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1958

SovietRxiv

Figure 1 schematic

Figure 1: Figure 1 schematic

Abstract

Full Text

Physical Chemistry

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INVESTIGATION OF THE MECHANISM OF INTERNAL DIFFUSION BY THE METHOD OF X-RAY DIASCOPY

(Presented by Academician M. M. Dubinin, April 26, 1958)

The movement of an adsorbed substance in porous sorbents during adsorption from a stream of carrier gas occurs by diffusion in the volume of the pores and along their surface. The role of each component may be greater or smaller depending on the character of the sorbent porosity, the nature of the surface, the nature of the adsorbed substance, the temperature, and a number of other conditions. Both types of transport, i.e., diffusion in the gas phase and migration along the surface, proceed simultaneously and in one direction, and therefore assessing the role of each type of transport presents considerable difficulties. In the present work an attempt is made to separate the fluxes in the gas and adsorption phases.

Fig. 1. Scheme of the movement of an adsorbed substance in the gas phase and along the pore surface.
a —in the absence of a counterflow of nonadsorbing gas; *b* —in the presence of a counterflow of nonadsorbing gas.

The idea underlying the research method is illustrated in Fig. 1, which schematically depicts a pore of the sorbent. Before adsorption begins, the pore is filled with air, nitrogen, or some other gas that is adsorbed very little (we shall regard it as nonadsorbing); its pressure is everywhere the same and equal to P_1. Let us create at one end of the pore a concentration C_0 of the adsorbed substance, and at the other end let $C = 0$. Owing to the difference in concentrations, a diffusion flux arises from left to right, with part of the substance moving in the gas phase and part along the surface of the pore (Fig. 1*a*). Now let us raise the pressure of the nonadsorbing gas to P_2. The pressure drop $\Delta P = P_2 - P_1$ will cause a counterflow of the nonadsorbing gas (Fig. 1*b*), and the conditions for transport of the substance in the gas phase will change sharply. At the same time, in the adsorption phase, if $\Delta P \ll P_1$, the transport conditions remain practically unchanged.

If the adsorbed substance moves predominantly along the surface of the pores, then in the presence of a counterflow of the nonadsorbing gas the rate of movement of the adsorption front inside the grain should not be appreciably slowed. If, however, transport of the substance occurs mainly in the gas phase, then a substantial influence of the flow of nonadsorbing gas should be expected. The effect of the counterflow will obviously occur only in those pores whose radii are greater than the mean free path of the molecules. In small pores, whose radii are smaller than the mean free path, the counterflows will pass independently of one another. In our experiments, pro-

introduced at atmospheric pressure, the mean free path was approximately 10^{-5} cm, and inhibition of transport in the gas phase occurred only in pores whose radii were greater than 10^{-5} cm.

Granulated wood charcoal of steam-gas activation, obtained at 32% burn-off, was used as the object of investigation. Its apparent specific gravity was 0.898 g/cm^3; the volumes of micro-, transitional, and macropores were, respectively, 0.27, 0.11, and 0.21 cm^3/g. The constants of the Dubinin and Radushkevich adsorption-isotherm equation were: $W_0 = 0.26$ cm^3/g, $B = 0.42 \cdot 10^{-6}$. Figure 2 gives the adsorption isotherm of ethyl bromide vapor, taken as the adsorbable substance.

Fig. 2. Adsorption isotherm of ethyl bromide vapor on activated carbon. $t = 20^{\circ}$.

A carbon grain in the form of a cylinder 5 mm in diameter and 6 to 9 mm long was placed in a sorption cell made of plexiglass, as shown in Fig. 3. Sealing of the grain mount was achieved by grinding its lateral surface against the wall of the tube. The grain was blown from the end face by a stream of a vapor-air mixture consisting of nitrogen containing ethyl bromide vapor, and at definite time intervals it was irradiated with X-rays. The position of the adsorption front inside the grain was recorded on X-ray film. To eliminate the influence of nonuniformity of the structure and surface properties of different carbon grains, a series of experiments was carried out with the same grain, which, after use, was regenerated directly in the tube by high-vacuum evacuation at room temperature for 72 hours.

Fig. 3. Diagram of the sorption cell

Labels in the figure: "Nitrogen + ethyl bromide" ; "Nitrogen" ; "Carbon grain."

The completeness of regeneration was monitored by X-ray radioscopy. The experiments were carried out at ethyl bromide vapor concentrations of 20.7 and 75.9 mg/l, vapor-air mixture velocities of 1.8 and 13.6 l/min $\cdot$ cm^2, and a temperature of $20 \pm 0.5^{\circ}$. The source of X-rays was an X-ray tube with a copper anticathode. The voltage at the anode was 30 kV, the current 10 mA, and the distance to the object 30 cm. The rate of nitrogen blowing through the grain

Figure 4: Position of the adsorption front in a coal grain

Figure 2: Figure 4: Position of the adsorption front in a coal grain

was 28 cm^3/min, which corresponded to a pressure drop at the ends of the grain of about 20 mm Hg. The nitrogen was supplied from a cylinder and was first passed through a column with cotton wool, silica gel, and activated carbon.

