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Abstract

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CHEMICAL REACTIONS IN A CHROMATOGRAPHIC REGIME

In studying chemical transformations in a flow, one usually seeks to maintain the system in a stationary state, reducing as far as possible the concentration gradients of the reacting substances ([1]). Under these conditions the kinetics of reactions under dynamic conditions is closest to static kinetics, but all the complications characteristic of the latter are preserved.

In papers by one of the authors and O. M. Todes ([2,3]), the features of the kinetics of catalytic reactions before the establishment of a stationary state throughout the entire bed and the dynamics of adsorption of radioactive substances were considered; in kinetic terms, the latter may be regarded as a model of a reaction carried out under conditions of frontal chromatography ([4]).

The kinetics of nonstationary chemical reactions with chromatographic separation has acquired particular importance in connection with the appearance of rapid methods for studying catalytic processes using pulse development chromatography ([5,6]). As was shown in 1961, when reacting substances move through a reactor in which chromatographic separation of the components of the mixture occurs simultaneously with the reaction, such unusual kinetic conditions are created that one may speak of special chromatographic regimes of reaction, differing substantially from both static and dynamic regimes ([7]). The study of cyclohexane dehydrogenation on supported platinum and certain alloy catalysts confirmed the feasibility of the chromatographic regime and the correctness of the conclusions concerning the distinctive qualitative features of chemical reactions in this regime. In particular, the possibility was demonstrated of eliminating self-poisoning by reaction products and of carrying out reversible reactions irreversibly ([8]).

In the chromatographic regime, many of the complications that hinder the study of true kinetics and of the stepwise mechanism of a reaction disappear. In principle, this regime can be realized for any particular variant of chromatography and for the most diverse types of homogeneous and heterogeneous reactions occurring in the gas phase, in the liquid phase, and on the surface of solids.

The present communication sets forth the theory of this method as applied to gas processes carried out under conditions of development chromatography with pulse introduction of the reacting substance. In studying a reaction in the chromatographic regime, a carrier gas is passed at constant velocity through a column of length L with a stationary phase. Beginning at time $t = 0$, the reacting gas is added to this gas, and after a short interval of time t_0 this addition is stopped. The reacting gas is carried by the carrier gas into the column, in which the chemical process takes place. At the outlet from the column, the degree of conversion and the shape of the curve of the concentration distribution of the initial substance and the reaction products can be measured. It is especially simple to record the time of appearance of the maxima of the peaks, $t_L^{\max}$. The problem is posed of relating these quantities to the constants of the chemical process.

Because of the difference in the adsorption properties of the initial substances and the reaction products, the molecules of the latter are continuously removed from the reaction zone, and in typical cases the effects associated with the presence in this zone of a small number of product molecules may be neglected without substantial error.

Below we consider a homogeneous first-order reaction in the gas volume and a heterogeneous catalytic first-order reaction with respect to the surface concentration of the adsorbed reacting substance. The surface is assumed to be homogeneous, the degree of surface coverage small, and the interaction of adsorbed molecules in the adsorption layer so weak that it does not change the adsorption coefficients and rate constants of the surface reactions. Under these assumptions the rate of adsorption is proportional to the partial pressure of the reacting gas, and the rate of desorption to its amount on the surface.

In the theory of chromatography ([9]), wall effects, edge effects, gas compressibility, and also the change in the carrier-gas velocity caused by introduction of the sample are usually neglected. The porosity of the bed and the carrier-gas velocity are assumed constant along the length of the column from $x = 0$ to $x = L$. In this work we shall also assume that the influence of gas diffusion may be disregarded.

The distribution of gas concentrations along the column satisfies the system of equations

$$\frac{\partial p}{\partial t} + \frac{\partial q}{\partial t} + u\frac{\partial p}{\partial x} + k_1 p + k_2 q = 0; \tag{1}$$

$$\frac{\partial q}{\partial t} = k_3 p - (k_2 + k_4) q, \tag{2}$$

where x is the distance through the charge from the place where the gas enters the column; p is the number of molecules of the reacting gas per unit volume of

the gas phase (this number is proportional to the partial pressure of the reacting gas); q is the number of adsorbed molecules of the reacting gas, referred to unit volume of the gas phase; u is the linear velocity of the carrier gas in the column ($u = u_0/\varepsilon$, u_0 is the linear velocity of the carrier gas before entering the column, ε is the porosity); k_1, k_2, k_3, k_4 are, respectively, the rate constants of the homogeneous reaction, the heterogeneous catalytic reaction, adsorption, and desorption. For adsorption within a monolayer, q and the degree of surface coverage θ are related by

$$q = n_s \theta S \rho (1 - \varepsilon)/\varepsilon,$$

where n_s is the number of vacant sites per unit surface; S is the surface area of the adsorbent, ρ is the density of the adsorbent. Equation (1) is the equation of conservation of matter with allowance for chemical reaction; equation (2) describes the sorption kinetics.

