GENERAL THEORY OF HOMO- HETEROGENEOUS PROCESSES IN MOVING MEDIA

(UDC 541.124)

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

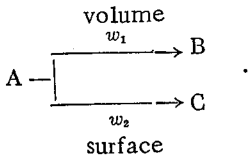
Lomonosov University, Moscow
Institute of Electrochemistry of the USSR Academy of Sciences

Translated from Doklady Akademii Nauk SSSR, Vol. 165, No. 3,
pp. 607-610, November, 1965
Original article submitted July 16, 1965

Until now the quantitative theory of chemical reactions in moving media has been developed mainly for the case of heterogeneous catalysis. Authors have discussed various cases of laminar flow (in particular, equal-access and non-equal-access surfaces) and turbulent flow [1, 2]. There have recently been many studies of the theory of macrokinetics of reactions in gas currents [3, 4] occurring on the surfaces of bodies flying rapidly through the air. These authors have found, in particular, that results obtained for liquids, in which the Prandtl diffusion number $\mathrm{Pr}_D = \nu/D$ is large by comparison with the thermal Prandtl number $\mathrm{Pr}_T = \nu/\chi$, can be transferred without great error to gases, for which $\mathrm{Pr}_D \sim \mathrm{Pr}_T$.

A somewhat different position is occupied by the theory of homo- heterogeneous processes, in which volume and surface reactions are joined into a single complex. These include many chain and radical processes, processes forming unstable products at the surface of a new phase, etc. Despite their importance, the macroscopic kinetics of these processes has been studied (if we ignore certain specific problems in the theory of combustion [5]) in the main only for the idealized case of a stationary medium, or (until recently) for laminar flow in tubes [6, 7]. However, it must be borne in mind that in liquids the stationary-medium approximation has generally no practical meaning. In practice, the important cases are those of liquids or gases in turbulent motion, broken external flow round variously-shaped reaction surfaces, etc. It is therefore of interest to study the general theory of the macrokinetics of homo- heterogeneous processes in moving media.

For general consideration, we shall take the simplest system in which stationary homogeneous and heterogeneous reactions are taking place according to the scheme



The concentration C of substance A (the number of particles per unit volume) obeys the equation of convective diffusion is a chemically active medium,

$$\operatorname{div}(\mathbf{v}C) = \operatorname{div}\mathbf{j} - k_1C^n. \tag{1}$$

In writing down (1) we were assuming that the velocity of the volume reaction can be expressed by the law $w_1 = -k_1C^n$, and were neglecting thermal effects. In the case of turbulent motion, we must understand that it is - the mean values of the velocity and concentration which are implied in (1) [1]. For simplicity and definiteness, we shall assume that the reaction vessel is a cylindrical tube of radius R and length L. We shall take the x axis along the tube. (We would emphasize that all our general results can easily be transferred to a reactor of arbitrary

---

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

shape.) In the tube, the flow velocity (the mean velocity of the turbulent current) has only one component, the longitudinal one, and (1) can be re-written as

$$\frac{\partial}{\partial x}\{v(r, x)C\} = \frac{1}{r}\frac{\partial}{\partial r}(rj_r) + \frac{\partial j_x}{\partial x} - k_1 C^n, \tag{2}$$

where j_r and j_x are the radial and longitudinal components of the current of substance; the variation of v(r, x) with the lengthwise coordinate allows for possible variation of the number of moles in the reaction. We shall also assume that on the tube walls there is taking place a surface reaction whose velocity w_2 is proportional to Γ^m, where Γ is the surface concentration of substance A. If we suppose that there is a relation holding of the form $\Gamma \sim C|_{r=R}$, the velocity of the surface reaction is given by the law[*]

$$w_2 = \gamma C^m|_{r=R}. \tag{3}$$

In stationary conditions, the following boundary condition must hold at the surface:

$$(j_r)_{r=R} = D(\partial C / \partial r)_{r=R} - \gamma C^m|_{r=R} = 0, \tag{4}$$

