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# Differential Pressure-Jump Method for Routine Measurement of Sorption Kinetics

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**Abstract.** A sensitive pressure-jump method has been developed for the measurement and characterization of material transport in porous solids. The apparatus is automatically operated and the data evaluation is performed by means of numerical methods based on the Crank-Nicholson procedure. As an example, the sorption of $n$-butane and ethene in spherical mesoporous silica gel pellets has been studied. In this way, it is possible to obtain uptake curves and in case of known particle shape to derive values for effective diffusion coefficients. From the pressure and temperature dependence of $D_e$, information on the transport mechanism by means of Knudsen and surface diffusion can be obtained as well as the tortuosity factor characterizing the pore network.

**Keywords:** porous solids, sorption kinetics, pressure-jump method, diffusion coefficient, tortuosity

## 1 Introduction

The material transport in porous solids plays a dominant role as the rate determining step for manyfold processes in nature and engineering. This is particularly relevant for the chemical industry with respect to the versatile and economically so important heterogeneous catalysis as well as for separation processes.

The determining factors for the material transport concern the surface area, porosity, distribution of pore sizes as well as pore texture and network, besides the molecular interaction between the sorptive and the interfaces of porous solids. The following transport mechanisms can be distinguished:

(i) Viscous Poiseuille flow in macropores with diameters $d_p > 50$ nm at a mean free path of molecules $l \ll d_p$,
(ii) Knudsen diffusion in mesopores $2 < d_p < 50$ nm and $l \gg d_p$ by means of molecular impacts with pore walls, and possibly, in addition, surface diffusion in adsorption layers, depending on molecular interaction, temperature, and pressure,
(iii) micropore diffusion in pores with $d_p < 2$ nm, in the order of the size of molecules by means of molecular place exchange processes between structural cavities.

In general, the pore system of a solid can be characterized by the porosity, the pore size distribution, and a tortuosity factor $\tau$ unless it is well defined by a regular pore texture. Correspondingly, the material transport is described by an effective diffusion coefficient $D_e$. An interpretation in terms of the various transport mechanisms requires systematic studies of the influence of pressure and temperature. On the other hand, conclusions with respect to pore and network textures can be drawn from the dynamics of the material transport.

For the study of the material transport in porous solids a number of stationary and non-stationary methods are at hand: the measurement of permeation, sorptions kinetics and self-diffusion (Kärger and Ruthven, 1992). In principle, the evaluation of stationary measurements is relatively simple, the experimental technique, however, may be more difficult, e.g. the tightening of the sample in permeation experiments. On the other hand, the evaluation of non-stationary measurements is considerably more involved, while the experimental set-up may be substantially simpler. In view of the nowadays available computer facilities, the latter aspect is, of course, particularly relevant for the development of a method which should also be suitable for routine measurements in industrial laboratories.

## 2 Sorption Kinetic Methods

Two measuring procedures are available:

(i) Batch methods: Determination of the amount sorbed or desorbed as a function of time under given boundary conditions;

(ii) Flow methods: Response to a step or pulse pertubation of the sorptive concentration in a chromatographic column.

The measuring device described in the following belongs to the first group and is based on a method described already much earlier (Haul and Schöning, 1953; Carman and Haul, 1954). The sorption process is measured by means of a differential manometer after an abrupt pressure change of the sorptive in a gas phase of constant volume. Convenient approximative solutions of the relevant diffusion equations were given for various shapes of the porous sample (Carman and Haul, 1954; Crank, 1979). The pressure-jump method has been further developed and improved with respect to instrumentation and data evaluation (Kärger and Ruthven, 1992; Bülow et al., 1980; Negishi et al., 1984; Dubinin, Gorlov and Voloshchuk, 1980). A fundamentally different realisation of the measuring principle has been introduced using periodic pressure changes (Naphtali and Polinsky, 1963; Yasuda, 1976). In the meantime, this "frequency response" method has been further elaborated and particularly applied to study diffusion and sorption in zeolite single crystals (Shen and Rees, 1994). A single step version of the frequency response method has been developed and applied to the measurement of fast diffusion processes (Van-Den-Begin and Rees, 1989).

On the basis of a well-proven measuring device for single point determinations of BET surfaces areas (Haul and Dümbgen, 1960), a variance of a single step method for the measurement of sorption kinetics has been developed. In both cases, the difference of pressure between two vessels, one containing the sample, is measured. This principle has also been applied to the measurements of diffusion in zeolite crystals (Dubinin, Gorlov and Voloshchuk, 1980). In comparison with this method, the essential differences of the device described here are the following (see Fig. 1).

