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PROBLEMS IN THE DETERMINATION OF EFFECTIVE DIFFUSION COEFFICIENTS OF GASES AND LIQUIDS USING THE UP-TAKE TECHNIQUE

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Abstract

Diffusion processes play an important role in many areas of science and technology. Since pore diffusion processes strongly depend on the pore texture of the porous solid, a desired value of an effective diffusion coefficient, D^{eff}, has to be determined experimentally. Although, several measuring techniques have been described in the open literature, only a few of them can be used to set up a routine procedure. One of these methods is the so-called Up-Take Technique. The evaluation of the experimental data in this case, however, can lead to difficulties which will be discussed in detail.

Keywords: effective diffusion coefficients up-take technique.

Introduction

The material transport by diffusion plays an important role as the rate determining step in many processes in nature and technology. Frequently, it proceeds within the pore space of a porous solid. In that case, the characteristic properties of the porous material, e.g. the porosity, the pore size distribution and the connectivity of the pore system, influence the diffusional transport very strongly.

While the diffusion velocity of a given fluid component migrating in a homogeneous system can be predicted sufficiently well on the basis of the molecular theory of gases and liquids, see, e.g., [1], [2], the calculation of pore diffusion coefficients is still restricted. The reason for this stems from the fact that the influence of the aforementioned parameters on the value of the pore diffusion coefficient of a given component is not known in detail. It is, however, common practice to assume that the influence of the pore texture on the values of these coefficients can be expressed by the permeability Ψ, an empirical parameter, given by the product of the porosity ε and the labyrinth factor χ:

$$\Psi = \varepsilon\chi. \tag{1}$$

While ε-values are easy to determine, χ-values have to be evaluated by diffusion measurements. In order to perform such experiments, a number of stationary and non-stationary methods are at hand, see, e.g., [3], [4]. Since it is not the aim of this contribution to discuss them, let us focus our attention, however, to their characteristic differences. First of all, it has to be mentioned that the equipments for the performance of stationary diffusion experiments are much more complex than those for the performance of non-stationary ones. The evaluation of the results obtained, however, is much easier for the stationary techniques. In addition, the porous specimen must have the geometrical shape of a plate in stationary measurements, a restriction which does not exist in the other case.

Since it is generally assumed that proper determined Ψ-values do not depend on the nature of the diffusing gas nor on the thermodynamic parameters of a given system, it seems to be worth-while to look for an experimental set-up suitable for the performance of routine measurements. Taking into account that the aforementioned methods can give only values of effective diffusion coefficients, D^{eff}, we have to realize a technique which, in addition, yields some information on the diffusion mechanism taking place under the chosen measuring conditions. With this additional information, we were able to calculate the diffusion coefficient, D, of the given component in the framework of the molecular theories mentioned above. With this result we obtain the desired Ψ-value by using the relation:

$$\Psi = \frac{D^{\text{eff}}}{D}. \tag{2}$$

Since the evaluation of the experimental results can be done relatively easily with nowadays available computer facilities, it seems useful to take the so-called up-take technique, i.e., a non-stationary method, for the development of such a routine procedure.

Using the example of a gas/solid system, the principle of this measuring technique is demonstrated in *Fig. 1* The given porous material, whose Ψ-value is of interest, is filled to a vessel closed by a piston. A gas which is adsorbed on the inner surface of the material is added. After the adsorption equilibrium has been reached, the total gas pressure is increased abruptly with the help of the piston. As a response of the system to this pressure jump it tends to establish a new adsorption equilibrium state whereby the total pressure p decreases with time. Assuming the pore diffusion process to be the rate determining step, the value of the effective diffusion coefficient for the chosen gas can be obtained from the registrated $p(t)$-function.

In order to use this principle for the investigation of the diffusional transport of gases in porous solids, V. LERCH [5] developed the experimental set-up shown schematically in *Fig. 2*

