frac{3\beta^3}{2}\frac{\delta}{\Delta}}$

A number of interesting conclusions follow from the table given.

1. With an increase in the rate of recombination of radicals in the bulk (increase in ε), the effective rate of formation of substance B decrease; ε also increases with a rise in δ ($\varepsilon \sim \delta^2$), which depends, generally speaking, on the hydrodynamic parameters of the flow and the roughness of the surface of the reactor, and therefore with an increase in δ (for example as a consequence of a decrease in the rate of flow) a decrease in w_{eff} should also be expected.

2. The magnitude w_{eff} depends differently on Δ (or on R) at different values of ε. It must, however, be borne in mind that δ, which is a function of the Reynolds number Re, also depends on Δ (or R) so that the total dependence of w_{eff} on Δ is fairly complex and is, generally speaking, determined by the value of Re.

For sufficiently small values of ε, the effective rate of the reaction does not depend on Δ (or on the radius R). In view of this it is understandable, for example, why in the investigation of cracking in the gas phase (i.e., at $\varepsilon \ll 1$) at low pressures w_{eff} depends only very slightly on Δ [4, 6]. The most pronounced dependence on Δ arises in the case $1 \ll \varepsilon \ll \Delta/\delta$, which is frequently realized in reactions taking place in the liquid phase. On passing to dimensionless magnitudes, we find for this case

$$w_{eff} = \frac{\varkappa a_v}{\Delta} \sqrt{\frac{6Dc_0}{k}}. \tag{15}$$

We may stress that it is particularly important to take into account the existence of a fundamental dependence of w_{eff} on the hydrodynamics of the flow and the geometrical characteristics of the reactor in scale transitions from laboratory to industrial apparatus.

3. With an increase in c_0 (which corresponds to a rise in ε) the magnitude w_{eff} first increases in proportion to c_0, and then this rise slows down ($w_{eff} \sim \sqrt{c_0}$, see (15)) and, finally, at sufficiently large values of c_0 (so that $\varepsilon \gg \Delta/\delta$) saturation takes place and it ceases to depend on c_0

$$w_{eff}^{\infty} = \varkappa a_v \frac{k\delta^2}{D} \sqrt{\frac{3\beta^2}{2} \frac{\delta}{\Delta}}. \tag{16}$$

We may note that all the conclusions drawn remain in force if the formation of substance B from A takes place by a reaction of higher order: $nA \rightarrow B$. The only change consists in the fact that in the expression for w_{eff}, a_v must be replaced by a_v^n.

In conclusion we may note that more complex chemical processes with the participation of various types of radicals formed and destroyed both in the bulk and at the wall can be considered in the same way.

LITERATURE CITED

1. Gas Dynamics and Heat Exchange in the Presence of Chemical Reactions [Russian translation], IL (1962).
2. V. G. Levich and A. M. Brodskii, Dokl. Akd. Nauk SSSR, 165, 604 (1965); 165, 1115 (1965); 166, 151 (1966).
3. A. M. Brodskii and V. G. Levich, Teoretich. Osnovy Khim. Tekhnol., 1, No. 2 (1967).
4. A. D. Stepukhovich, The Kinetics and Mechanism of Thermal Cracking [in Russian], Saratov (1965).
5. E. Yanke and F. Émde, Tables of Functions with Formulas and Curves [in Russian], Moscow (1959).
6. R. Martin, M. Dzierzjnski, and M. Miclaus, J. Chim. Phys., 61, 287, 790, 802 (1964).
7. V. G. Levich, Physicochemical Hydrodynamics [in Russian], (1959).