

PERMEATION OF SIMPLE GASES THROUGH A POROUS MEDIUM

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Weber equation (2) was employed for deriving a relation for permeation of non-adsorbing gases through a porous medium described by the model of distributed pores (Eqs (4), (7), (8)). A procedure was proposed according to which the derived equations may be used for determining tortuosity of a porous material from measurements of permeation of simple gases. The procedure takes into account the increased inaccuracy of frequency curves of the pore-volume distribution for very wide pores. The method was verified by evaluating permeation measurements of hydrogen, helium, methane, nitrogen, oxygen and argon through the Cherox 36-00 commercial catalyst.

Description of practically all processes which take place in porous catalysts during heterogeneous catalytic reactions of gases¹ is based on the conception of effective diffusion coefficients. A detailed analysis² has shown that such diffusion coefficients always depend on concentration, so that their experimental determination for necessary concentration ranges would be very laborious and, moreover, these diffusion coefficients would have to be determined from kinetic measurements of the given catalytic reaction affected by diffusion of reactants in the porous catalyst. A more rational procedure is based on the assumption of certain model of the porous structure of the catalyst: it is *e.g.* assumed that the actual porous structure of the catalyst may be replaced by a bundle of straight circular capillaries of equal radii (mean pore model³), or that capillaries in the bundle have different radii and that the number of capillaries with a certain radius is given by the pore size distribution (model of distributed pores⁴). The diffusion coefficient in the bundle of capillaries \mathcal{D}_A^* , which may be *e.g.* determined by use of Stefan–Maxwell equations for diffusion in the transition region², is then connected with the effective diffusion coefficient by a simple relation

$$D_A = (\epsilon/q) \mathcal{D}_A^*, \quad (1)$$

in which tortuosity q appears as a geometric constant of the catalyst. This constant can be of course determined only experimentally but, essentially, from an arbitrary process which is affected by the porous structure of the catalyst. It is however desirable that the experimental observation of the selected process be sufficiently simple and adequately accurate. Permeation of simple and non-adsorbing gases through a porous particle fulfills obviously these criteria.

This work has been aimed at showing a method for determining tortuosity in porous catalysts from permeation measurements which would not be affected too much by the uncertainty in determination of the pore-size distribution. The method has been illustrated by evaluating permeation measurements of hydrogen, helium,

methane, nitrogen, oxygen and argon through pellets of the industrial Cherox 36-00 catalyst.

Permeability of a Bundle of Capillaries

Permeation of simple and nonadsorbing gases in a circular capillary of radius r is well described by the Weber⁵ equation

$$\mathcal{N} = - \left[\mathcal{D}_K \frac{\pi/4 + K}{1 + K} + \frac{r^2 p}{8\mu} \right] \frac{d(p/RT)}{dz}, \quad (2)$$

where \mathcal{N} is the molar density of gas flux through the capillary, \mathcal{D}_K is the Knudsen diffusion coefficient ($\mathcal{D}_K = (2/3)rv$ with v being the mean thermal velocity of gas molecules), μ is the gas viscosity, p its pressure, $d(p/RT)/dz$ the gradient of total molar gas concentration in the direction of the capillary axis, and K is the Knudsen number, *i.e.* the ratio of the mean free path of molecules and the capillary diameter ($K = \lambda/2r$). As the mean free path is inversely proportional to the gas pressure, the Knudsen number depends on both r and p ($K = K(r, p)$). The term in the bracket on the RHS of Eq. (2) is usually denoted as the permeability coefficient and it depends on pressure and the capillary radius.

If the porous medium is replaced by the model of distributed pores, the density of the molar flux through the capillary bundle, \mathcal{N}^* , may be described as

$$\mathcal{N}^* = -\mathcal{B}^* d(p/RT)/dz, \quad (3)$$

where \mathcal{B}^* is the permeability coefficient of the capillary bundle which depends only on pressure and is defined as

$$\mathcal{B}^* = \int_{r_{\min}}^{r_{\max}} \left[\mathcal{D}_K \frac{\pi/4 + K}{1 + K} + \frac{r^2 p}{8\mu} \right] f(r) d \log r, \quad (4)$$

with r_{\min} and r_{\max} being the radii of narrowest and widest pores in the porous catalyst. Function $f(r)$ is the frequency function of the pore-volume distribution which is defined so that the product $f(r) d \log r$ represents the fraction of pore volumes with radii from the interval corresponding to $(\log r, \log r + d \log r)$ from the total pore volume. As a result, $f(r)$ is normalized, *i.e.*

