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Fig. 1. Apparatus layout

Figure 1: Fig. 1. Apparatus layout

Abstract

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DIFFUSION COEFFICIENTS IN SECONDARY PORES OF GRANULATED ZEOLITES

(Presented by Academician M. M. Dubinin on 22 XI 1962)

The rate of diffusion in granulated zeolites depends on the diffusion coefficients in the primary pores (“entrance windows” and sorption cavities of the cells) and in the secondary pores (gaps between crystals). To establish the relation between the overall diffusion coefficient and its particular values in the primary and secondary pores, direct measurement of these quantities is desirable.

In the present work we describe the method and the results of measuring diffusion coefficients in the secondary pores of granulated zeolites of type A. The measurements were carried out by the method of stationary diffusion. The layout of the apparatus is shown in Fig. 1. The carrier gas (helium) leaving the cylinder is divided into two streams: one of them, through capillary K_1 and metal valve 1, enters vessel 8, containing the liquid under investigation, and then passes into diffusion cell 9; at the outlet from this cell, by valve 4, it is directed either into the measuring chamber of katharometer 10 or, through flowmeter 5, to exhaust. The other stream, through capillary K_2 and metal valve 2, passes through the comparison chamber of the katharometer and the diffusion cell, washing the granule from the rear side. Vapors of the liquid that have diffused through the grain are carried off by the helium stream and directed either into the measuring chamber of the katharometer or to exhaust. Before flowmeter 5, both streams are connected in order to equalize the pressures in both lines. Constancy of the gas pressure at the ends of the grain is monitored by means of differential manometer 3. Sealing of the side surface of the zeolite granule was carried out by fusing the granule into a lead shell (after preliminary dehydration) with the aid of the device shown in Fig. 2. Granule 1 is placed inside a metal bomb and held by rod 4. After the granule has been fixed and pieces of lead have been introduced into bath 2, the bomb is connected to vacuum and slowly heated (about 3 hours) to 400° C. The lead melts and flows along capillary 3 into

Fig. 1. Apparatus layout: 1, 2 –metal valves; 3 –differential manometer; 4 –

Fig. 2. Device for casting granules

Figure 2: Fig. 2. Device for casting granules

distributing valve; 5 —flowmeter; 6 —mercury pressure regulator; 7 —evaporator; 8 —manometer; 9 —diffusion cell; 10 —katharometer; 11 —reservoir.

the lower part of the device and fills the gap between the granule and the walls of the apparatus, forming a casting corresponding to the dimensions of the diffusion cell.

The diffusion coefficient was calculated from the equation:

$$D = \frac{VL}{F} \cdot \frac{C_2}{C_1}, \tag{1}$$

where V is the helium flow rate at the rear side of the grain in cm^3/s, F and L are the cross section and length of the granule, C_2 is the concentration in the stream at the rear side of the grain, and C_1 is the concentration in the stream at the front side of the grain. To record the concentration of the substance, the previously described (1) catharometer with an EPP-09 electronic potentiometer was used.

Fig. 2. Device for casting granules

The experiments were carried out with benzene and carbon tetrachloride, whose critical molecular dimensions are larger than the entrance windows into the sorption cavities of type-A zeolites. The objects of study were granulated zeolites of the Linde firm, MS-4A and MS-5A, and samples obtained by Ya. V. Mirskii, Mr-296 and Mr-297. The experiments were performed at a pressure of 760 mm Hg and at temperatures of 50, 100, 150, and 200°C.

The results obtained are given in Table 1.

The diffusion coefficients under the conditions investigated range from 0.016 to 0.055 cm^2/s. If the porosity of the samples (ε) and the tortuosity of the capillaries (k_2) are taken into account, higher values are obtained:

$$D_2 = D\frac{k_2^2}{\varepsilon}.$$

Figure 3 shows the dependence of the diffusion coefficient D_1 on temperature (the tortuosity coefficient was taken as 1.5). The same figure gives, by a dotted line, the temperature dependence of D_1 for the case of gas diffusion in gas and molecular diffusion. Comparison of the curves shows that the experimental data correspond more closely to the curve for Knudsen flow.