The symmetrical construction of the set-up warrants identical flow rates of the sorptive after the pressure step in both tubes leading to the two equal vessels. Furthermore, this construction minimises disturbing influences on the measuring process due to temperature changes between the thermostated vessels and the other parts of the experimental set-up. Instead of using two valves, the pressure step is achieved in both parts of the measuring system by means of an abrupt volume change of two bellows, operated e.g. pneumatically.

## 3 Differential Pressure-Jump Apparatus

The set-up of the measuring device is illustrated in Fig. 1. Two identical vessels ($F$ and $F'$), one containing the sample, are connected with metal bellows ($B$ and $B'$). The two parts of the measuring system can be connected or separated by means of valve (1). Volume differences due to the construction of the system and/or the volume of the sample can be equalized by means of a spindle driven piston $C$. The bellows can be instantaneously compressed or expanded by means of a short-stroke double acting piston $A$. In this way, the pressure of the sorptive can be changed abruptly and simultaneously to the same extent in both thermostated vessels. The valves as well as the piston are pneumatically operated, in the present set-up. The measuring system can be evacuated to a residual pressure $<10^{-2}$ hPa, depending on the vacuum equipment. The initial pressure of the sorptive is measured with a sensitive pressure transducer $E$. After closing the valves (1) and (2), a pressure jump is released and the pressure change is recorded by means of an especially sensitive differential pressure transducer $D$. The

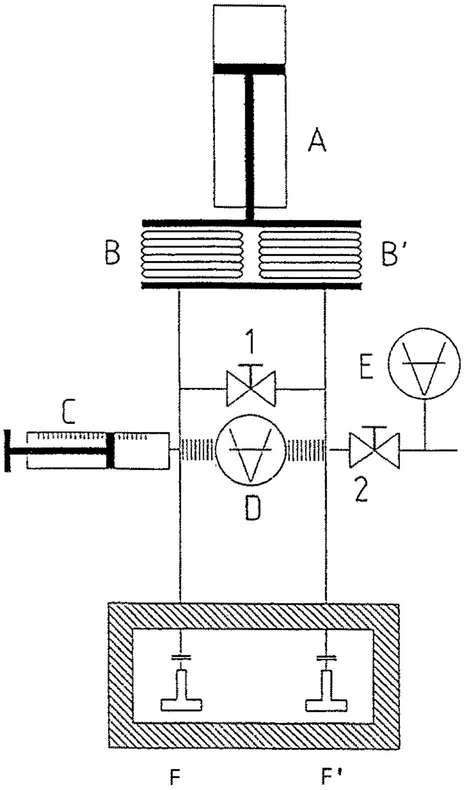

*Fig. 1.* Schematic set-up of the measuring device (see section 3).

various steps of a measuring process are automatically operated by means of a computer programme (Lerch, 1993).

The following measurements can be performed: registration of ad- and desorption curves from the measured $\Delta p(t)$-function, evaluation of effective diffusion coefficients $D_e$ for various shapes of porous particles and pellets, as well as measurements of adsorption isotherms.

## 4 Evaluation of Measurements

The determination of the sorption kinetics of *n*-butane in spherical pellets of the porous silica gel material AF 125 (see Table 1) may serve as a typical example. Starting from sorption equilibrium at a given temperature $T$ and gas concentration $c_a$ in the pellets, valves 1 and 2 (see Fig. 1) will be closed. At $\Delta p = 0$, an identical abrupt volume change (e.g., $-\Delta V$) in both parts of the measuring system is applied by means of compression of the bellows. This abrupt pressure increase causes a fast tuning process of the transducer which is recorded as a very narrow $\Delta p$ signal (Fig. 2). Subsequently, $\Delta p$ increases continuously up to a time independent value (see Fig. 2, curve *a*). In case of a blank experiment (curve *b*) this tuning process is exactly reproduced. In both cases, however, the $\Delta p$ values after the pressure-jump are negative. This is due to a volume difference between the two parts of the measuring system. Negative $\Delta p$-values can be avoided by equalisation of the volume in the two parts of the measuring system by means of the adjustable piston $C$ (see Fig. 1). In order to get information on the time constant of the initial tuning process, blank experiments with *n*-butane and helium were performed. As is shown in Fig. 3, the delay time of this initial process is about 100 ms, while the new sorption equilibrium state with concentration $c_b$ is reached within about 50 seconds (Fig. 2). Under the given conditions the influence of the tuning process can be eliminated by means of a subtraction of the results obtained with and without the porous sample, provided the volume of the sample can be neglected.

