MASS TRANSFER IN A THREE-PHASE SYSTEM UNDER CONDITIONS OF MECHANICAL AND PNEUMATIC AGITATION

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Mass transfer between a solid and a liquid, accompanied by the evolution of a gaseous phase, is studied experimentally in the presence of mechanical agitation. It is shown that for low concentrations of the reagent pneumatic agitation is more effective than mechanical.

Chemical reactions taking place under diffusion control between a solid material and a liquid, with the evolution of a gaseous phase, are distinguished by the fact that, in growing and becoming detached from the solid surface, the gas bubbles make the liquid boundary layer turbulent, and hence accelerate mass transfer. The kinetic characteristics of such reactions were considered in [1-3]. In many ways such processes are analogous to those involved in the bubble-type boiling of a liquid.

The mechanism of mass transfer between a solid and a liquid, complicated by the evolution of a gas phase, may be expressed as follows. Molecules of the reagent diffuse to the surface of the solid and a rapid chemical reaction takes place, as a result of which the concentration of the reagent at the solid surface tends to zero [1]. The stoichiometrically evolving gas has a maximum concentration at the solid—liquid interface and diffuses into the liquid. The distribution of the concentrations in this case is indicated in Fig. 1a.

If $c_g > c_{eq}$ and the difference $c_g - c_{eq}$ (supersaturation) reaches a certain specific value, evolution of the third (gas) phase will occur.

The most favorable conditions for the formation and growth of bubbles exist on the solid surface. By analogy with heat transfer, these conditions include a maximum concentration of the gas and the presence of microasperities, acting as centers for gas formation. Furthermore, when a bubble is formed on the solid surface, the work against the forces of

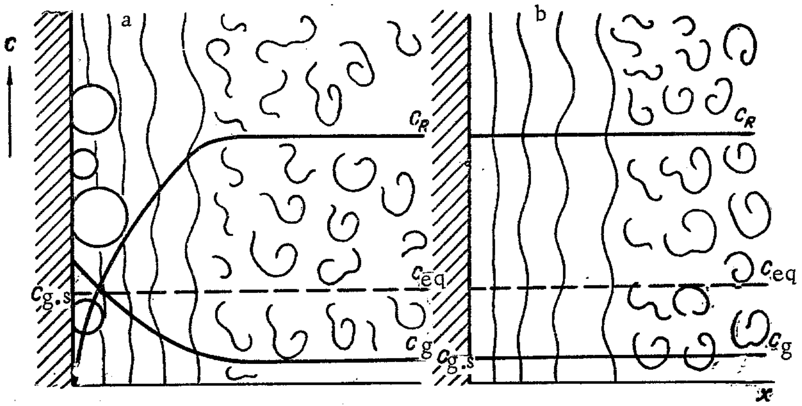

Fig. 1. Distribution of the reagent and gas concentrations at the solid surface: a) steady-state process; b) at the initial contact between the reagent and the renewed solid surface.

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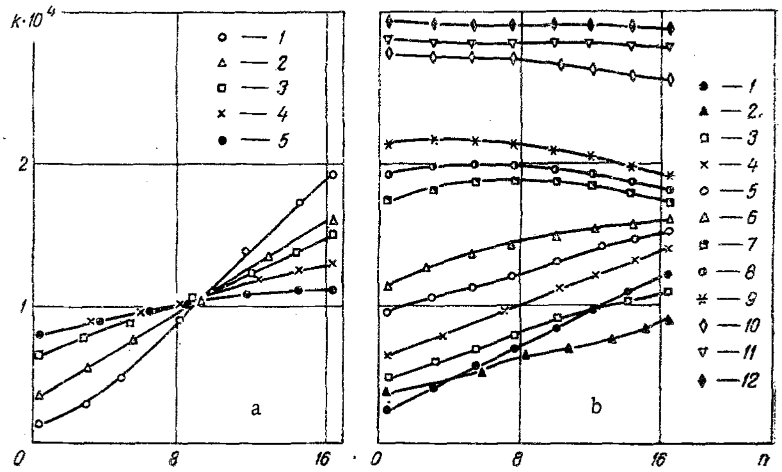

Fig. 2. Mass-transfer coefficients k (m/sec) in relation to the number of revolutions of the stirrer n (1/sec) for various concentrations of the reagent: a) interaction of calcite with HCl of concentration: 1) 0.07; 2) 0.14; 3) 0.227; 4) 0.33; 5) 1.12 g-eq/liter; b) interaction of magnesium with sulfuric acid of concentration: 1) 0.1; 2) 0.25; 3) 0.53; 4) 0.68; 5) 0.91; 6) 1.1; 7) 1.48; 8) 1.67; 9) 1.85; 10) 2.40; 11) 2.60; 12) 2.78 g-eq/liter.

surface tension will be less than in the case of a liquid [5, 6]. Thus a gas phase may arise at a smaller supersaturation on a solid surface.

