GENERAL THEORY OF HOMOGENEOUS-HETEROGENEOUS PROCESSES IN MOVING MEDIA

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Abstract

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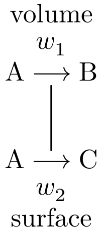
GENERAL THEORY OF HOMOGENEOUS-HETEROGENEOUS PROCESSES IN MOVING MEDIA

Up to the present time, the quantitative theory of chemical reactions in moving media has been developed chiefly for the case of heterogeneous catalytic reactions. Various cases of laminar motion have been considered—in particular, cases of an equally accessible and an unequally accessible surface—and turbulent flows (^{1,2}). Recently a large number of studies have been carried out on the theory of the macrokinetics of reactions in gas flows (^{3,4}), occurring on the surface of bodies at high flight speeds in air. It follows from the cited works, in particular, that results obtained for a liquid medium, in which the diffusion Prandtl number $\mathrm{Pr}_D = \nu/D$ is large in comparison with the thermal Prandtl number $\mathrm{Pr}_T = \nu/\chi$, may be transferred without large errors to gases, for which $\mathrm{Pr}_D \sim \mathrm{Pr}_T$.

The theory of homogeneous-heterogeneous processes, in which bulk and surface reactions are coupled into a single complex, is in a somewhat different state. Such reactions include many chain and radical processes, processes proceeding with the formation of unstable products that form a new phase on the surface, etc. Despite their importance, the macroscopic kinetics of these processes has been considered—apart from certain specific problems of combustion theory (^{5}) —for the most part only for the idealized case of a stationary medium, or, very recently, in laminar flow in a tube (^{6,7}). It must be borne in mind, however, that in liquids the approximation of a stationary medium has no real meaning in general. In practice, both for liquids and for gases, the case of a turbulent flow regime, separated external flow around reaction surfaces of varied form, etc., is of primary importance. Therefore it is expedient to investigate the general theory of the macrokinetics of homogeneous-heterogeneous processes in moving media.

For carrying out general arguments, let us take the simplest system in which stationary homogeneous and heterogeneous reactions proceed according to the scheme



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

$$\operatorname{div}(\mathbf{v}C) = \operatorname{div}\mathbf{j} - k_1 C^n. \tag{1}$$

In writing (1) we have assumed that the rate of the bulk reaction is expressed by the law $w_1 = -k_1 C^n$ and have neglected thermal effects. In the case of turbulent motion, the velocity and concentration in equation (1) should be understood as their mean values (^{1}). For definiteness and simplicity of notation, we shall assume that the reaction vessel is a cylindrical tube of radius R and length L. We direct the x-axis···

along the axis of the tube. We emphasize that all the general results can be readily transferred to a reactor of arbitrary shape. In a tube, the flow velocity (the mean flow velocity in turbulent flow) has only one (longitudinal) component, and (1) can be written in the form

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

where j_r and j_x are the radial and longitudinal components of the flux of matter, while the dependence $v(r,x)$ on the longitudinal coordinate takes into account the possible change in the number of moles in the reaction. We shall further assume that a surface reaction occurs on the tube walls, whose rate w_2 is proportional to Γ^m, where Γ is the surface concentration of substance A. If it is assumed that a relation of the form $\Gamma \sim C|_{r=R}$ holds, then the rate of the surface reaction can be characterized by the law*

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

Under stationary conditions, the following boundary condition must be satisfied at the surface

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

and at the reactor inlet the initial value of the concentration is specified:

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

As is known, at large Reynolds numbers the entire flow can be divided into a main core, in which the velocity is constant over the cross section, and a hydrodynamic boundary layer, where the velocity decreases to zero at the solid surface. Analogously, at large Péclet numbers, when considering transport phenomena, a main region and a diffusion boundary layer are distinguished. In the main region, turbulent mixing ensures a distribution of the concentration velocity and temperature close to the cross-sectional average. Indeed, outside the entrance section of the tube, the entire dependence of the velocity and concentrations on the longitudinal coordinate is associated with the presence of volume chemical reactions w_1. A substantial change in concentration and velocity along the axis occurs on a scale comparable with the total length of the reactor L. If this change were to occur over a substantially smaller distance, the concept of a spatial reactor would lose its meaning. Thus, the characteristic length of volume reactions is the size L. Since the reaction length $L \gg R$, the change in concentration across the thickness of the reactor in the main region is small. The concentration in the main region may be regarded as a slowly varying function of the radius r, and for the law of radial variation one may use a relation valid in a chemically inactive medium. Under this assumption, averaging (1) over the cross section leads to the following approximate equation for the concentration in the main region Cv:

$$\frac{duCw}{dx} = \frac{2}{R} j_r\big|_{r=R-\delta} - k_1 C_v^n, \tag{6}$$

where u is the averaged value of the velocity in the main region.