at the entrance to the reactor the initial concentration is given as

$$C = C_0|_{x=0,\ 0<r<R}. \tag{5}$$

At large Reynolds numbers, the flow as a whole can of course be divided into a main kernel in which the velocity is constant over the cross-section, and a hydrodynamic boundary layer where the velocity decreases to zero at the solid wall. Similarly, for large Peclet numbers the transport phenomena are divided into a main region and a boundary diffusion region. In the main region, turbulent mixing ensures velocity, concentration and temperature distributions close to the mean for the cross section. In fact, outside the input section of the tube, the variation of velocity and concentration with x will depend entirely on the presence of volume chemical reactions w_1. The actual variation of concentration and velocity along the axis takes place on a scale comparable with the entire reactor length L. If this variation occurred over a substantially shorter length, the idea of the reactor space would lose its meaning. Thus the characteristic length of the volume reactions is L. Since the reaction length L >> R, the variation of concentrations across the width of the reactor will be small in the main region. The concentration in the main region can be taken as a slowly varying function of the radius r, so that for the law of radial variation we can use the relation which is valid in a chemically inactive medium. The assumption of cross-sectional averaging (1) leads to the following approximate equation for the concentration C_V in the main region:

$$\frac{duC_w}{dx} = \frac{2}{R} j_r \mid_{r=R-\delta} - k_1 C_V^n, \tag{6}$$

where u is the mean velocity in the main region.

Let us now consider the boundary-layer region, $R \geq r \geq R-\delta$. In this region the derivatives along the normal to the surface are very large, because the concentration changes from C_V (at the outer boundary) to C_S (at the reaction surface) across a thin layer. At the same time, the flow velocity v(x, r) decreases with closeness to the wall, and the effective Peclet number diminishes. Thus, in the boundary layer, we cannot neglect the term in (1) containing the radial derivatives. However, two terms are negligibly small: that in the lengthwise flow of the susbstance and that expressing the velocity of the main volume reaction. The first is smaller than the complete flow by the factor R/L. The second is small because the variation in concentration caused by the volume reaction over a length δ can be neglected. Below we shall formulate the quantitative conditions whose satisfaction enables us to omit the term representing the volume reaction in the boundary layer. Thus the transfer equation in the boundary layer takes the form of the equation in a chemically inactive medium,

$$\frac{\partial}{\partial x} uC = \frac{1}{r}\frac{\partial}{\partial r}(rj_r). \tag{7}$$

---

[*] The course of a surface process can be determined not only by the catalytic action of the surface, but also, in the non-isothermal case, by superheating near the wall. In these different cases, the physical meaning of γ will be different.

The concentration distribution in the boundary layer can be represented to a good approximation [1] (in any case, sufficient for calculating the qualitative pattern of the phenomena, which is our main aim in this note) in the form*

$$C=\frac{C_V-C_S}{\delta'}y+C_S \quad (0\leqslant r\leqslant R-\delta'). \tag{8}$$

The expression for the thickness of the diffusion boundary layer was found in [1] for a number of concrete problems. Then

$$j_r=D\frac{C_V-C_S}{\delta'}=\text{const.} \tag{9}$$

Substituting (9) in the boundary condition (4) we find an equation which relates the surface and volume concentrations:

$$D\frac{C_V-C_S}{\delta'}=\gamma C_S^m. \tag{10}$$

To get a qualitative picture, we shall confine ourselves to the case of a monomolecular reaction,

$$C_S=\frac{D}{\delta'}\frac{C_V}{(D/\delta'+\gamma)}=\frac{C_V}{1+\delta'/\delta_S}, \tag{11}$$

where we are putting $\delta_S=D/\gamma$. Then

$$C=C_V\frac{y}{\delta'+\delta_S}+C_S,\quad R>y>R-\delta'; \tag{12}$$

$$j_r=\gamma C_V\,/\,(1+\delta'\,/\,\delta_S). \tag{13}$$

In our approximation the flow of substance is constant in the boundary-layer region. The quantity $\delta_S=\gamma/D$ is called the reaction length of the surface reaction. In the limiting case of a very rapid surface reaction (diffusion conditions), $\gamma\to\infty$, $\delta_S\to 0$ and $C_S\to 0$. All the variation of the concentration takes place in the region $\sim\delta'$. For a low surface-reaction rate, the main role is played by the thickness δ_S of the reaction layer.