It should be realized that the particles or pellets of the porous samples need to be readily accessible to the

*Table 1.* Characteristic data of the porous materials.

| | AF 125 | T 1571 |
|---|---|---|
| Shape | spherical | spherical |
| Diameter [mm] | 2.5 | 4.5 |
| $S_g$ [m$^2$/g] | 300 | 113 |
| $V_p$ [cm$^3$/g] | 0.91 | 0.91 |
| $\varepsilon$ | 0.64 | 0.64 |
| $\rho_p$ [g/cm$^3$] | 0.79 | 0.79 |
| $\rho_s$ [g/cm$^3$] | 2.2 | 2.2 |
| Mean pore radius [Å] | 50 | 90 |

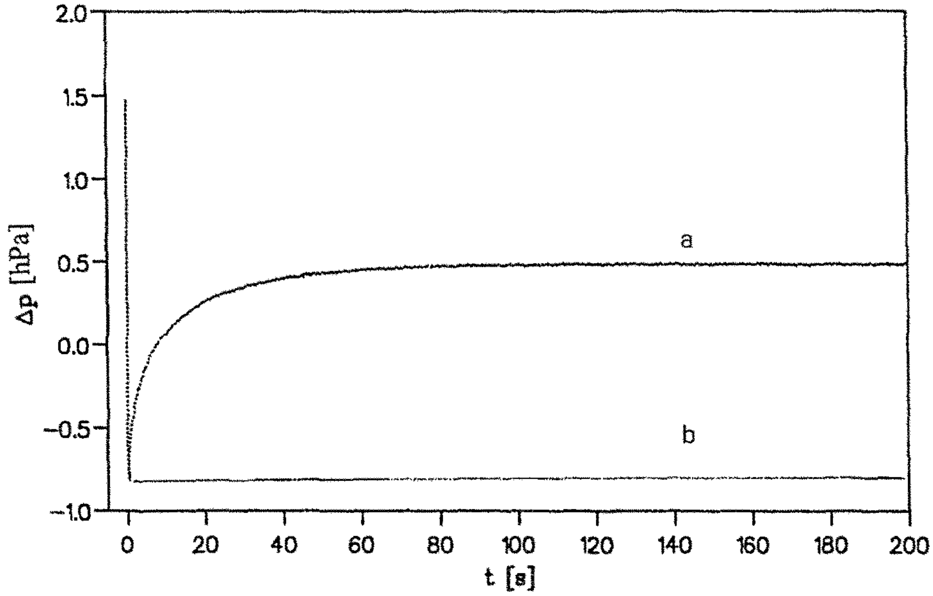

*Fig. 2.* Up-take curve for sorption of *n*-butane in spherical pellets of silica gel, 273 K. a) AF 125, b) blank experiment (section 4).

