

A QUASI-STATIONARY RELATION FOR THE CAPILLARY-POROUS ELEMENTS OF CHEMICAL REACTORS

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The authors set up quasi-stationary relations between the concentration of the reactant and the reaction product for a definite type of reactor with chemical transformations. The relationship established can be used in an analytical investigation of the transient operation of such reactors.

The problems associated with the unsteady operation of chemical reactors are of considerable theoretical and practical interest. Their solution involves serious mathematical difficulties and demands a number of assumptions of various types. Hence any justifiable simplification of the analytical investigation of the transient operation of chemical reactors represents a considerable step forward.

Let us now consider chemical reactors incorporating elements with a capillary-porous structure (column packing, electrodes, etc.). We restrict ourselves to elements\* in which the transfer processes are effected by molecular diffusion alone or by forced flow. In addition, for the former case we assume that the changing content of the product in the reactor during the period in which steady working conditions are attained is determined only by the stoichiometric reactant content during the same period; in the latter case in a continuously working reactor the contents of the reactant and the product are kept constant. A chamber from which the reactor is fed with reactant and which takes the product of the reaction is attached to the reactor.

In order to simplify the mathematical derivations, we assume a two-component type of reactor (reactant  $\rightleftharpoons$  product) in the system considered and also the existence of conditions permitting transition to the one-dimensional problem. \*\*

In this case the equations expressing the law of conservation of matter, which are contained in the

system of differential equations describing the unsteady working conditions of such reactors, can be written as follows:

$$\frac{\partial c_r(x, \tau)}{\partial \tau} = D_r \frac{\partial^2 c_r(x, \tau)}{\partial x^2} - Q_r(x, \tau),$$

$$\frac{\partial c_p(x, \tau)}{\partial \tau} = D_p \frac{\partial^2 c_p(x, \tau)}{\partial x^2} + Q_p(x, \tau); \quad (1)$$

$$\frac{\partial c_r(x, \tau)}{\partial \tau} = v \frac{\partial c_r(x, \tau)}{\partial x} - Q_r(x, \tau),$$

$$\frac{\partial c_p(x, \tau)}{\partial \tau} = v \frac{\partial c_p(x, \tau)}{\partial x} + Q_p(x, \tau). \quad (2)$$

The capacities of the reactant and product sources are linked by the following relation:

$$Q_r/\nu_r = Q_p/\nu_p. \quad (3)$$

Here  $\nu_r$  and  $\nu_p$  are the corresponding stoichiometric coefficients in the equation of the reaction taking place in the reactor  $\nu_r R + \dots \rightleftharpoons \nu_p P + \dots$ . It should be noted that  $Q_j$  are not only functions of the coordinate and time, but may also depend on the concentrations of the reactant and the product, the temperature, and a number of other factors (determined by the particular type of chemical process).

The problem is to establish a relationship between the concentrations of reactant and product for the following initial and boundary conditions.

For the system of equations (1) the initial conditions are

$$c_r(x, 0) = c_r^0 = \text{const.}$$

$$c_p(x, 0) = c_p^0 = \text{const.} \quad (4)$$

Boundary conditions: assuming the boundary  $x = 0$  to be closed we obtain

$$\left. \frac{\partial c_r(x, \tau)}{\partial x} \right|_{x=0} = 0, \quad \left. \frac{\partial c_p(x, \tau)}{\partial x} \right|_{x=0} = 0. \quad (5)$$

The same conditions are satisfied by a reactor which is open on both sides and symmetric with respect to the left-hand and right-hand boundaries: in this case zero flowrates are observed in the central plane.

The second boundary condition is determined from the equation of material balance during the time

\*In the following discussion by reactor we mean its porous element.

\*\*E.g., catalytic heterogeneous reaction in an isotropic fine-porous medium in which the depth of the actively operative layer is much greater than the dimensions of the structural element concerned (particles of material, pores). As suggested by Zel'dovich [1] this medium may be considered to be homogeneous with certain effective parameters, while the chemical transformation may be assumed to take place in the entire volume.

needed for the reactor to reach steady working conditions:

$$D_r \int_0^{\infty} \left. \frac{\partial c_r(x, \tau)}{\partial x} \right|_{x=L} d\tau = \int_0^L \{c_r(x, \infty) - c_r(x, 0)\} dx + \int_0^L \int_0^{\infty} Q_r(x, \tau) dx d\tau,$$

$$D_p \int_0^{\infty} \left. \frac{\partial c_p(x, \tau)}{\partial x} \right|_{x=L} d\tau = \int_0^L \{c_p(x, \infty) - c_p(x, 0)\} dx - \int_0^L \int_0^{\infty} Q_p(x, \tau) dx d\tau. \quad (6)$$

For the system of equations (2) the initial conditions are

$$c_r(x, 0) = c_r^0 = \text{const}; \quad c_p(x, 0) = c_p^0 = \text{const}. \quad (7)$$

