# GAS PERMEABILITY OF POROUS SUBSTANCES

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A dependence of the amount of gas passed $Q$ on the input pressure $P_{\text{in}}$ has been derived for turbulent flow in a model material with an artificially prepared porous texture. For the ratio $Q/\Delta P$, where $\Delta P$ is the pressure gradient equal to the difference of an input $P_{\text{in}}$ and output $P_{\text{out}}$ pressures, the dependence on $P_{\text{in}}$ is linear with a positive slope value, while for $Q/\Delta P^2$ for the pressure gradient expressed by $P_{\text{in}}{}^2 - P_{\text{out}}{}^2$ it is linear as well, but with a negative slope value, which contradicts the experimental results. The ratio $Q/\Delta P$ has been introduced as a quantity determining the permeability. The dependence of permeability on the path length of the flow $L$ satisfied the power function $Q/\Delta P = CL^{-b}$, where the constant $C$ corresponds to the value $(Q/\Delta P)_{(1)}$ for $L = 1$, $C$ is characteristic of a given system. Helium has been chosen as a standard gas for studying gas permeability in real porous systems.

**Keywords**: Gas permeability; Real porosity; Turbulent flow.

Permeability is understood as the ability of a fluid (liquid, gas) to pass through a pore system of material along a decreasing concentration gradient, or pressure gradient in the case of gas permeability. There are two types of porous systems: a real one, which is an integral structural part of a material, and a simplified model system, which would enable, based on individual properties, to derive basic parameters for expressing permeability as a physical process.

A model system has been constructed for a laminar flow, composed of a bundle of straight capillaries, not necessarily parallel and of an equal diameter in general case; however, according to definition, their walls are smooth to allow formation of continuous flow lamellae. The evaluation of permeability by the mechanism of laminar flow is based on Darcy's equation in the rational form[1,2]

$$k = \eta \frac{L}{A} \frac{Q}{\Delta P} , \tag{1}$$

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where $k$ is Darcy's coefficient of permeability, $\Delta P$ is the pressure gradient given by the difference of input $P_{\mathrm{in}}$ and output $P_{\mathrm{out}}$ pressures, or in the form[3,4]

$$k = \eta \frac{2 P_{\mathrm{o}} L}{A} \frac{Q}{\Delta P^2} , \qquad (2)$$

where $\Delta P^2$ is the pressure gradient expressed by the difference the squared pressures $P_{\mathrm{in}}{}^2 - P_{\mathrm{out}}{}^2$, if the average pressure of gas within its passage through a porous system is introduced as a correction. $P_{\mathrm{o}}$ is the pressure of gas surrounding the measuring equipment. In both equations, the differences $\Delta P$ and $\Delta P^2$ are independent variables and the amount of gas $Q$ passed per time unit is a dependent variable. Other quantities are constants, which define a test body by the height $L$ and the cross-section area $A$ and the applied gas or liquid is characterized by viscosity coefficient $\eta$. The unit of permeability coefficient $k$ is 1 Darcy [D], whose dimension conforms to dimensions of all quantities included in cited equations[3,5,6].

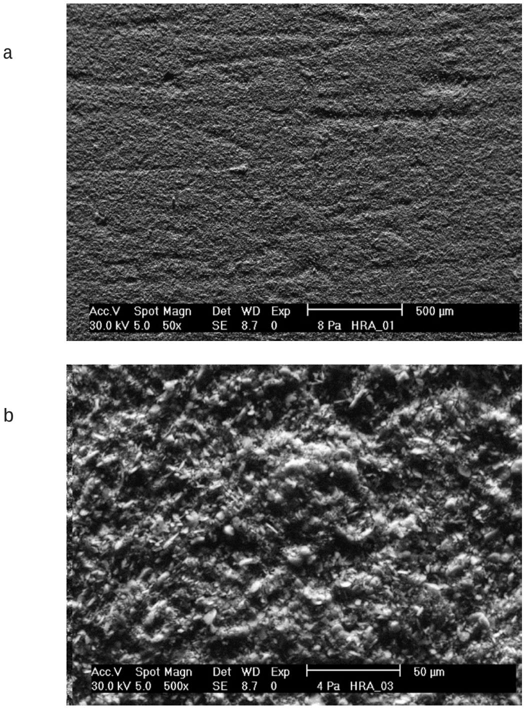

FIG. 1
Omnidirectional cavity arrangement in real porous substance by SEM, secondary electrons. Magnification 50× (a), magnification 500× (b)