We must now complete the solution in the main flow and in the boundary layer. To this end, let us substitute the expression (12) for the current of substance into (7). We then get

$$\frac{duC_V}{dx}=\frac{2}{R}\frac{\gamma C_V}{1+\delta'/\delta_S}-kC_V^n. \tag{14}$$

This formula shows that, in our approximation, a hollow tubular reactor with homo- heterogeneous reactions can be considered as an ideal displacement reactor with terms depending on the hydrodynamics (8) and geometry (R).

Let us now consider the limits of applicability of the above approximations. The principal approximation is the neglect of the volume reaction in the boundary layer. Let us set up the mass balance in the boundary layer per unit length, $\Delta x=1$. For this purpose let us consider the current of substance flowing into the boundary diffusion layer from unit volume, and the current leaving the boundary layer across its cross section. Since, in the main current, $j_r=0$ when $R-\delta>y>0$, the first quantity reduces simply to j_r. The amount of substance reacting in the boundary layer is

$$2\pi R\int_0^{\delta'} k_1C^n dr\leqslant 2\pi k_1 C_V^n R\delta'.$$

---

*We shall neglect gas flow to the surface associated with changes in the number of moles, the Stefan current, and other side effects.

The sufficient condition for neglecting the volume reaction in the mass balance of the boundary layer reduces [cf. (7)] to

$$2\pi R \frac{2}{R} j_r = \frac{2}{R} \frac{\gamma C_V}{1+\delta'/\delta_S} > k_1 C_V^n \, 2\pi R \delta' \approx 2\pi R \frac{u\delta'}{L}; \tag{15}$$

$$\frac{u}{\gamma}\left(1+\frac{\delta'}{\delta_S}\right) \ll \frac{L}{\delta'}. \tag{16}$$

Inequality (16), which is always satisfied for a sufficiently extended system, is the quantitative criterion for the applicability of (14) (the equation of an ideal displacement reactor) to an extended reactor with homo-heterogeneous processes. It means that the surface reactions with reaction and diffusion lengths δ_S and δ lead to appreciable concentration changes at distances which are very small in comparison with the length and width of the reactor.

So far we have been considering isothermal reactions. The above method can be directly transferred to any non-isothermal reaction, when the temperature distribution is given by

$$\frac{duT}{dx} = \frac{1}{r}\frac{\partial}{\partial r}(r i_T) - Q k_1(T) C^n. \tag{17}$$

As in the case of the volume reaction, the thermal effect of a reaction at the surface can in many cases be neglected, and the equation for the temperature distribution in the reactor can be written by analogy with (14) as

$$\frac{duT_V}{dx} = \frac{2}{R}\frac{T_V - T_S}{\delta_T} - Q k_1(T_V) C_V^m. \tag{18}$$

The solutions to (14) and (18) must be derived with due account of the boundary conditions, $T = T_S$ for $r = R$, $T = T_0$ for $x = 0$.

In conclusion, we must note that further development of this theory awaits the consideration of more realistic schemes for the chemical reactions, and will require account to be taken where necessary of the volume reactions of secondary and side products in the boundary layer.

LITERATURE CITED

1. V. G. Levich, Physicochemical Hydrodynamics [in Russian], Moscow (1959).
2. M. Leighthill, Proc. Roy. Soc., A 202, 359, 377 (1950).
3. D. Rosner, AIAA J., 2, 593 (1964).
4. Symposium: Gas Dynamics and Heat Exchange in Chemical Reactions [in Russian], IL (1962).
5. Th. Karman and G. Millan, IV Symposium on Combustion (1953), p. 173.
6. A. Gill, Am. Inst. Chem. Eng. J., 8, No. 2 (1962); P. Chunej and S. Lin, AIAA J., 1, 929 (1963); J. Katz, Chem. Eng. Sci., 10, 202 (1959).
7. N. N. Semenoff, Acta physicochim. URSS, 18, 93 (1943).