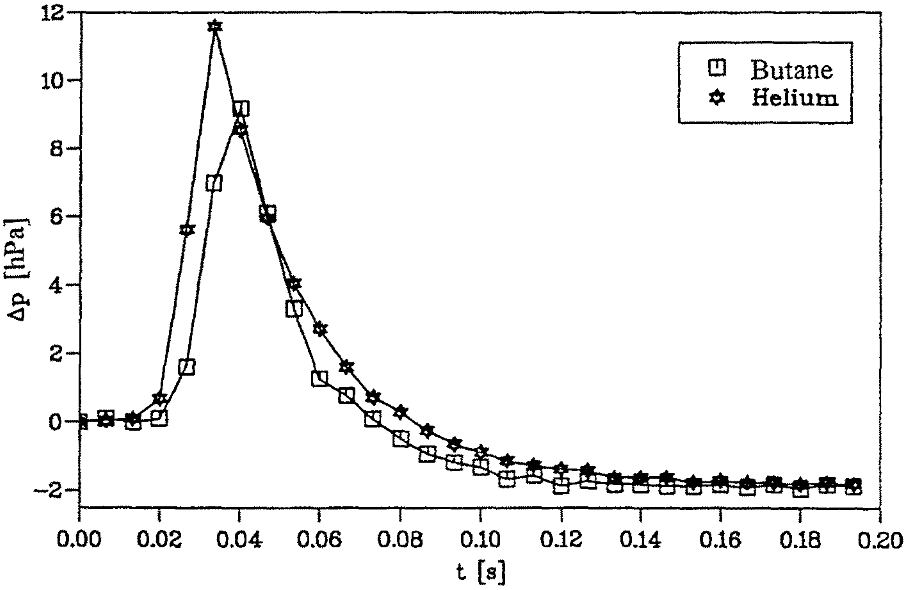

*Fig. 3.* Initial period of $\Delta p(t)$ curve, blank experiments with $n$-butane and helium.

sorptive, anyway, as far as the evaluation of diffusion coefficients is concerned.

The evaluation of effective diffusion coefficients from experimental $\Delta p(t)$ data starts from the material balance equation. For spherical particles, as an example, assuming a constant effective diffusion coefficient, and taking into account that the gas is adsorbed on the inner surface of the porous pellets, we have the equation:

$$\varepsilon\left(\frac{\partial c}{\partial t} + \frac{\partial c_s}{\partial t}\right) = D_e^*\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \tag{1}$$

wherein $D_e^*$ is given by

$$D_e^* = \frac{\varepsilon D_p}{\tau} = \varepsilon D_e \tag{2}$$

In this equation $D_p$ denotes the overall diffusion coefficient of the sorptive in a straight cylindrical capillary. In general, the $D_p$-values are influenced by the molecular mobilities of the sorptive in the mobile phase, i.e. in the gas as well as in the adsorption phase. $\varepsilon$ is the pellet porosity and $\tau$ the turtuosity. Assuming adsorption equilibrium to be established, we have the equation:

$$c_s = f(c) \tag{3}$$

Denoting the derivative of this function by $\beta$:

$$\beta = \frac{\partial c_s}{\partial c} \tag{4}$$

we have, instead of Eq. (1), the relation:

$$\varepsilon\frac{\partial c}{\partial t} = \frac{\varepsilon D_e}{1+\beta}\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \tag{5}$$

Formulating Eq. (1), it has been taken into account that the accumulation of the sorptive as well as the sorptive transport both take place within the pore space of the pellet. Thus, Eq. (1) as well as Eq. (5) are independent of the pellet porosity, $\varepsilon$ (Wicke, 1973). $D_e$ is the measured effective diffusion coefficient in this type of experiments.

The balance Eq. (5) has to be integrated under the following initial and boundary conditions:

$$\begin{array}{lll} c & = c^0 & \text{for } t = 0,\ r = R \\ c & = c_a & \text{for } t = 0,\ 0 \le r < R \\ \dfrac{\partial c}{\partial r} & = 0 & \text{for } t > 0,\ r = 0 \\ V\dfrac{dc}{dt} & = 4\pi R^2 D_e^* \dfrac{\partial c}{\partial r} & \text{for } t > 0,\ r = R \end{array} \tag{6}$$

The solution of Eq. (5) for $\beta = $ const. and $D_e = $ const. is (Carman and Haul, 1954; Crank, 1979):

$$\frac{c^0 - c(t)}{c^0 - c_b} = 1 - \sum_{n=1}^{\infty} \frac{6\lambda(1+\lambda)}{9(1+\lambda) + \lambda^2 q_n^2} \exp\left\{-q_n^2 \tau^*\right\} \tag{7}$$

with

$$\left.\begin{aligned} \lambda &= \frac{V}{v(1+\beta)}; \quad \tau^* = \frac{D_e t}{R^2(1+\beta)} \\ tg(q_n) &= \frac{3q_n}{3+\lambda q_n^2} \end{aligned}\right\} \quad (8)$$

The experiments can be performed in such a way that $\beta$ as well as $D_e$ become independent of $c$, e.g. by taking $\Delta p$ sufficiently small. Nevertheless, for a more general application the evaluation of the experimental result was based on a numerical procedure which uses the well-known Crank-Nicholson method (Lerch, Haul and Hesse, 1992). In that case the $D_e$-value in Eq. (5) must be changed until the calculated concentration at the pellet surface, $c(R, t)$, is equal to the concentration in the pellet surroundings, $C(t)$, which is experimentally measured (Lerch, Haul and Hesse, 1992).