Cavity arrangement in a real porous substance is omnidirectional, cavities are not shape-delimited and are of various diameters and lengths (Fig. 1a). From the macroscopic standpoint they are randomly connected and their inner surface consists of a layer of primary particles forming the solid matter of the porous body (Fig. 1b). That is why the gas flow within a porous substance as a real system cannot be defined as laminar and its character approaches to turbulent.

By comparison with a model for laminar flow it is obvious to what degree the equations derived for laminar flow in separate and mutually unconnected channels could be applied in a real porous substance for undirected cavities whose interconnection creates a spatially undefined porous entity.

This partial study has been aimed at examining applicability of commonly used relations to laminar flow in a material with a real pore system, finding differences in interpretation, and deriving appropriate relations allowing to characterize gas permeability of these materials. It has been focused on the dependence of permeability on the form of the pressure gradient and the path length of the flow.

## EXPERIMENTAL

### Material

Measurements were carried out for cylinders prepared of corundum specially for this purpose and fired at 1100 °C. Their inner texture is identical with that shown on microphotographs in Fig. 1. For cylinders with diameter 30 mm and heights 30, 20 and 10 mm, real methanol and apparent mercury densities have been measured, open porosity and pore distribution determined by high-pressure mercury porosimetry (Porosimeter 2000 Carlo Erba), and specific surface by nitrogen adsorption at –196 °C (Sorptomatic 1990 Carlo Erba). The respective values are presented in Table I, the pore distribution in Fig. 2. Gases with var-

TABLE I
Textural parameters of ceramic body with real porous system

| $d_r$ g cm$^{-3}$ | $d_a$ g cm$^{-3}$ | Por % | $V_{meso}$ cm$^3$ g$^{-1}$ | $V_{macro}$ cm$^3$ g$^{-1}$ | $V_o$ cm$^3$ g$^{-1}$ | $r_{mode}$ nm | $S_{BET}$ m$^2$ g$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 3.9158 | 2.37 | 39.5 | 0.001 | 0.166 | 0.167 | 365 | 1.5 |

$d_r$, real helium density; $d_a$, apparent mercury density; Por, porosity according to mercury porosimetry; $V_{meso}$, volume of mesopores ($3.7 < r < 40$ nm); $V_{macro}$, volume of macropores (40–7500 nm); $V_o$, volume of open pores; $r_{mode}$, mode of pores radii; $S_{BET}$, specific surface area ($N_2$, 77 K) according to the BET theory.

ious molecular size and different physical properties have been chosen. Their list is given in Table II.

### Instrumental

The apparatus depicted in Fig. 3 was used for measurements, which has been constructed for a standard sample width of 30 mm. The principal part forms a massive two-piece hollow cylinder 2, 5 with gas inlet 1 and outlet 7 in its bases. A sample 4 is tightened between both parts by a system of sealing 3 with rubber rings 6, so that gas could flow freely within a measured sample through a well-defined cross-section area. At the low part, the sample is cemented to the ring border with a plastic material. The apparatus has been adapted for measuring both gas and liquid permeability.