$$\int_{r_{\min}}^{r_{\max}} f(r) d \log r = 1. \quad (5)$$

Permeability of Porous Medium

Because the molal density of the gas flux through porous medium, N , per unit cross

section of the porous medium, may be expressed as

$$N = (\varepsilon/q) \mathcal{N}^* \quad (6)$$

the effective permeability coefficient B defined by

$$N = -B d(p/RT)/dx, \quad (7)$$

(where x is the length coordinate measured in the direction of gas flow) is related to the permeability coefficient of the capillary bundle, \mathcal{B}^* , by relation (8)

$$B = (\varepsilon/q) \mathcal{B}^*, \quad (8)$$

which is analogous to Eq. (1) for diffusion.

Thus, if we want to determine tortuosity q from Eq. (8), we must have at our disposal effective permeability coefficients B determined experimentally according to definition (7) and permeability coefficients of the capillary bundle \mathcal{B}^* (knowledge of porosity ε is tacitly assumed). Coefficients \mathcal{B}^* can be determined according to Eq. (4) provided that the experimentally determined frequency function $f(r)$ of the pore size distribution is known.

The frequency functions f of the pore-size distribution is usually determined by connecting frequency functions obtained from the desorption branch of the adsorption isotherm of an inert gas (nitrogen, argon, in some cases benzene) and the frequency function from mercury porosimetry. (Adsorption data yield frequency functions for mesopores with radii from 1 nm to several tens of nm; mercury porosimetry provides data for macropores from several tens of nm to possibly 10^4 nm). For common porous catalysts, the contribution of macropores with large radii to the total pore volume is usually low and consequently of limited accuracy. It is obvious from Eq. (4) that frequency function f is weighed by squared radius in the second term of the integral on the RHS (term for the viscous flux). The inaccuracy in $f(r)$ is thus considerably amplified for large pore radii. It would be therefore suitable to eliminate these terms in determination of tortuosity.

After introducing mean integral values according to the following definitions,

$$\langle r \rangle = \int_{r_{\min}}^{r_{\max}} r f(r) d \log r, \quad (9)$$

$$\langle r^2 \rangle = \int_{r_{\min}}^{r_{\max}} r^2 f(r) d \log r, \quad (10)$$

$$\left\langle \frac{\pi/4 + K}{1 + K} \right\rangle = \Phi(p) = (1/\langle r \rangle) \int_{r_{\min}}^{r_{\max}} \frac{\pi/4 + K}{1 + K} f(r) d \log r \quad (11)$$

the equation for effective permeability coefficient B assumes the form of (compare with Eqs (4) and (8))

$$B = (\varepsilon/q) [(2/3) v\langle r \rangle \Phi(p) + \langle r^2 \rangle p/8\mu]. \quad (12)$$

Dimensionless function $\Phi(p)$ characterizes the interaction of contributions due to the Knudsen flow and slip at the pore wall and its values are $\Phi = 1$ in the Knudsen region, (where $K \rightarrow \infty$ because of $p \rightarrow 0$), and $\Phi = \pi/4$ in the region where the flowing gas has the properties of continuum ($K \rightarrow 0$, $p \rightarrow \infty$). Dependences $\Phi(p)$ (calculated according to definition (11)) for the catalyst Cherox 36-00 are plotted on Fig. 1 for helium and methane which exhibit largest differences in mean free paths λ . Curves $\Phi(p)$ for the remaining gases (hydrogen, nitrogen, oxygen, argon) lie between these two curves. It is obvious from this figure that at atmospheric pressure the lower limit $\Phi(p) = \pi/4$ has not been attained with any of the gases; the upper limit is valid only for pressures lower than 1 Torr. If the experiments are performed at approximately 150–760 Torr, $\Phi(p)$ may be expressed by an empirical linear dependence

$$\Phi = \alpha - \beta p, \quad (13)$$

where $\alpha = 0.843$ and $\beta = 30.1 \cdot 10^{-6} \text{ Torr}^{-1}$ for helium and the catalyst used.