Furthermore, the numerical method can be used to evaluate diffusion experiments performed with porous pellets of cylindrical shape. In this case an approximative analytical solution is only available for a cylinder of infinite length (Carman and Haul, 1954; Crank, 1979). In practice, however, the case of finite length is of particular importance, since adsorbents or catalysts are frequently produced by extrusion processes in this shape. Since in this case the material transport occurs in radial as well as axial direction, the twodimensional transport problem requires the numerical solution of the following differential equation (Lerch, Haul and Hesse 1992):

$$\varepsilon\frac{\partial c}{\partial t} = \frac{D_e^*}{1+\beta}\left(\frac{\partial^2 c}{\partial z^2} + \frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \quad (9)$$

The initial and boundary conditions are:

$$\left.\begin{aligned} c &= c^0 && \text{for } t = 0, r = R, z = \tfrac{1}{2}L \\ c &= c_a && \text{for } t = 0, 0 \le r < R, 0 \le z < \tfrac{1}{2}L \\ \frac{\partial c}{\partial r} &= 0 && \text{for } t > 0, r = 0, \text{ all } z \\ \frac{\partial c}{\partial z} &= 0 && \text{for } t > 0, z = 0, \text{ all } r \\ V\frac{dc}{dt} &= D_e^* \int_v \text{div grad } c\,dv && \end{aligned}\right\} \quad (10)$$

The numerical solution of the differential Eq. (9) by means of the Crank-Nicholson method requires, however, excessive computation time.

In case of very fast diffusion, i.e., a very small diffusion time constant,

$$t_D = R^2(1+\beta)/D_e, \quad (11)$$

the evaluation would require a rather involved unfolding of the following contributions: the tuning of the pressure transducer, the propagation of the initial pressure-jump along the tubes leading to the measuring vessels and the actual material transport within the porous solid.

## 5 Examples for Application of the Measuring Technique and Discussion

In order to illustrate the feasibility of the measuring technique a few examples will be given for the study of sorption kinetics.

Two samples of porous spherical particles of different silica gels will be considered: sample 1 (AF 125), rather monodisperse with a mean pore radius of about 5 nm and sample 2 (T1571), with a rather broad pore size distribution around 9 nm (Fig. 4, Table 1). For sample 1 the $\Delta p(t)$ uptake curve for $n$-butane as shown in Fig. 2 was converted to $C(t)$, the time dependent concentration of the sorptive in the pellet surroundings. The numerical calculation as indicated in section 4 leads to a value of $7.1 \cdot 10^{-3}$ cm$^2$/s for the effective diffusion coefficient, $D_e$. The corresponding calculated concentration at the pellet surface $c(R, t)$ agrees well with the experimentally obtained $C(t)$-curve, as required (see Fig. 5). In order to obtain information on the transport mechanism, the dependence of $D_e$ on pressure and temperature has been measured also with ethene. From Fig. 6, it can be seen that for both sorptives at about 330 K $D_e$ is independent of pressure in a wide range. This result together with indications for a temperature dependence on $\sqrt{T}$ are evidence for Knudsen diffusion to be the rate determining mechanism. In this case, $D_e$ is an effective Knudsen diffusion coefficient, $D_e = D_e^K$. The Knudsen diffusion coefficient $D_K$ for a straight cylindrical pore of width, $d_p$, is:

$$D_K = \frac{d_p}{3}\sqrt{\frac{8RT}{\pi M}} \quad (12)$$

On the basis of this model, it is possible to obtain information on the tortuosity $\tau$ of the pore network by using the relation:

$$\tau = \frac{D_K}{D_e^K} \quad (13)$$

It is well-known that silica gel material exhibit a texture corresponding to a random agglomeration of spheres