TABLE II

Properties of used gases

| Gas | M<br>g mol$^{-1}$ | $b$<br>cm$^3$ mol$^{-1}$ | $V_1$<br>cm$^3$ molecule$^{-1}$ | $d_1$<br>cm molecule$^{-1}$ | η<br>g cm$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| He | 4.003 | 23.7 | $0.98 \times 10^{-23}$ | $2.66 \times 10^{-8}$ | $186 \times 10^{-6}$ |
| $H_2$ | 2.016 | 26.6 | $1.104 \times 10^{-23}$ | $2.76 \times 10^{-8}$ | $84 \times 10^{-6}$ |
| $CO_2$ | 44.01 | 42.7 | $1.722 \times 10^{-23}$ | $3.23 \times 10^{-8}$ | $138 \times 10^{-6}$ |
| n-$C_4H_{10}$ | 58.12 | 117.9 | $4.894 \times 10^{-23}$ | $4.54 \times 10^{-8}$ | $74 \times 10^{-6}$ |

$M$, molecular weight; $b$, van der Waals constant; $V_1$, volume of a molecule; $d_1$, diameter of a molecule; η, viscosity coefficient (298 K).

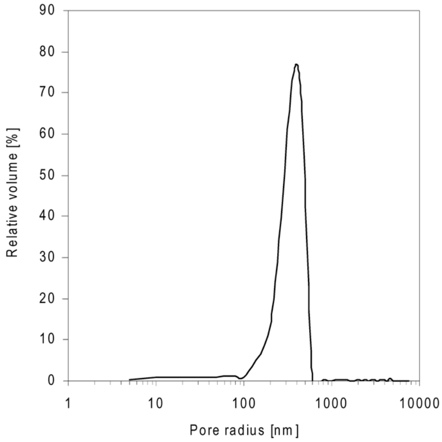

FIG. 2

Pore distribution by Hg-porosimetry, mode of pores radii $r_{\text{mode}}$ = 365 nm

The measuring equipment is illustrated in Fig. 4. To the upper cover 4, gas inlet from a gas tank 1 is connected through a gas pressure regulator 2 and a digital pressure transducer 3 connected to a recording unit. Gas outlet is routed through a check pressure transducer 6 into a water reservoir 7 with a pressure preset to outer atmospheric pressure by bend of an outlet capillary 8. By increasing pressure over the water in the reservoir, water is expelled until the inner and outer pressures become equal. The volume of gas retained is determined from the mass of water expelled from the isobaric reservoir.

### Measuring Procedure

The jacket of cylindrical sample is gas-tight sealed with an insulation tape. After fixation in the measuring cylinder, the input pressure is adjusted and gas is allowed to pass through a

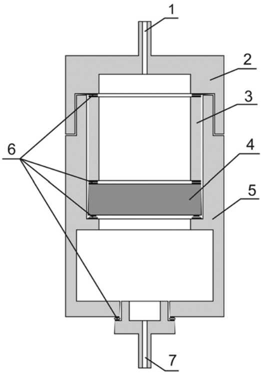

FIG. 3
Scheme of laboratory apparatus for permeability measurement: 1, gas inlet; 2, cover; 3, distance piece; 4, sample; 5, jacket; 6, packing; 7, gas outlet

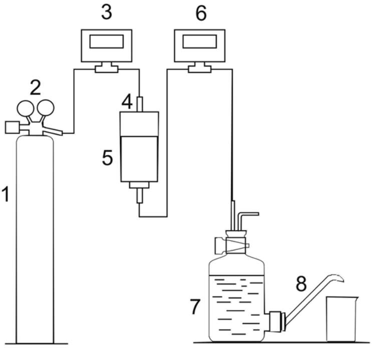

FIG. 4
Scheme of measuring equipment: 1, gas tank; 2, gas pressure regulator; 3, pressure transducer; 4, cover; 5, apparatus jacket; 6, check pressure transducer; 7, water reservoir; 8, outlet capillary

sample for 20–50 min and flow out freely outside the sampling flask. In this way saturation of the material with gas is achieved via both adsorption and absorption mechanisms, and gas molecules occupy, within the porous flow system, the same position as in a true permeability measurement. Thus an additional pore filling associated with gas losses on its passage through the body is prevented. After attaining static and dynamic equilibria between the flowing gas and the porous structure, a certain stage of the steady state the flow is chosen for measuring, at which the outlet is switched to the sampling flask where gas sampling is performed without any change in the flow conditions as a volume of water forced out under isobaric conditions.