By combining Eq. (12) with Eq. (13) in the region of its validity, an expression for the pressure dependence of the effective permeability coefficient $B(p)$ is obtained

$$B = a + bp, \quad (14)$$

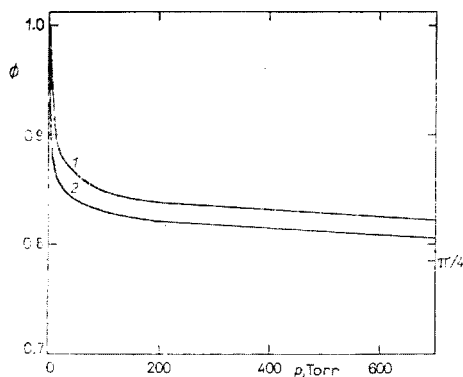


FIG. 1
Function $\phi(p)$ for Helium 1 and Methane 2
for the Cherox 36-00 Catalyst

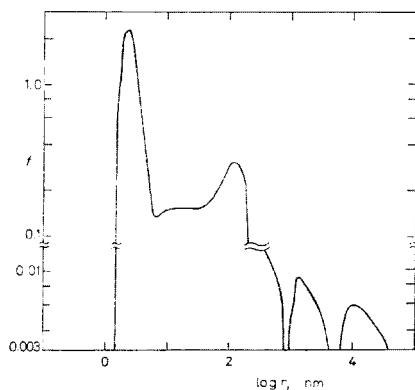


FIG. 2
Frequency Function of the Pore Distribution
Catalyst Cherox 36-00.

where

$$a = (\varepsilon/q) (2/3) v \langle r \rangle \alpha, \quad (15)$$

$$b = (\varepsilon/q) [(\langle r^2 \rangle / 8\mu) - (2/3) v \langle r \rangle \beta]. \quad (16)$$

For simple gases and common porous catalyts, the second term on the RHS of Eq. (16) is usually substantially lower than the first term (a difference of three orders for the Cherox 36-00 catalyst) and so it may be neglected; then it holds

$$b = (\varepsilon/q) \langle r^2 \rangle / 8\mu. \quad (17)$$

No such simplification for $\Phi(p)$ is possible in the low pressure region. For $p \rightarrow 0$, the limiting value of $B(p)$ is $(\varepsilon/q) (2/3) v \langle r \rangle$ and on increasing the pressure, curve $B(p)$ approaches the straight line $B = a + bp$. Function $B(p)$ may pass through a minimum in some cases. Such a minimum is usual for permeation of gases through glass capillaries⁶. It can be shown easily that on using the model of distributed pores this minimum may occur only if the following inequality is satisfied

$$-(d/dp) [(\varepsilon/q) (2/3) v \langle r \rangle \Phi(p)] \Big|_{p=0} > (d/dp) [(\varepsilon/q) \langle r^2 \rangle p / 8\mu] \Big|_{p=0}, \quad (18)$$

i.e.

$$- d\Phi/dp \Big|_{p=0} > 3 \langle r^2 \rangle / (16 \mu v \langle r \rangle). \quad (19)$$

EXPERIMENTAL

Catalyst Cherox 36-00 (12% MoO₃ + 3% CoO/Al₂O₃) is a product of Chemické závody, Záluží, Krušné Hory. Texture characteristics of the nonactivated catalyst are summarized in Table I.

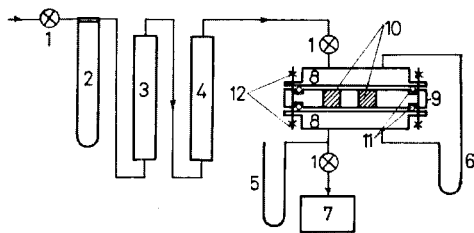


FIG. 3

Apparatus for Permeation Measurements

1 Needle valves, 2 differential flowmeter, 3 bubble flowmeter, 4 drying tower, 5 mercury manometer, 6 differential manometer, 7 vacuum pump, 8 upper and lower flange of the cell, 9 metal plate, 10 catalyst pellets, 11 rubber tightening rings, 12 connection bolts.

The frequency function of the pore distribution (Fig. 2) was obtained by combining mercury porosimetry (porosimeter Carlo Erba, model 65a) and the evaluation of the desorption branch of the adsorption isotherm of benzene at 20°C by the Roberts method⁷.

Gases: Electrolytic hydrogen (Technoplyn, Kyje), bulb nitrogen (Tesla, Vrchlábi), argon (Moravské chemické závody, Ostrava), medicinal oxygen (Technoplan, Kyje), helium (Schuchardt, München) and methane (Schuchardt, München) were taken from pressure cylinders.