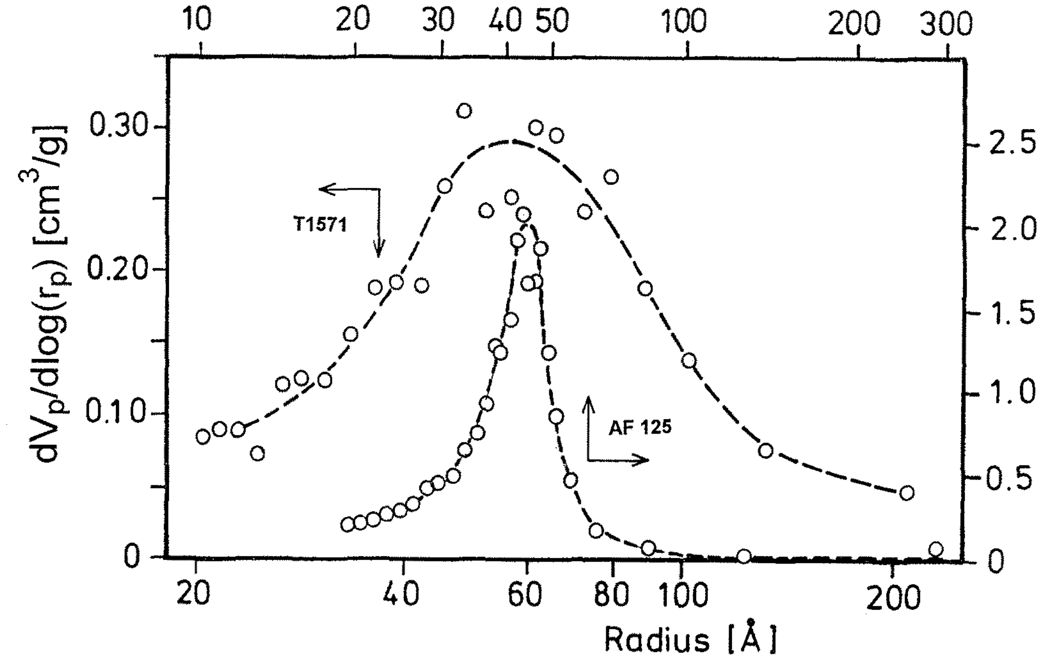

*Fig. 4.* Pore size distribution of the silica gel samples. 1) AF 125, 2) T1571 (see Table 1).

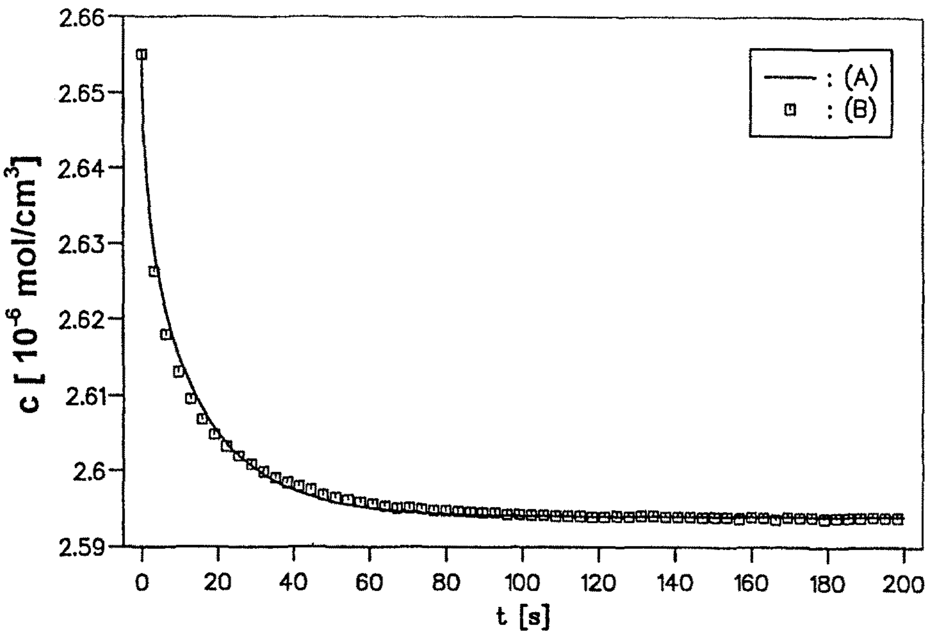

*Fig. 5.* Comparison of the numerically calculated concentration values $c(R, t)$ at the pellet surface $(A)$ with the experimental concentration values $C(t)$ in the pellet surroundings $(B)$.