The measurement was carried out within the pressure range 100 to 300 kPa.

## RESULTS

### *Dependence of Permeability on the Pressure Difference*

As already mentioned in introduction, when adhering to all material constants, the ratio $Q/\Delta P$ determines the extent of permeability in dependence on the gas pressure. $\Delta P$ is an independent variable. The pressure difference $\Delta P$ has been determined both as the difference in linear values of input and output pressures $\Delta P = (P_{in} - P_{out})$, and the difference of their squared values $\Delta P^2 = (P_{in}^2 - P_{out}^2)$. In the arrangement described, permeability was measured against the atmospheric pressure so that, after a slight correction, $P_{out} = 1$.

An example of evaluation of values measured for helium permeability is presented. As shown in Fig. 5, the dependence $Q/\Delta P$ [cm$^3$ s$^{-1}$ Pa$^{-5}$] vs

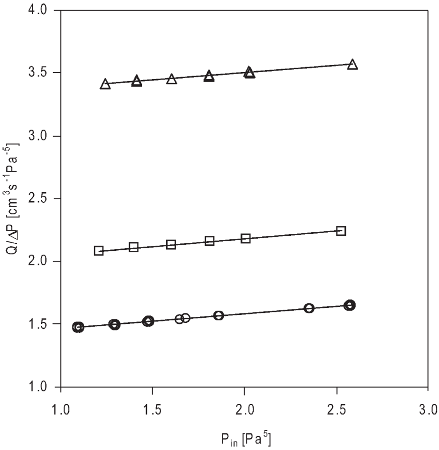

FIG. 5
Dependence of $Q/\Delta P$ on the pressure for He; sample heights 10 (△), 20 (□) and 30 (○) mm

$P_{in}$ [Pa[5]] is linear for all sample heights and, within the framework of individual heights the $Q/\Delta P$ values can be considered very near within limits of a systematic experimental error. Based on this finding, helium has been introduced as a standard gas for gas permeability examination. For helium, an interaction with a tested material is precluded, both the chemical and adsorption one, due to its deep critical temperature.

By analogy, for helium the dependence $Q/\Delta P^2$ [cm$^3$ s$^{-1}$ Pa$^{-10}$] vs $P_{in}$ [Pa[5]] has been constructed, depicted in Fig. 6. This dependence is also roughly linear. However, it is inversely proportional, the value of $Q/\Delta P^2$ decreases with increasing pressure and in parallel, also Darcy's coefficients of permeability $k$ according to Eq. (*2*) in accordance with a former observation[5]. It is clear that while the course of individual linear values $\Delta P$ quite roughly corresponds with the trend of the direct dependence of the gas amount passed $Q$ on pressure, the opposite trend is observed by $\Delta P^2$, which could be explained as an inadequate value of this amount in relation to the flow intensity.

The same pairs of the dependence $Q/\Delta P$ or $Q/\Delta P^2$ on $P_{in}$ have been observed also for other gases, as seen in Figs 7 and 8. In all the cases, the shapes of the dependences are quite analogous, with a positive slope for $Q/\Delta P$ and with a negative one for $Q/\Delta P^2$. Since after substituting the ratio $Q/\Delta P^2$ into Eq. (*2*) the resulting value cannot be corrected additionally with