Apparatus (Fig. 3). Five cylindrical pellets of catalyst (diameter \times height: 0.72 cm \times 0.75 cm) were fixed in cylindrical holes of a circular 0.75 cm-high metal plate, which was fixed between the lower and upper flange of the metal permeation cell. The gases entered the cell after passing through a differential flowmeter, bubble flowmeter, drying tower (molecular sieve Calsit 5A) and a fine needle valve. From the cell exit they passed through a further needle valve which served for adjusting the total pressure, and entered the vacuum pump. The pressure gradient between front faces of pellets was measured by an U-manometer filled with oil. The total pressure in the bottom part of the cell was measured by a mercury manometer. Permeability B was calculated

TABLE I

Texture Properties of the Cherox 36-00 Catalyst

True density, g/cm ³	3.72 ^a
Apparent density, g/cm ³	1.29 ^b
Porosity, cm ³ /cm ³	0.653
Pore volume, cm ³ /g	0.506
Specific surface, m ² /g	255 ^c

^a Determined pycnometrically with helium, ^b determined pycnometrically with mercury, ^c cumulative surface determined from the distribution curve.

TABLE II

Mean Thermal Velocity (v), Mean Free Path (λ), Viscosity (μ) and Constant α for Permeation of Gases through the Cherox 36-00 Catalyst (20°C, 760 Torr)

Gas	$v \cdot 10^5$ cm/s Eq. (19)	$\lambda \cdot 10^6$ cm Ref. ⁸	$\mu \cdot 10^6$ g/cm s Ref. ⁹	α
Hydrogen	1.764	11.8	88.6	0.839
Helium	1.252	18.6	196	0.843
Methane	0.625	5.2	108	0.825
Nitrogen	0.473	6.3	174	0.828
Oxygen	0.443	6.8	203	0.829
Argon	0.396	6.7	222	0.828

from Eq. (7) with the differentials replaced by differences between both faces of the pellet and it was measured at room temperature in dependence on the mean pressure in the pellet in the range 100–700 Torr.

RESULTS AND DISCUSSION

To illustrate the experimentally obtained $B(p)$ dependences, the permeability of nitrogen is plotted on Fig. 4 versus the mean pressure in the pellet p (arithmetic mean of pressures on both pellet faces). Analogous dependences hold for the other gases. Constants a and b of Eq. (14) were obtained from the straight line passing through the experimental points. It is obvious from expression (15) that in a versus $(2/3)v\alpha$ coordinates, the points for different gases must lie on a straight line passing through the origin; its slope is equal to the product $(\epsilon/q)\langle r \rangle$. Fig. 5 comprises our results plotted in these coordinates; the mean thermal velocity was calculated from the relation

$$v = (8RT/\pi M)^{1/2} \quad (20)$$

and constants α from Eq. (13) were evaluated by linearizing functions $\Phi(p)$, which were calculated numerically according to definition (11) for 150–700 Torr. The mean free paths of molecules λ , which appear in the Knudsen number K , were taken from the literature⁸ (Table II). Points in Fig. 5 are well described by the linear dependence with standard deviation equal to 5% of the value of the slope $((\epsilon/q)\langle r \rangle = 6.474 \text{ nm})$.

Among the gases used for permeation measurements, pronouncedly inert nonadsorbing types (helium, argon) as well as gases containing multiatomic molecules for which the adsorption cannot be excluded beforehand (methane) were considered.

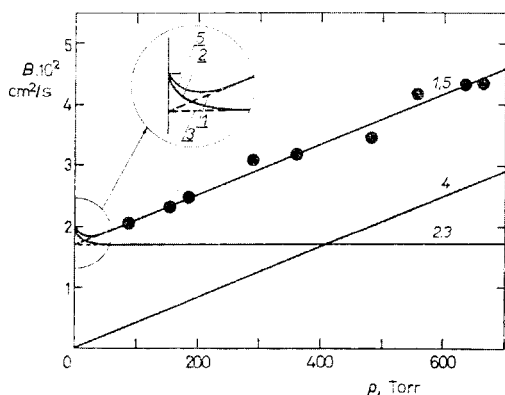


FIG. 4

Pressure Dependence of Nitrogen Permeability (B) for the Cherox 36-00 Catalyst

1 Dependence $B = a + bp$; 2 dependence $(\epsilon/q)(2/3)v\langle r \rangle \phi(p)$, inequality (19) is satisfied; 3 dependence $(\epsilon/q)(2/3)v\langle r \rangle (\alpha - \beta p)$; 4 viscous flux bp ; 5 dependence $(\epsilon/q)(2/3)v\langle r \rangle \phi(p) + bp$.