Table 1

Diffusion coefficients in secondary pores ($\mathbf{cm^2/s}$)

Zeolite	Benzene 50°	Benzene 100°	Benzene 150°	Benzene 200°	Carbon tetrachloride 50°	Carbon tetrachloride 100°	Carbon tetrachloride 150°	Carbon tetrachloride 200°
MS-4A	0.038	0.044	0.050	0.055	0.032	0.037	0.042	0.047
MS-5A	0.025	0.029	0.033	0.037	0.018	0.021	0.024	0.027
Mr-296	0.021	0.024	0.027	0.030	0.016	0.018	0.021	0.030
Mr-297	0.028	0.033	0.037	0.042	0.023	0.026	0.030	0.033

The ratio of the experimental values of the diffusion coefficients

$$\left(\frac{D_{\mathrm{C_6H_6}}}{D_{\mathrm{CCl_4}}}\right)_{\mathrm{op}}$$

is also closer to the ratio

$$\frac{D_{\mathrm{C_6H_6}}}{D_{\mathrm{CCl_4}}},$$

calculated for molecular flow. For diffusion of gas in gas,

$$\frac{D_{\mathrm{C_6H_6}}}{D_{\mathrm{CCl_4}}} = \frac{\sqrt{\dfrac{1}{m_1} + \dfrac{1}{m_2}}}{\sigma_{1,2}^2} \cdot \frac{\sigma_{1,3}^2}{\sqrt{\dfrac{1}{m_1} + \dfrac{1}{m_3}}}. \tag{2}$$

where

$$\sigma_{1,2} = \frac{d_1 + d_2}{2}, \qquad \sigma_{1,3} = \frac{d_1 + d_3}{2}, \qquad m_1,\ m_2,\ m_3,\ d_1,\ d_2,\ d_3$$

are the masses and gas-kinetic diameters, respectively, of the molecules of helium, benzene, and carbon tetrachloride. Substituting into equation (2) the numerical values of m and σ (the diameters σ adopted for helium, benzene, and carbon tetrachloride are 2.14; 7.02 and 7.3 Å for a temperature of 100° C (2)), we find

$$\frac{D_{C_6H_6}}{D_{CCl_4}} = 1.06.$$

For molecular diffusion

$$\frac{D_{C_6H_6}}{D_{CCl_4}} = \sqrt{\frac{m_3}{m_1}} = 1.4.$$

From experiment at a temperature of 100° C, for the samples studied, on the average

$$\left(\frac{D_{C_6H_6}}{D_{CCl_4}}\right)_{\text{exp}} \approx 1.3,$$

i.e., the character of the transfer corresponds mainly to the Knudsen region.

The radii of the secondary pores of the zeolites MS-4A (MS-5A) and Mr-296 (Mr-297), according to data (3), are respectively equal to 2500 and 5000 Å. Since under the adopted experimental conditions the mean free path is $\sim 10^{-5}$ cm, i.e., much smaller than the radius of the secondary pores, it would seem that diffusion in the secondary pores should proceed as ordinary diffusion. Meanwhile, the experimental data indicate the presence of molecular flow. This circumstance is apparently connected with the fact that the main diffusional resistance in the secondary pores is due to smaller pores with radii $< 10^{-5}$ cm, which serve as connecting links for larger pores. Such a character of the connection between pores in other sorbents has been noted in works (4–6).

Fig. 3. Dependence of the coefficient in the secondary pores on temperature: 1—zeolite MS-4A, benzene; 2—MS-4A, carbon tetrachloride; 3—MS-5A, benzene; 4—MS-5A, carbon tetrachloride; 5—Mr-296, benzene; 6—Mr-297, carbon tetrachloride; 7—Mr-297, benzene; 8—Mr-296, carbon tetrachloride. The dashed curves were calculated according to the equation $D \sim T^{1.75}$ ( ) and $D \sim T^{0.5}$ (a).

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