(Unger, 1972). For a close packing of spheres, a tortuosity value of $\tau = \sqrt{2}$ is to be expected (Wicke, 1973). For sample 1, Eq. (13) leads to a value of 1.6 and 1.5 for the *n*-butane and ethene system, respectively. These results are in agreement with the random pore model (Wakao and Smith, 1962) which states that the

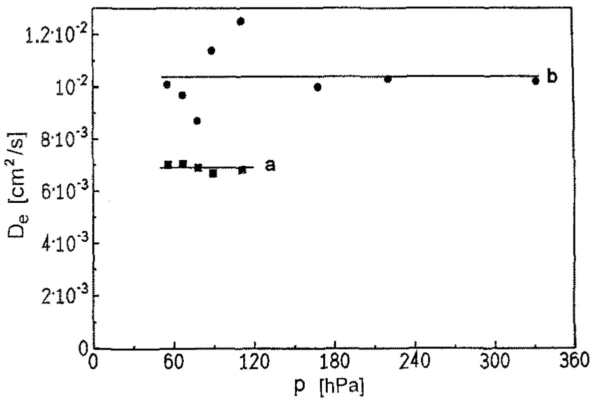

*Fig. 6.* Pressure dependence of the effective diffusion coefficient $D_e$ for a) $n$-butane (330 K) and b) ethene (330 K), AF 125.

tortuosity is given by the equation:

$$\tau = \frac{1}{\varepsilon} \tag{14}$$

With a porosity value of 0.64 (see Table 1), a $\tau$-value of 1.56 is obtained. With sample 2 (Fig. 4) similar results were obtained at temperatures above 300 K, i.e. $\tau = 1.4$ and 1.5 for $n$-butane and ethene, respectively.

Surprisingly, for lower temperature values distinctly smaller $\tau$-values were calculated. For sample 2, the result is $\tau = 1.16$ for ethene at 273 K. For $n$-butane a $\tau$-value even smaller than 1 is obtained at 268 K.

Thus, an additional transport process has to be considered leading to an increased rate of sorption. Since the amount of gas adsorbed on the pore walls of the material is significantly larger at lower temperatures, e.g. 268 K (Fig. 7), it is obvious to suggest that the material transport proceeds simultaneously by Knudsen and surface diffusion. The contributions of these mechanisms to the total sorptive transport within the pore space, however, have to be studied by further experiments.

In this more complex case, the evaluation of the experimental $C(t)$-curve for spherical pellets is based on the following material balance equation:

$$\frac{\partial c}{\partial t} = \frac{1}{1+\beta}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left[\left(r^2 D_e^K + r^2\beta D_s\right)\frac{\partial c}{\partial r}\right]\right\} \tag{15}$$

In formulating this equation it has been assumed that adsorption equilibrium is established. Taking $\Delta p$ sufficiently small in the pressure-jump experiments, $D_s$ as well as $\beta$ both can be considered as constant. Setting:

$$D_e = D_e^K + \beta D_s \tag{16}$$

Equation (15) leads to Eq. (5). The evaluation of the experimental results in the case of superposition of two transport mechanisms, thus, does not lead to any further difficulties.

Plotting $D_e$ versus $\beta$, for $n$-butane a straight line is obtained in this example (Fig. 8) resulting in $D_e^K = 1.2 \cdot 10^{-2}$ cm²/s and $D_s = 5.2 \cdot 10^{-4}$ cm²/s. Using

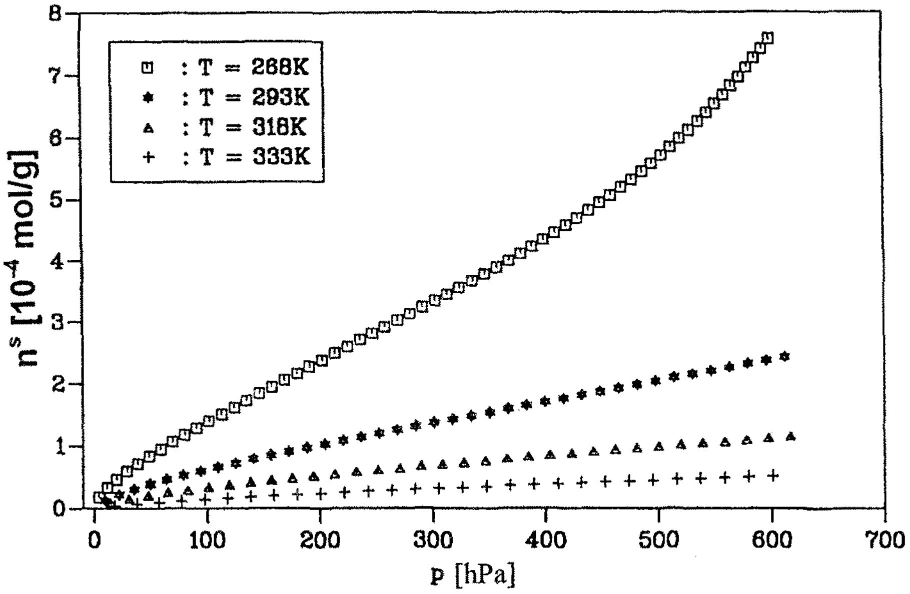

*Fig. 7.* Adsorption isotherms of $n$-butane/T1571.