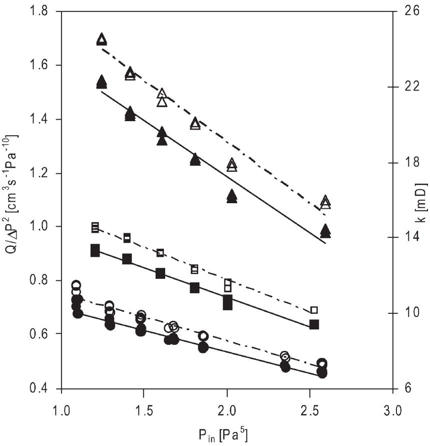

FIG. 6

Dependence of $Q/\Delta P^2$ and coefficient of permeability $k$ on the pressure for He; sample heights 10 (△, ▲), 20 (□, ■) and 30 (○, ●) mm ($k$, empty symbols; $Q/\Delta P^2$, full symbols) any variable parameter, the coefficients of permeability $k$ decrease with increasing pressure[5] in proportion to corresponding ratios $Q/\Delta P^2$, as illustrated by the diagrams.

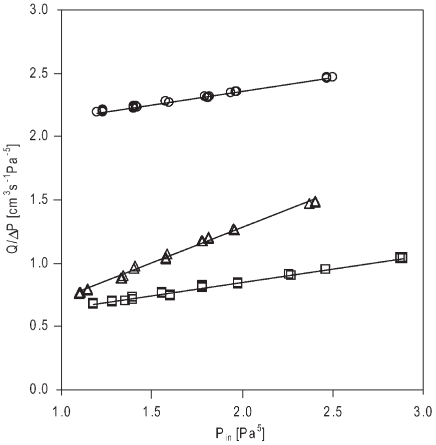

FIG. 7
Dependence of $Q/\Delta P$ on the pressure for $H_2$ (○), $CO_2$ (□) and n-$C_4H_{10}$ (△); sample height 30 mm

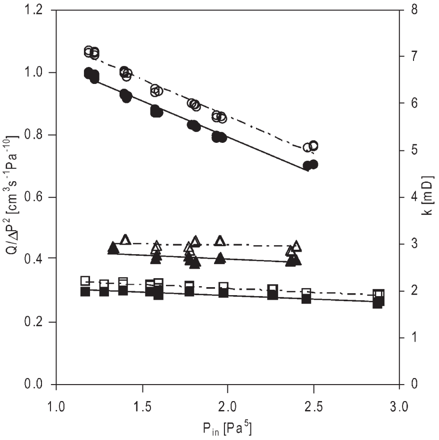

FIG. 8
Dependence of $Q/\Delta P^2$ and coefficient of permeability $k$ on the pressure for $H_2$ (○, ●), $CO_2$ (□, ■) and n-$C_4H_{10}$ (△, ▲); sample height 30 mm ($k$, empty symbols; $Q/\Delta P^2$, full symbols)

*Dependence of Permeability on the Pressure*

In this connection, the dependences of the amount of gas passed $Q$ [cm$^3$ s$^{-1}$] on the input pressure $P_{in}$ [Pa$^5$] were determined for all three samples with different heights, as shown in Fig. 9. In the range of applied pressures the dependence is linear, however the linearity was observed also at markedly higher pressures[7]. The direct proportionality between both quantities does not apply as can be derived from a new dependence.

Considering that for $P_{in} = 0$ also $Q = 0$ holds true, the experimental determined amount $Q_{(1)}$ corresponding to the lowest pressure $P_{in(1)}$ becomes a basis for calculation of subsequent $Q_{calc(n)}$ corresponding to pressure $P_{in(n)}$. According to a simple relation

$$Q_{calc(n)} = Q_{(1)}P_{in(n)}/P_{in(1)}\,, \tag{3}$$

where the ratio $Q_{(1)}/P_{in(1)}$ denotes the slope of linear dependence, a series of correlating values is obtained, from which the dependences $Q_{calc}$ vs $P_{in}$ have been constructed, which are presented whit dot-and-dash also in Fig. 9. These are linear as well, but they lie under the dependence $Q$ vs $P_{in}$, from which it follows that the calculated values $Q_{calc}$ are generally lower than the experimental values $Q$. The difference between $Q$ and $Q_{calc}$ presented is due to the fact that the gas entering a porous system at a pressure $P_{in}$ and get-