The gas bubbles detached from the surface draw the adjacent liquid with a very slight concentration of the reagent after them (Fig. 1a). At this point a flow of liquid with a concentration c_R flows out of the interior. Thus, at the initial instant of time the concentration of the reagent on the surface at the point of bubble detachment is not equal to zero, but c_R (Fig. 1b). The transient process so created leads to high flow densities. As we shall later show, the bubbles have the greatest turbulizing effect on the boundary layer at the instant of generation and during their initial development.

It was demonstrated in [4] that the injection of an inert gas intensified these processes, especially in the region of low concentrations. However, in addition to the agitating effect, the inert gas so introduced creates an additional effect — that of screening the surface of the solid particle. Mechanical agitation is frequently employed in practice in order to intensity heat and mass transfer. It would appear that, for the systems which we are considering, this kind of agitation ought to create a better effect than pneumatic agitation, in view of the fact that no additional screening (isolation) of the solid surface then occurs. It is accordingly of great interest to compare the effects of these two forms of agitation.

Experiments with mechanical agitation of the liquid were carried out in a cylindrical glass apparatus with a flat bottom, 160 mm in diameter, filled with an acid solution to a height of 160 mm. The agitating device was a three-bladed stirrer of the propeller type, 50 mm in diameter, with the blades inclined at 30°. The distance between the bottom of the apparatus and the stirrer was 40 mm. Single solid samples were fixed in the liquid at a height of 1/2 H and at 1/4 D from the walls. We studied the dissolution of calcite spheres in hydrochloric acid and magnesium spheres in sulfuric acid. All the experiments were carried out under isothermal conditions at 17°C.

The experimental method was as follows. The apparatus was filled with acid of a particular concentration, thermostated to a specified temperature, the stirrer was connected, and the liquid was agitated for 5-7 min at a constant rate of rotation in order to establish steady-state conditions. Dried, weighed, and measured spherical particles were then fixed in the vessel, and the starting time was recorded. After a specified period of time (depending on the concentration of the solution), the samples were removed, carefully washed with

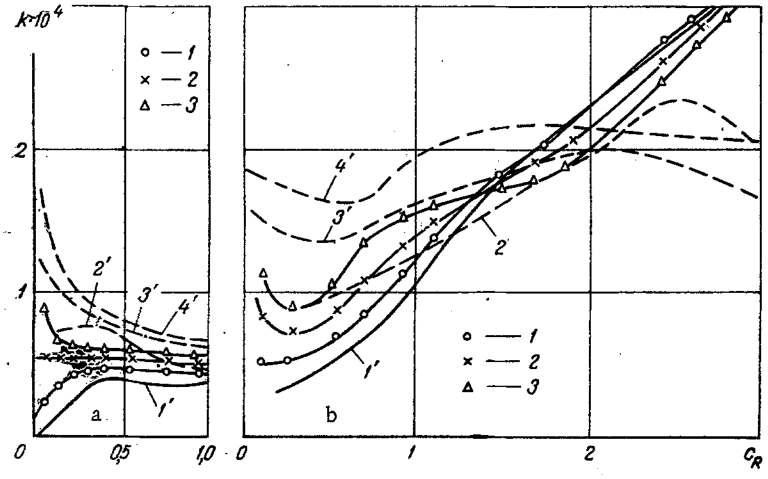

Fig. 3. Mass-transfer coefficient k (m/sec) as a function of the motive force of the process c_R (g-eq/liter) under conditions of mechanical and pneumatic agitation: 1) without agitation; 1-3) mechanical agitation at n (1/sec) values of 1) 4; 2) 10; 3) 16; 2'- 4') pneumatic agitation at various gas-flow rates (m^3/sec), as follows : a) interaction of calcite with HCl : 2') 0.00033; 3') 0.0016; 4') = 0.0085; b) interaction of magnesium with sulfuric acid : 2') 0.0005; 3') 0.0016; 4') 0.0064.

water, and again dried to constant weight. Since the sample surface area and the concentration of the solution altered very little in all the experiments, the mass-transfer coefficient was determined from the equation

$$k = \frac{\Delta G}{\alpha c_R F \Delta\tau} . \tag{1}$$

We see from the curves relating the mass-transfer coefficient k to the number of revolutions n (Fig. 2) that, in the low-concentration range, the mass-transfer coefficient increases with increasing n, in agreement with the results presented in [7]. At higher concentrations no such relationship is obeyed. In order to establish a qualitative estimate of the various methods of agitation, Fig. 3 shows the mass-transfer coefficient as a function of the motive force of the process c_R for three cases : 1') agitation effected by the evolving gas bubbles only; 1-3) liquid agitated by the stirrer; 2-4) liquid agitated by an inert gas. (The experimental apparatus, the method of conducting the experiments, and the results of the latter are presented in [4].) A comparison between the results obtained (Fig. 3a and b) shows that for the evolution of both H_2 (which is poorly dissolved in the acids) and CO_2 (which is far more soluble than H_2) the curves are of entirely the same character. At low concentrations, in fact, mechanical and pneumatic agitation both increase the mass-transfer coefficient in each case by comparison with the case of no agitation. At high concentrations agitation by the chemically evolved gas is so strong that there is no point in using either mechanical or pneumatic agitation.

