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Abstract

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CONDUCTING A TOPOCHEMICAL DIFFUSION PROCESS AT A CONSTANT RATE

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Chemical decomposition of solids, accompanied by the formation on their surface of a porous layer of solid products, is often retarded by the diffusion of reacting substances through this layer into the reaction zone. Such processes include the oxidation of a number of metals, the combustion of high-ash fuel, the burning-out of coke from aluminosilicate cracking catalysts, the leaching of melts, the production of porous glass by the action of acids on sodium borosilicate glass, and a number of others. In those cases where the rate-determining stage of the process is diffusion in the porous layer, the concentrations of the reacting substance in the bulk (solution, gas) and at the outer surface of the porous layer have time to become equalized and do not differ from one another.

Let us introduce the following notation: D is the effective diffusion coefficient of the reacting substance in the porous product layer; h is the thickness of the porous product layer; x is the current coordinate along the thickness of the porous layer ($0 < x < h$); dc/dx is the concentration gradient of the diffusing substance; dm/dt is the reaction rate; t is time; M is the stoichiometric coefficient equal to the amount of reacting substance consumed in the formation of 1 cm^3 of porous layer; k is the rate constant of the chemical reaction; c_h is the effective concentration of the reacting substance at the boundary porous layer —unreacted layer; c_0 is the concentration of the reacting substance in the bulk of the gaseous (or liquid) phase at the outer boundary of the porous layer.

According to Fick' s second law,

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \tag{1}$$

boundary conditions:

$$x = 0, \qquad c_{0,t} = f(t); \tag{2}$$

$$x = h, \qquad c_h \simeq 0. \tag{3}$$

Under steady-state conditions, the magnitude of the diffusion flux of the reacting substance through the porous layer to the reaction zone is equal to the reaction rate:

$$-D\frac{dc}{dx} = \frac{dm}{dt} = M\frac{dh}{dt} = kf(c_h). \tag{4}$$

The exact solution of the problem for the case $c_{0,t}$ = const, given by L. A. Vulikom (1), in many cases may be replaced by an approximate solution in the boundary conditions. At $c_{0,t}$ = const a quasi-stationary process usually takes place,

$$-\frac{dc}{dx} = \frac{c_{0,t} - c_{h,t}}{h} \simeq \frac{c_0}{h}. \tag{5}$$

The condition of quasistationarity means that, although the quantity c_0/h decreases as h grows, the gradient $\partial c/\partial x$ at any given moment is practically the same throughout the entire layer. Hence, taking into account (4) and (5),

$$-D\frac{dc}{dx} = C\frac{c_0}{h} = M\frac{dh}{dt}. \tag{6}$$

From (6) follows the so-called “quadratic”(or “parabolic”) law found by Tammann (^{2}):

$$h^2 = \frac{2c_0D}{M}t. \tag{7}$$

The rate of the process is variable. As the layer thickness increases, the concentration gradient decreases and, consequently, so does the effective concentration, which is the result of the establishment of a mobile equilibrium in the reaction zone at the boundary of the unreacted solid. Thus, with the concentration of the reacting substance in the bulk remaining constant, its effective concentration in the reaction sphere will decrease during the process, and the chemical conditions for the formation of the porous layer of products will change. This circumstance, which has not attracted attention, is manifested in the layered structure of porous glasses (^{3,4}), outwardly resembling Liesegang-ring patterns. Hence the question arises of how to ensure constancy of the concentration of the reacting substance in the reaction zone during the process, which should automatically lead to its proceeding at a constant rate, not changing as the porous layer grows. The problem consists in finding the form of the function $f(t)$ describing the change in the concentration of the reacting substance in the bulk (gas or solution) that ensures fulfillment of these conditions.

The exact solution involves a number of difficulties, and carrying it out appears expedient after clarifying the question by means of an approximate solution and experimental verification.

Let us turn to an approximate solution. According to the condition

$$\frac{dh}{dt} = A = \text{const}, \tag{8}$$

whence

$$h = At. \tag{9}$$

Substituting (5), (8), and (9) into the boundary conditions (2), (4), we find the sought function:

$$c_{0,t} = \frac{MA^2}{D} t = Bt. \tag{10}$$

Thus, the condition for constancy of the process rate and of the effective concentration in the reaction zone is a linear increase in the concentration of the reacting substance in the bulk during the process.

It is evident from (10) that the rate of formation of the porous layer ($A = dh/dt$) increases in proportion to the square root of the rate of increase of the concentration of the reacting substance in the bulk (B). The result obtained is connected with the following basic assumptions: quasistationarity of the process and linear distribution of the concentration of the reacting substance in the porous layer, as well as independence of the porous structure of the product layer from its thickness, or, more precisely, practical constancy of the effective diffusion coefficient over the thickness of the porous layer and over the duration of the process. It should be especially emphasized that these very same assumptions also underlie the "parabolic" law; the good obedience of a large number of processes to this law convincingly shows that these conditions are indeed fulfilled in experiment.