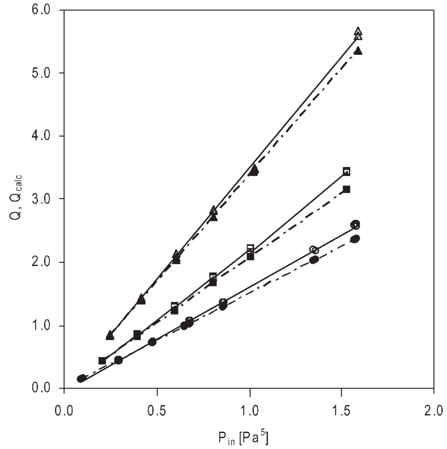

FIG. 9

Dependence of the registred gas amount $Q$ and the calculated gas amount $Q_{calc}$ on the pressure for He; sample heights 10 (△, ▲), 20 (□, ■) and 30 (○, ●) mm ($Q$, empty symbols; $Q_{calc}$, full symbols) ting out at a pressure $P_{out}$, while $P_{in} > P_{out}$, must by the passage increase its input volume $V_{in}$ to an output volume $V_{out}$ for which, according to the equation of state, $V_{in}P_{in} = V_{out}P_{out}$ holds $V_{out} > V_{in}$, and thus also $Q > Q_{calc}$. Since, with respect to the flow continuity, the volume $V_{in}$ and $V_{out}$ enter and get out of the porous system simultaneously, due to expansion an acceleration of the gas flow through material must occur, which is reflected in that the recorded quantity $Q$ leaving the porous system in a time unit is larger than $Q_{calc}$ proportional to corresponding $P_{in}$.

### *Dependence of Permeability on the Path Length*

The dependence of permeability on the path length, which the gas must travel on the passage within a porous system, has been verified only for the relation $Q/\Delta P$ vs $L$ on samples with the height $L$ = 30, 20 and 10 mm. The real length of transport routes, however, can be greater than $L$ due to arrangement of a porous system.

For $Q/\Delta P$ values corresponding to the above given heights, the average value $(Q/\Delta P)_{av}$ of the entire set of $Q/\Delta P$ values has been introduced representing members of this group as regards their dependence on the pressure. In this way, three-point dependences have been obtained for all gases, as shown summarily in Fig. 10. These dependences fitted very well with a simple power function

$$Q/\Delta P = CL^{-b} , \tag{4}$$

where $C$ and $b$ are constants. This equation in numerical form has been presented for each gas in a corresponding diagram. Its validity has been verified by solving for limiting cases.

For $L = 1$, $Q/\Delta P = C$ where the constant $C$ stands for an average value $(Q/\Delta P)_{av(1)}$ which, for continuity, the system would acquire at the unit sample height $L$ = 1 mm. For the limiting condition $L \to 0$, when the volume of a porous system is effectively zero, the permeability concept loses its physical sense, the pressures in the expression $P_{in} - P_{out}$ will be equal, so that $\Delta P = 0$ and the ratio $Q/\Delta P \to \infty$, which corresponds to the value $Q/\Delta P$ according to Eq. (*3*) solved for the given condition. On the other hand, on the condition of zero permeability, i.e. $Q = 0$ and thus also $Q/\Delta P = 0$, then $L \to \infty$ according to Eq. (*4*), as also corresponds with the problem logic.

In the case of dependence relates to only a single pressure $P_{in}$, it is interpolated from the dependence in Fig. 10 invariable of height $L$. Corresponding points on the ordinate are calculated, a curve analogous to the dependence in Fig. 10 is constructed whose form is expressed by Eq. (*4*). The only quantity required is the constant $C$ determining in this case the ratio $(Q/\Delta P)_{(1)}$ specially for a selected pressure $P_{in}$, and thus characterizing the value of standard permeability for given conditions.