The boundary conditions are

$$c_r(L, \tau) = c_r^0; \quad c_p(L, \tau) = c_p^0. \quad (8)$$

By dividing the first equation of system (1) by  $\nu_r$  and the second equation by  $\nu_p$  and adding the results, we obtain

$$\frac{\partial}{\partial \tau} \left[ \frac{c_r(x, \tau)}{\nu_r} + \frac{c_p(x, \tau)}{\nu_p} \right] = \frac{\partial^2}{\partial x^2} \left[ D_r \frac{c_r(x, \tau)}{\nu_r} + D_p \frac{c_p(x, \tau)}{\nu_p} \right]. \quad (9)$$

Below we consider systems for which it may be assumed with a known approximation that the effective diffusion coefficients of reactant and product are equal:

$$D_r \approx D_p = D.$$

In this case Eq. (9) becomes

$$\frac{\partial u(x, \tau)}{\partial \tau} = D \frac{\partial^2 u(x, \tau)}{\partial x^2}, \quad (9')$$

where  $u(x, \tau) = [c_r(x, \tau)/\nu_r + c_p(x, \tau)/\nu_p]$  is a new combined variable.

The initial and boundary conditions for (9') take the following forms, respectively:

$$u(x, 0) = c_r^0/\nu_r + c_p^0/\nu_p, \quad (4')$$

$$\left. \frac{\partial u(x, \tau)}{\partial x} \right|_{x=0} = 0, \quad (5')$$

$$\int_0^{\infty} \left. \frac{\partial u(x, \tau)}{\partial x} \right|_{x=L} d\tau = 0. \quad (6')$$

We solve Eq. (9') by the Fourier method [2, 3]. The particular integral of the equation is

$$u(x, \tau) = \exp(-\lambda^2 \tau) \left[ A \cos \frac{\lambda}{\sqrt{D}} x + B \sin \frac{\lambda}{\sqrt{D}} x \right].$$

The general solution of Eq. (9'), after satisfying boundary conditions (5') and (6'), may be written as follows:

$$u(x, \tau) = \sum_{n=0}^{\infty} A_n \exp \left( -\frac{\pi^2 n^2 D}{L^2} \tau \right) \cos \frac{\pi n}{L} x,$$

where coefficients  $A_n$  are determined from the initial condition (4'):

$$A_n = \frac{2u(x, 0)}{L} \int_0^L \cos \frac{\pi n x}{L} dx = \begin{cases} 2u(x, 0) & \text{for } n = 0 \\ 0 & \text{for } n > 0. \end{cases}$$

The general solution of Eq. (9') in its final form for the specified initial and boundary conditions (4')-(6') is as follows:

$$u = A_0/2 = u(x, 0) = c_r^0/\nu_r + c_p^0/\nu_p.$$

Thus, we have shown the quasi-stationary properties of the following relationship between the concentrations of reactant and product:

$$c_r(x, \tau)/\nu_r + c_p(x, \tau)/\nu_p = c_r^0/\nu_r + c_p^0/\nu_p = \text{const}. \quad (10)$$

The relation thus obtained means that during the period which the reactor requires to reach steady working conditions, at any moment of time the sum of the reduced concentrations of the system\* remains constant and equal to the initial value. In addition, from relation (10) follows the stoichiometric equality of the reactant and the product flowrates at the reactor inlet ( $x = L$ ) at any moment of time:

$$\left| D \frac{\partial c_p(x, \tau)}{\partial x} \right|_{x=L} = \left| \frac{\nu_p}{\nu_r} D \frac{\partial c_r(x, \tau)}{\partial x} \right|_{x=L}.$$

For a reactor with forced feed and removal of reactant and product (boundary value problem (2, 7, 8)) a similar relation is obvious without mathematical proof being required.

As an example of the reactors considered we may cite simple electrodes used in applied electrochemistry (fuel cells, electrolyzers, etc.). Investigation of the steady working conditions of such electrodes [4, 5] gave a relation of type (10):

$$c_r(x)/\nu_r + c_p(x)/\nu_p = c_r^0/\nu_r + c_p^0/\nu_p,$$

where  $c_j^0 \equiv c_j^0$  is the concentration of the  $j$ -th component of the system in the volume of the electrolytic chamber; this concentration is continuously maintained (by the large volume of the chamber or by continuous supply of reactant and removal of product).

\*The "sum of the reduced concentrations of the system" is the sum of the concentrations of reactant and product divided by the corresponding stoichiometric reaction coefficients.

## NOTATION

$c_r$  and  $c_p$ —concentrations of reactant and product, respectively, mole/cm<sup>3</sup>;  $D_j$ —effective diffusion coefficient of  $j$ -th component of system (in the region of concentrations considered it is assumed to be constant);  $v$ —velocity of forced flow of mixture of reactant and product;  $Q_j$ —capacity of source of  $j$ -th component of reaction;  $c_j(x, \infty)$ —value of concentration of  $j$ -th component during steady operation of reactor,  $L$ —linear dimension of reactor.

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