The fact that all the gases satisfy the linear dependence on Fig. 5 proves that permeation in pores is not accompanied by surface migration of adsorbed molecules and that the product $(\varepsilon/q) \langle r \rangle$ is the actual geometric constant of the catalyst which does not depend on the kind of the permeating gas.

By comparing the value $(\varepsilon/q) \langle r \rangle$ with the mean radius $\langle r \rangle$ determined by numerical integration according to definition (8) ($\langle r \rangle = 34.7 \text{ nm}$), tortuosity $q = 3.50$ has been obtained.

Slopes b of the linear dependences of permeability on pressure (Eq. (14)) are plotted in Fig. 6 versus inverse of viscosity ($1/8\mu$). Even in this case a straight line with the slope of $(\varepsilon/q) \langle r^2 \rangle$ (compare Eq. (17)) and passing through the origin is obtained. It is possible to calculate the mean value $\langle r^2 \rangle = 2.87 \cdot 10^5 \text{ nm}^2$ by numerical integration

FIG. 5
Dependence of Intercepts a on $(2/3) v\alpha$ for the Cherox 36-00 Catalyst

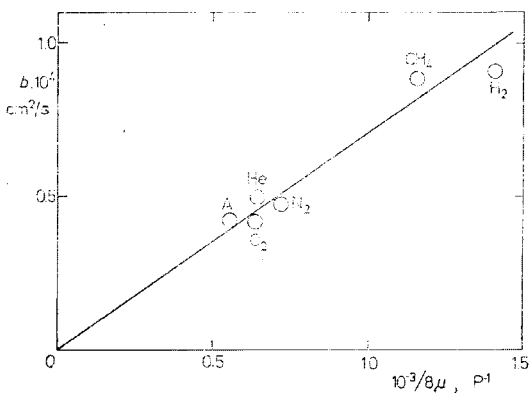
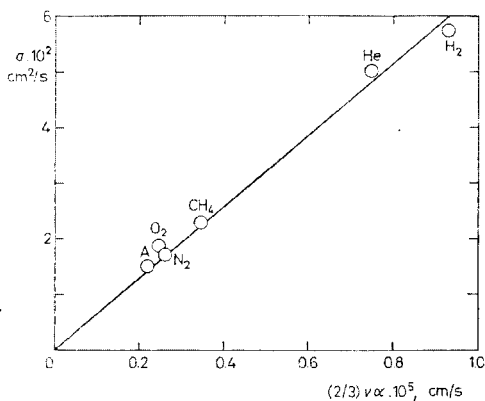


FIG. 6
Dependence of Slopes b on $(1/8\mu)$ for the Cherox 36-00 Catalyst

of (Eq. (10)) employing the frequency function f . The value of resulting tortuosity is then $q = 3.55$ which compares well with the former value $q = 3.50$.

The frequency function of the pore distribution, which is plotted in Fig. 2 in log-log coordinates, includes also very wide pores (50000 nm). However, the contribution of these pores to the total pore volume is very low; the frequency function f is in this region by two orders lower than for meso- and macropores with radii up to several hundreds of nm. In the region of largest pores the frequency function is consequently loaded with high error. Mean values $\langle r \rangle$ and $\langle r^2 \rangle$ (Eq. (8), (9)) are therefore determined with a definite uncertainty. If this is taken into account, the range of $34.7 - 1.2 + 3.8$ nm must be considered for the mean radius $\langle r \rangle$. The asymmetry of the interval results from using $\log r$ as the independent variable in frequency function f . The analogous interval for $\langle r^2 \rangle$ is of course much wider: $2.87 - 0.8 + 4.13 \cdot 10^5 \text{ nm}^2$. These intervals of mean values correspond to the interval $q = 3.50 - 0.12 + 0.39$ for tortuosity determined by using intercepts a of linear dependences $B(p)$, whereas this interval is equal to $3.55 - 1.0 + 3.9$ for tortuosity evaluated from slopes b of these dependences. Thus, the preference of intercepts of linear dependence (14) for the determination of tortuosity becomes here obvious; tortuosities evaluated from the slopes are loaded with a ten times larger error.

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