The results of one series of experiments are presented in Fig. 4. In the first two horizontal rows the position of the adsorption front (the darkened band) in the grain is shown in the absence of a flow of non-sorbing gas; in the 3rd and 4th rows, in the presence of a counterflow of non-sorbing gas. In the 5th row are given the results of desorption experiments, in which the carbon grain was first treated in a stream of the vapor-air mixture at a velocity of 1.8 l/min $\cdot$ cm^2 and an ethyl bromide vapor concentration of 20.7 mg/l; then the feed of ethyl bromide was stopped, i.e., the end face was blown only with pure nitrogen, and purging of the grain with nitrogen at a rate of 28 cm^3/min from the side of the other end face was begun. The exposure time of the grain in the stream of vapor-air mixture and the other experimental conditions are indicated in the figure.

$\tau = 5$ 10 25 36 49 64 min.

$\tau = 0$ 30 min.

Fig. 4. Position of the adsorption front in a coal grain. **1, 2** –in the absence of a counterflow of non-sorbing gas: **1** $-C_0 = 20.7$ mg/l, **2** $-C_0 = 75.9$ mg/l; **3, 4** –in the presence of a counterflow of non-sorbing gas. Velocity of the vapor-air mixture: **3** –1.8 l/min $\cdot$ cm^2, **4** –13.6 l/min $\cdot$ cm^2, **5** –desorption. Nitrogen flow rate at the end face of the grain, 1.8 l/min $\cdot$ cm^2; through the grain, 28 cm^3/min.

From the data obtained it follows that the depth of treatment of the grain in the presence of a counterflow of a non-sorbing gas is considerably smaller than in its absence. This result cannot be explained by dilution of the concentration of the vapor-air mixture at the end of the grain by the nitrogen emerging from the grain, since increasing the velocity of the vapor-air mixture by more than a factor of 7 did not lead to any appreciable change in the rate of advance of the adsorption front (cf. the photographs in the 3rd and 4th rows). Nor can this be the result of a secondary phenomenon, i.e., of the substance being transported along the surface, then passing into the gas phase and being carried back by the nitrogen stream. Such an assumption is inconsistent with the results of desorption experiments. Over 30 min of desorption, even in the very initial section of the grain, complete desorption of ethyl bromide is not observed. It should also be noted that pores with radii $r > 10^{-5}$ cm have a surface area expressed in tens of square meters per gram, whereas the surface area of the remaining, smaller pores amounts to hundreds of square meters per gram; and although in them the counterflow does not affect transport of the substance in the gas phase, along their surface transport of the substance should occur in a considerably larger amount than along the surface of pores with $r > 10^{-5}$ cm.

The depth of treatment of the grain in the presence of a counterflow, 20–30 min after the start of the experiment, remains almost constant (equal to ~ 0.7 mm), i.e., the motion of the adsorption front, initially rather rapid, slows sharply. This circumstance indicates that the adsorbed substance moves mainly in the gas phase. From the Einstein-Smoluchowski relation $x^2 = 2Dt$, where x is the path traversed by a particle in time t, and D is the diffusion coefficient, it follows that the adsorption front (if the substance moves in the gas phase) will be stopped when the linear velocity of the counterflow $w > 2D/x$. For the conditions indicated above, the linear velocity of the gas in the grain was 2.3 cm/sec, or, taking porosity into account, 3.7 cm/sec. Taking approximately $D = 0.1$ cm^2/sec, we find $x = 0.54$ mm, which is quite close to the experimental value (0.7 mm). With time the adsorption front shifts somewhat in the direction of the diffusion flux, which is quite natural, since the movement of the substance along the surface, as well as in pores whose radii are smaller than the mean free path, is not impeded by the stream of non-sorbing gas.

When the concentration of the vapor–air mixture is increased from 20.7 to 75.9 mg/l, a substantial increase is observed in the rate of advance of the adsorption front inside the grain. Since the magnitude of adsorption in this case increased from 265 to 270 mg/g, i.e., by only 2%, and consequently the gradients of the adsorption values in the grain changed little, this fact can be explained only by assuming that the principal type of transport is diffusion in the gas phase.

Thus, on the basis of the results obtained, it may be concluded that for the system considered, transport of the substance in the gas phase is of primary importance, and the role of large pores as transport paths is very significant for the rate of internal diffusion.

The authors express their gratitude to Academician M. M. Dubinin for valuable comments during the discussion of the results of the work.

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Received
12 IV 1958

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