From the practical point of view, the low-concentration behavior is of greatest importance, for example, in connection with hydrometallurgical production [8]. We see from Fig. 3 that, for low concentrations, agitation by an inert gas is the more effective means of intensification, despite the additional insulation of the solid surface.

This may clearly be explained in the following way. A bubble is only able to break away spontaneously from the solid surface if it reaches a certain diameter. By analogy with heat transfer [5, 6] we may assume that the following time dependence of the growth of the bubble will occur:

$$R = A\sqrt{\tau}. \tag{2}$$

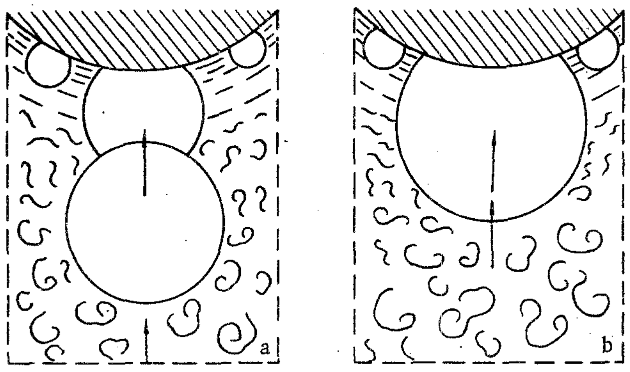

Fig. 4. Interaction of inert-gas bubbles with gaseous reaction products on arriving at the reaction surface: a) Development of contact between the bubbles; b) elimation of the reaction-product bubble and screening of the solid surface.

Some of the inert gas introduced, rising up in the liquid in the form of large bubbles, will pass very close to the surface of a solid particle, make contact with the developing gas bubble, link up with the latter, and so detach them, drawing along some of the liquid (with a low concentration of the reagent) from the surface (Fig. 4a). In this case detachment may occur for bubble diameters smaller than the normal value corresponding to detachment.

The degree of turbulization of the boundary layer by the developing gas bubbles may be characterized by the rate of growth of the bubble

$$v = \frac{dR}{d\tau} = \frac{A^2}{2R}, \tag{3}$$

derived from Eq. (2).

It follows from Eq. (3) that during the growth of the bubbles the boundary layer is turbulized more for small values of R. The probability that the larger bubbles will be removed from the surface of the solid phase by the inert gas is quite high. Thus those evolving gas bubbles which make only a minor contribution to the turbulization of the boundary layer are the first to be removed from the surface.

Over a particular time interval, a certain proportion of large inert-gas bubbles will arrive directly at the solid surface, displacing the surface layer of liquid (which contains only a very small concentration of the reagent) (Fig. 4b). During this period of time, some of the surface is screened by the inert gas. Such screening may then remain absent for quite a long time. As a result of new contact with the liquid, reagent with a high concentration c_R will appear on the solid surface. Conditions are created for transient mass transfer (Fig. 1), considerably accelerating the process.

When the liquid is agitated by the stirrer, the liquid flows so developing pass around the gas bubbles formed on the solid surface and not the surface itself (Fig. 5). Since the bubble detachment diameter diminishes very little with increasing flow rate [9], this leads to only a slight increase in k (Fig. 3). An analogous type of flow around surface protruberances (in particular hydrogen bubbles on the surface of a rotating disk electrode), leading to a fall in the mass-transfer rate behind these protruberances, was described in [10], following the work of a number of authors.

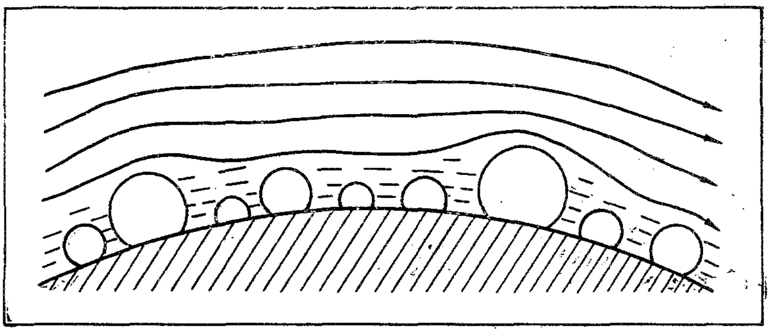

Fig. 5. Flow of reagent around a solid with gas bubbles forming on its surface in the case of mechanical agitation.

A comparison between all these results and a qualitative assessment of their significance leaves no doubt that, in the case of diffusion-controlled chemical reactions in a solid—liquid system, complicated by the evolution of a gas phase, the use of an inert gas for agitating the liquid is a more effective method than mechanical agitation for a low concentration of the reagent.

NOTATION

c_g, c_{gs}, gas concentration in the liquid and on the solid surface; c_{eq}, equilibrium gas concentration in the liquid; c_R, concentration of the reagent; H, height of the vessel; D, diameter of the vessel; k, mass-transfer coefficient, m/sec; ΔG, weight lost by the solid sample, kg; F, surface area of the sample, m^2; τ, time, sec; α, stoichiometric coefficient; n, number of revolutions of the stirrer, 1/sec; R, radius of a gas bubble; A, constant; x, coordinate.

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