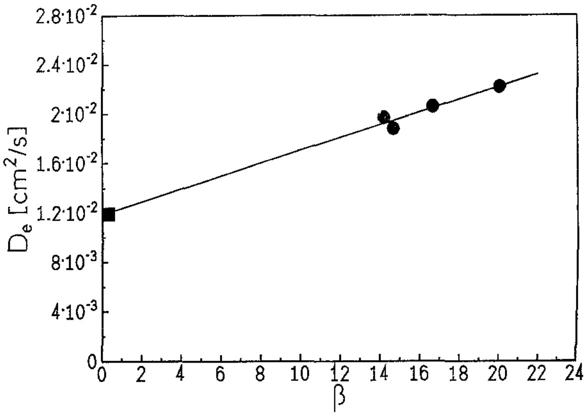

*Fig. 8.* Plot of $D_e$ versus $\beta$, dots: experimental values, square: extraploated value.

Eqs. (12) and (13) the $D_e^K$-value leads to a tortuosity $\tau = 1.5$. Since, in addition, the $D_s$-value is also of the expected order of magnitude (Kärger and Ruthven, 1992), the given interpretation of the experimental results is self consistent.

## 6 Conclusions

It has been shown that the non-stationary differential pressure-jump method and the measuring device described are well-suited for the investigation of sorption kinetics in porous solids. The symmetrically constructed and automatically operated set-up described here as well as the numerical data evaluation are advantageous for routine measurements. In this way, it is possible to obtain up-take curves, effective diffusion coefficients as well as adsorption isotherms. In most cases of practical interest, an unfolding of the experimental results is not required in the evaluation procedure.

The study of diffusion in microporous solids has been particularly devoted to diffusion in single crystals of zeolites, in view of the wide spread interest in this group of materials (Kärger and Ruthven, 1992). In the diversative industrial applications of these materials, however, the use of compacted pellets is required. Thus, in addition to the intra-particle diffusion the inter-particle transport processes and the tortuosity of the pore network are of vital interest. With this aspect in mind, diffusion in pellets of silica gel samples with different pore size distribution were studied. The results indicate that it is possible to obtain information on the transport mechanism (Knudsen and surface diffusion) as well as on the tortuosity by means of the differential pressure-jump method.

## 7 Nomenclature

| | | |
|---|---|---|
| $A$ | m$^2$ | outer surface of a pellet |
| $A_s$ | m$^2$/g | BET surface area |
| $C$ | mol/m$^3$ | concentration in the gas phase in the pellet surroundings |
| $c$ | mol/m$^3$ | concentration within the pellets |
| $c_s$ | mol/m$^3$ | concentration in the adsorption phase of the pellet |
| $d_p$ | nm | pore diameter |
| $D_e$ | cm$^2$/s | effective diffusion coefficient |
| $D_K$ | cm$^2$/s | Knudsen diffusion coefficient for a straight cylindrical pore |
| $D_e^K$ | cm$^2$/s | effective Knudsen diffusion coefficient |
| $D_s$ | cm$^2$/s | surface diffusion coefficient |
| $L$ | m | length of a cylindrical pellet |
| $l$ | m | mean free path of molecules |
| $M$ | g/mol | molar mass |
| $n^s$ | mol/g | amount adsorbed |
| $p$ | h Pa | pressure |
| $R$ | gm$^2$/s | gas constant |
| $R$ | m | pellet radius |
| $r$ | m | radial coordinate |
| $r_p$ | nm | mean pore radius |
| $T$ | K | temperature |
| $t$ | s | time |
| $V$ | m$^3$ | volume of gas in pellet surroundings |
| $V_p$ | cm$^3$/g | specific pore volume |
| $v$ | m$^3$ | volume of a pellet |
| $z$ | m | axial coordinate |
| $\beta$ | | slope of adsorption isotherm |
| $\varepsilon$ | | porosity of the pellets |
| $\tau$ | | tortuosity |

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