The partial pressure of the reacting gas before entering the column is a known function of time $\varphi(t)$. This function may be taken to be zero at $t = 0$ and $t > t_0$.

At the entrance to the column the condition of material balance must be satisfied,

$$\frac{u_0}{\varepsilon}\varphi(t) = u p_{x=0}$$

or, since $\varepsilon u = u_0$,

$$\varphi(t) = p(x,t) \quad \text{for } x = 0. \tag{3}$$

At the initial moment of time the column is free of the reacting gas. The first molecules of the reacting gas arrive at point x at the time $t_x = ux$. The solution of the system of equations (1), (2) must satisfy the condition

$$p(x,t) = 0 \quad \text{for } t = t_x. \tag{4}$$

Let us first consider the case of adsorption equilibrium $k_3 \to \infty$, $k_4 \to \infty$, $k_3/k_4 = a$ (where a is the adsorption coefficient). In this case

$q = ap$, and equation (1) takes the form

$$\frac{\partial p}{\partial t} + u_p \frac{\partial p}{\partial x} + \gamma p = 0, \tag{5}$$

$$u_p = \frac{u}{1+a}, \qquad \gamma = \frac{k_1 + a k_2}{1+a}. \tag{6}$$

The solution of equation (5) is the function

$$p(x,t) = \varphi\left(t - \frac{x}{u_p}\right)\exp\left(-\gamma\frac{x}{u_p}\right). \tag{7}$$

Under adsorption equilibrium, all molecules of the initial gas move along the column with the constant velocity u_p. Molecules from the beginning of the column arrive at the point x after the time $t_x = x/u_p$. The quantity u_p is measured experimentally, and from the first relation in (6) it is possible to calculate the adsorption coefficient. It follows from (7) that the decrease in the amount of the reacting substance occurs according to the same law as in a first-order reaction under static conditions with the constant γ. The dependence of the logarithm of the fraction of undecomposed substance at the gas outlet from the column on the time of gas passage through the column is linear. From the slope of the line the constant γ can be found; after this, from the second of formulas (6), one of the kinetic constants k_1 or k_2 is calculated, provided that the other constant is equal to zero. In the general case, when $k_1 \neq 0$ and $k_2 \neq 0$, measurements at different temperatures should be made to determine these constants.

When studying the kinetics of heterogeneous reactions under dynamic conditions, chromatographic effects caused by the difference in the velocities of motion of the components of the gas mixture through the reactor cannot be detected by ordinary methods (these effects can be observed by special methods, for example, by adding a pulse of a labeled gas to the gas stream). From experimental data obtained under dynamic conditions, only the product of the reaction-rate constant and the adsorption coefficient can be found. When studying the kinetics of a reaction in the chromatographic regime, in addition to the quantities determined in a dynamic reactor, the true passage time of the reacting substance through the column is measured, and as a result it is possible to calculate both the reaction-rate constant and the adsorption coefficient.

From the graph of the dependence of $\ln\gamma$ on $1/T$, the observed activation energy E_n is calculated. In the case when the reacting substance is strongly adsorbed on the surface and $a \gg 1$, $\gamma = k_1/a + k_2$; if only a heterogeneous reaction occurs and $k_1 = 0$, then E_n is equal to the true activation energy E_ist; if only a homogeneous reaction occurs and $k_2 = 0$, then $E_\text{n} = E_\text{ist} + Q_\text{ads}$. In the case of weak adsorption of the reacting substance, when $a \ll 1$ and $\gamma = k_1 + ak_2$, measurements in the chromatographic regime lead to the same results as measurements under ordinary dynamic conditions; for a homogeneous reaction $E_\text{n} = E_\text{ist}$, and for a heterogeneous reaction $E_\text{n} = E_\text{ist} - Q_\text{ads}$.

Equation (5) and its solution (7) remain valid also for an energetically nonuniform surface, provided that the degree of filling for any group of sites is small; however, in this case the relation between the observed and the true activation energy becomes more complicated.