## DISCUSSION

In determination of gas permeability of porous materials, there are two possibilities of defining an appropriate value:

(*a*) By a quantity, e.g. coefficient of permeability $k$, which would have a universal validity and for individual gases would be a constant independent of pressure gradient and varying size of a tested body. For validity of this quantity as a constant, a mathematical model would be required including necessary parameters characterizing transmission and transport properties of gas, flow character including retardation effects and spatial arrangement of the capillary system of a porous material[8–13]. This is a complex model, which requires values of input parameters obtained by other independent methods. Such a model would express theoretical relations between all quantities involved, although with certain restriction of its experimental validity and practical applicability.

(*b*) As a special value representing the amount of certain gas passing in certain time interval through a porous body of given dimensions under preselected boundary conditions. The permeability determined in this way

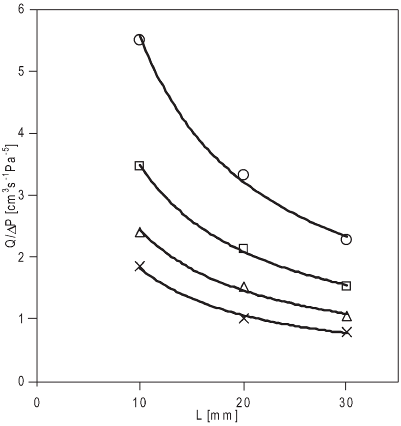

FIG. 10

Dependence of $Q/\Delta P$ on the sample height $L$ for He (□, $y = 18.921x^{-0.7335}$), $H_2$ (○, $y = 34.366x^{-0.7894}$), $CO_2$ (×, $y = 10.868x^{-0.7726}$) and n-$C_4H_{10}$ (△, $y = 13.122x^{-0.7295}$)

is of individual validity for a concrete material and if necessary, it can be supported by characteristics of a measured porous system, i.e., total pore volume and pore distribution in dependence on diameter and/or size of their surface.

Porosity, which characterizes the presence of cavities in a material, is usually considered open, i.e., the included pores are accessible from outside, or closed, and the included pores are inaccessible. Summing their volumes provides total porosity. For the flow of a fluid through a porous system only the open porosity is of importance, both practical and physical. The volume of open pores $V_o$, representing the open porosity, is given as the difference of the apparent volume $V_a = (V_s + V_c + V_o)$ and real volume $V_r = (V_s + V_c)$ of material, where $V_s$ is the volume of solid phase and $V_c$ the volume of closed pores, both inaccessible to gas and liquid from standpoint of pycnometric analysis. For calculation of $V_o$, the equation $(d_a - d_r)/d_r d_a$ is commonly used, where the densities are substituted for the respective volumes. The correct value of real density $d_r$ is defined by the relation $d_r = m/(V_s + V_c)$ and the apparent density by the relation $d_a = m/(V_s + V_c + V_o)$, where $m$ is the mass of sample. The most accurate values of $d_a$ will be obtained using the stereometric method by accurate measuring basic dimensions of the geometric regular body prepared from the tested material. This procedure is mostly technically challenging, its results however are almost exact. The unavailable closed porosity cannot be determined even by pycnometric methods in a density form, as each of them contains it in an inseparable state. The only method allowing determination of the closed porosity is X-ray analysis, which is able to distinguish between filled and empty phase within certain size range.

## CONCLUSION

Basic parameters of the turbulent flow in terms of gas permeability have been studied on a model substance with a real porous system. Gases with various molecular characteristics were used and, based on the results obtained, helium has been chosen as a standard gas for gas permeability characterization. It has been found that the dependence of the amount of the gas passed $Q$ on the pressure gradient $\Delta P$ is linear with a positive slope, which allows both inter- and extrapolation within a broad pressure range. The ratio $Q/\Delta P$ has been introduced for expressing the dependence of gas permeability on measured parameters, which contains, within one determination, single variable quantities. Variation in gas permeability on the path length of the flow has been described with a power function.

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