Let us now consider the region of the boundary layer $R \ge r \ge R - \delta$. In this region the derivatives in the direction normal to the surface are very large, since in the thin layer the concentration changes from the value C_v at its outer boundary to the value C_s at the reaction surface.

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* The development of surface processes may be caused not only by the catalytic action of the surface but also, in the nonisothermal case, by near-wall superheating. In each of these cases the specific physical meaning of γ is different.

At the same time, the flow velocity $v(x, r)$ decreases as the wall is approached, and the effective Peclet number decreases. Therefore, in equation (1), in the region of the boundary layer one cannot omit the term containing radial derivatives. However, in it two terms may be omitted as small: the term with the longitudinal flux of substance and the term expressing the rate of the principal bulk reaction. The first is small in comparison with the radial flux in the ratio

R/L. The second is small because the change in concentration caused by the bulk reaction over the length δ may be neglected. Below we formulate a quantitative condition whose fulfillment makes it possible to omit the term describing the bulk reaction in the boundary layer. Thus, the transport equation in the boundary layer takes the form of the equation in a chemically inactive medium

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

As is known (1), the concentration distribution in the boundary layer can, to a good approximation (in any case, one quite sufficient for clarifying the qualitative picture of the phenomenon, which is our main aim within the framework of this note), be represented in the form*

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

The expression for the thickness of the diffusion boundary layer was found earlier (1) for a large number of particular problems. Accordingly

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

Substituting (9) into the boundary condition (4), we find an equation for determining the relation between the surface concentration and the bulk concentration:

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

To obtain a qualitative picture, we shall restrict 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 $\delta_S = D/\gamma$ is denoted. In this case

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

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

The flux of substance in our approximation has a constant value in the region of the boundary layer. The quantity $\delta_S = \gamma/D$ is called the reaction length of the surface reaction. In the limiting case of a very fast (diffusion regime) surface reaction $\gamma \to \infty$, $\delta_S \to 0$ and $C_S \to 0$. In this case the entire change in concentration occurs in the region $\sim \delta'$. At a low rate of the surface reaction, the thickness of the reaction layer δ_S plays the principal role.

We must now match the solutions in the main flow and in the boundary layer. For this purpose we substitute the expression for the flux of substance (12) into (7). Then we obtain

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

Formula (14) shows that in our approximation a hollow tubular reactor with homogeneous-heterogeneous reactions may be regarded as an ideal-displacement reactor with a term depending on the hydrodynamics (8) and the geometry (R).

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* We neglect the gas flow toward the surface associated with the change in the number of moles, Stefan flow, and other side effects.

Let us turn to an estimate of the limit of applicability of the approximations made. The basic approximation consists in neglecting the volume reaction in the region of the boundary layer. Let us write the material balance in the boundary layer, referred to unit length $\Delta x = 1$. To do this, consider the flux of substance entering the diffusion boundary layer from the bulk, and the flux leaving the boundary layer in a cross section of the boundary layer. Since in the main stream for $(R - \delta > y > 0)$, $j_r = 0$, the first quantity reduces simply to j_r. The amount of substance that has reacted in the boundary layer is equal to

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

A sufficient condition for neglecting the volume reaction in the material balance in the boundary layer reduces to the fulfillment of the inequality (see (7))

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

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

Inequality (16), which is always fulfilled for sufficiently long systems, is a quantitative criterion for the applicability of equation (14)—the equation of an ideal-displacement reactor—to extended reactors with homogeneous-heterogeneous processes. Its meaning is that surface reactions, characterized by the reaction and diffusion lengths δ_S and δ, lead to substantial changes in concentration over distances that are very small in comparison with the length and width of the reactor.

Up to this point we have considered isothermal reactions. The method developed above can be transferred directly to arbitrary nonisothermal reactions, when the temperature distribution is given by the equations

$$\frac{duT}{dx} = \frac{1}{r}\frac{\partial}{\partial r}(ri_T) - Qk_1(T)C^n. \qquad (17)$$

The heat effect of the reaction on the surface can in many cases, just as earlier for the volume reaction, be neglected, and the equation for the temperature distribution in the reactor can be written analogously to (14) in the form

$$\frac{duT_V}{dx} = \frac{2}{R}\frac{T_V - T_S}{\delta_T} - Qk_1(T_V)C_V^n. \qquad (18)$$

Equations (14) and (18) must be solved with allowance for the boundary condition: $T = T_S$ at $r = R$; $\quad T = T_0$ at $x = 0$.

In conclusion, we note that for the further development of the theory under consideration it is necessary to consider more realistic schemes of chemical reactions, and also to take into account, where necessary, the volume reactions of secondary and by-product species in the boundary layer.

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