Let us turn to the case where the adsorption and desorption rate constants are comparable with the reaction-rate constants. The solution of equations (1), (2) for the case $k_1 = k_2 = 0$ is given in [10]; in paper [11] diffusion effects in adsorption are taken into account. The solution of equations (1), (2) with account of the chemical reaction can be obtained by ordinary methods [12].

The relative amount of unreacted gas at the point x, g/g_0, is determined by the relation

$$g/g_0 = \int_{t_x}^{\infty} p(x,t)\,dt \Big/ \int_0^{t_0} \varphi(t)\,dt.$$

From equations (1), (2) it can be established that

$$g/g_0 = \exp(-\mu x/u), \tag{8}$$

where μ is the following combination of kinetic constants

$$\mu = \frac{k_1k_2 + k_1k_4 + k_2k_3}{k_2 + k_4}. \tag{9}$$

If the duration t_0 of introducing the reacting gas into the column is close to zero, then for times t considerably exceeding t_0, the function $p(x,t)$, found by solving equations (1), (2), is written in the form

$$p(x,t) = \frac{2g_0k_3k_4 \exp\{[(k_2 - k_1 + k_3 - k_4)x/u - (k_2 + k_4)t]\}\, I_1(z)}{uz}, \tag{10}$$

$$z = 2\sqrt{k_3k_4\,\frac{x}{u}\left(t - \frac{x}{u}\right)},$$

where $I_1(z)$ is the Bessel function of the first kind, first order, of imaginary argument.

In the region of large values of the argument, for the Bessel function one may take the asymptotic expression

$$I_1(z) = \frac{e^z}{\sqrt{2\pi z}},$$

after which it can be established that, for values of x satisfying the relation

$$\frac{x}{u} > \frac{3(k_2 + k_4)}{k_3k_4},$$

the function $p(x,t)$ reaches a maximum at the value $t_x^{\max}$, determined by the formula

$$t_x^{\max} = \frac{x}{u} + \frac{k_3 k_4 x}{2(k_2+k_4)^2}\left(1+\sqrt{1-\frac{3u(k_2+k_4)}{k_3 k_4 x}}\right). \qquad (11)$$

The time at which the peak maximum leaves the column can be found experimentally. By determining the velocity of peak motion and the degree of conversion at a variable carrier-gas velocity and using formulas (8)–(11), one can calculate the constants of sorption and of the chemical reaction.

In many technically important topochemical and catalytic processes (for example, in a fluidized bed of dust-like particles) the composition of the gas around the particle changes with time; in laboratory study of such processes it is necessary to investigate the kinetics of the reaction under a rapidly changing, controlled gas composition around the particle. Possibilities of this kind are opened up by the chromatographic mode of carrying out the reaction. In particular, as the present consideration shows, the difficult experimental problem of simultaneously determining sorption kinetics and reaction kinetics can be solved comparatively simply when the reaction is carried out in the chromatographic mode.

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CITED LITERATURE

1. M. I. Temkin, S. L. Kiperman, P. S. Luk' yanova, DAN, **74**, 763 (1950); G. P. Korneichuk, M. Ya. Rubanik, *Kinetics and Catalysis*, **3**, No. 4, 633 (1961).

2. S. Z. Roginskii, O. M. Todes, Izv. AN SSSR, OKhN, **1946**, No. 4, 381.

3. S. Z. Roginskii, O. M. Todes, Izv. AN SSSR, OKhN, **1946**, No. 5, 475.

4. S. Z. Roginskii, O. M. Todes, *Radiochemistry*, **4**, issue 1, 39 (1962).

5. R. J. Kokes, H. Tobin, P. H. Emmett, *J. Am. Chem. Soc.*, **77**, No. 22 (1955).

6. G. A. Gaziev, O. V. Krylov et al., DAN, **140**, No. 4, 863 (1961).

7. S. Z. Roginskii, M. I. Yanovskii, G. A. Gaziev, DAN, **140**, No. 5, 1125 (1961).

8. S. Z. Roginskii, M. I. Yanovskii, G. A. Gaziev, *Kinetics and Catalysis*, **3**, No. 2 (1962).

9. J. J. Van Deemter, F. J. Zuiderweg, A. Klinkenberg, *Chem. Eng. Sci.*, **5**, 271 (1956).

10. A. A. Zhukhovitskii, A. N. Tikhonov, Ya. L. Zabezinskii, ZhFKh, **19**, 253 (1945).

11. L. Lapidus, N. R. Amundson, *J. Phys. Chem.*, **56**, 984 (1952).

12. A. N. Tikhonov, A. A. Samarskii, *Differential Equations of Mathematical Physics*, 1953.

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