As follows from the "parabolic" law, the time required for the establishment of diffusion equilibrium and of the quasi-stationary regime is of the order of h^2/D. The distance over which the concentration is equalized in a given time will be of the order of $\sqrt{Dt}$ and must be large in comparison with the distance $h = At$ through which the reacting substance must diffuse; hence

$$t < \frac{D}{A^2} = \frac{M}{B}. \tag{11}$$

After this time has been reached, a violation of the simple law (10) found above should occur.

It follows from (10) and (11) that the maximum permissible concentration ($C_{0,t} = Bt$) of the reacting substance in the volume must be less than the volumetric stoichiometric coefficient M; the maximum permissible rate of increase of concentration B must be less than the quotient obtained by dividing M by the total process time t, during which a porous layer of thickness h has time to form on the solid; and the maximum thickness of the porous layer is

$$h = At = A\frac{C_{0,t}}{B} < \frac{AM}{B} = \frac{D}{A^2}. \tag{12}$$

A convenient object for experimental verification of the correctness of the results obtained was the preparation of porous glass by leaching sodium borosilicate glass Na = 7/23 in acid (composition in mole %: Na_2O 7, B_2O_3 23, SiO_2 70).

The values of D needed for preparing the experiments were calculated from equation (7) using the experimental data of O. S. Molchanova, Z. G. Slavyanskaya, and A. V. Kruglova on the kinetics of growth of the porous layer on Na = 7/23 glass during its leaching in acid solutions of constant concentration. For temperatures of 24 and 25° and solutions of sulfuric and hydrochloric acids from 0.1 to $3N$, they varied from 0.00013 to 0.008 cm^2/h. From the composition of the initial and porous glass, the value $M = 4.71 \cdot 10^{-3}$ $\text{equiv/cm}^3 \cdot \text{h}$ was calculated.

Starting from all the values of D obtained (from 0.0438 to 0.114 cm^2/h) and the values of A drawn from experimental data (from 0.005 to 0.04 cm/h), the required values of the rate of increase of the acid concentration B (from 0.000012 to 0.70 $\text{equiv/cm}^3 \cdot \text{h}$) were calculated with the aid of equation (10). By assigning various values to the duration of the experiment (from 5 to 72 h), we determined that the limiting permissible values of B are from 0.000065 to 0.00094 $\text{equiv/cm}^3 \cdot \text{h}$.

For experiments at room temperature with sulfuric acid, assuming $D = 0.001 \div 0.005$ cm^2/h and $A = 0.01$ cm/h, we obtain $B = 0.000094 \div 0.00047$ $\text{equiv/cm}^3 \cdot \text{h}$ and $h < 0.1 \div 0.5$ cm.

Table 1

Experiment No.	$B, \left(\frac{\text{equiv}}{\text{cm}^3\text{h}}\right) \cdot 10^4$	t_{lin}, h	h_{lin}, cm	A_{lin}, cm/h	D, cm^2/h	$\sqrt{\frac{B_1}{B_2}}$	$\frac{A_{1\text{lin}}}{A_{2\text{lin}}}$	$\frac{h_{2\text{lin}}}{t_{1\text{lin}}}$, exp.	$\frac{h_{2\text{lin}}}{t_{1\text{lin}}}$, calc.
1	1.07	4–4.5	0.045–0.50	0.0112	0.0055	1.44	1.54	1.20–1.33	1.37
2	0.516	8.5	0.060	0.0074	0.0050	1.44	1.54	1.20–1.33	1.37

The experiments were carried out at room temperatures on polished specimens of Na = 7/23 glass. The thickness of the porous layer was measured during the leaching process with the aid of a measuring microscope. A linear increase in the

Fig. 1. Kinetic curves of experiments under the linear regime. 1 $-h(t)$, experiment 1; 2 $-h(t)$, experiment 2; 3 $-c_0(t)$, experiment 1; 4 $-c(t)$, experiment 2

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acid concentration was achieved by continuously adding concentrated sulfuric acid dropwise from a manostated graduated cylinder into one or another volume of vigorously stirred distilled water. The results of two such experiments are given in Table 1. As can be seen from the kinetic curves $h(t)$ and $c_0(t)$ of the two experiments (see Fig. 1), during the first several hours the thickness of the porous layer does indeed increase at a constant rate. Then the rate of the process, as was to be expected, falls. It is interesting to note that the first semitransparent layer (“strata”) appears at the moment when the linear regime breaks down and the rate decreases in connection with this. The rate of leaching in the linear regime, in accordance with (10), increases in direct proportion to the square root of the rate of increase of the concentration.

Fig. 1. Kinetic curves of experiments under the linear regime.
1 $-h(t)$, experiment 1; 2 $-h(t)$, experiment 2; 3 $-c_0(t)$, experiment 1; 4 $-c(t)$, experiment 2.

The experimentally observed ratio of the thicknesses of the layers processed under the linear regime ($h_{2\text{lin}}/h_{1\text{lin}}$ = 1.20-1.33) agrees fairly closely with the value 1.37, calculated from the approximate relation

$$h_{2\text{lin}}/h_{1\text{lin}} \simeq A_2 B_1 / A_1 B_2,$$

which follows, under a simplifying assumption, from equation (12).

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