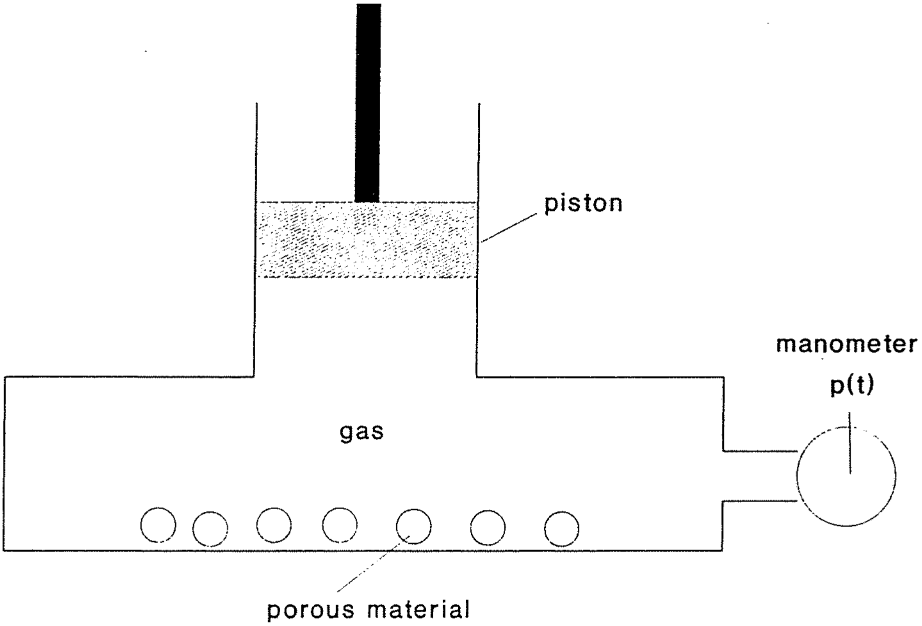

Fig. 1. Sketch of a set-up for the performance of gas up-take experiments

In this apparatus, he employed the so-called differential measuring technique to obtain a highly available experimental set-up. In this case, two identical vessels, labeled by 1 and 1', one containing the porous sample, are connected with the metal bellows B and B'. These bellows can be suddenly compressed to increase the gas pressure in the vessels. If the two vessels are seperated from another by valve 1, the pressure change in the vessel, containing the porous specimen, can be followed as a pressure difference between the vessels by the sensitive difference pressure sensor D.

The described up-take technique can also be taken to determine the effective diffusion coefficients of given liquid/solid systems. In *Fig. 3* a realisation is shown which was used to study the diffusion process of a dye in the pore space of porous SiO_2 material. In this set-up, the porous sample is fixed to a stirrer in order to reduce the influence of the boundary layer diffusion on the process of interest. In order to determine the effective diffusion coefficient the time change of the dye concentration in the solution, $C_D(t)$, was followed by a photometer.

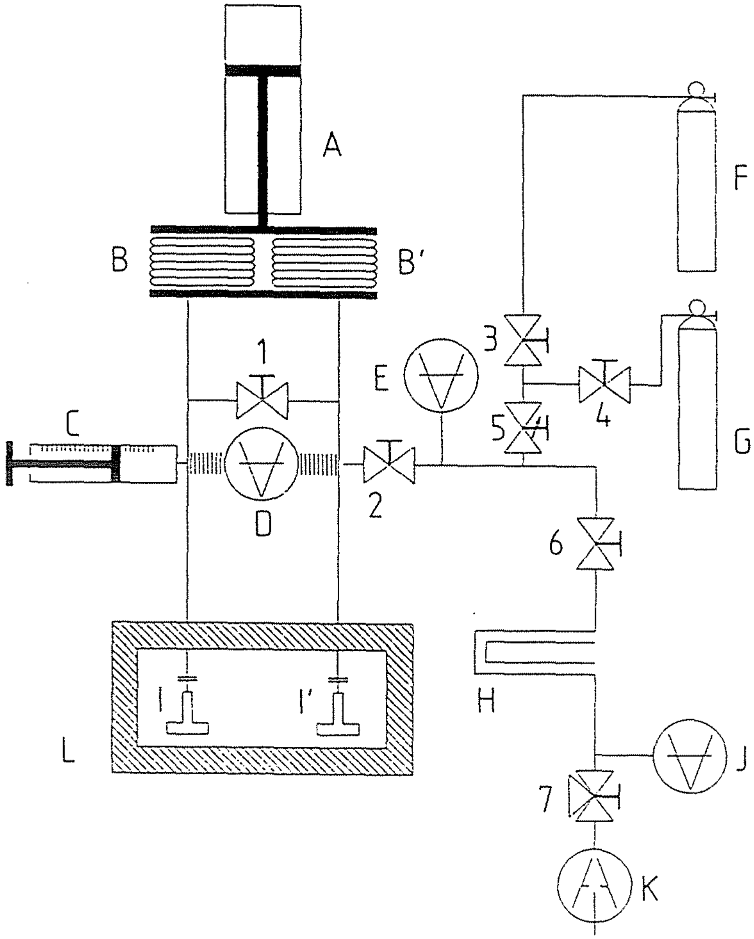

Fig. 2. Realization of an experimental set-up for performing gas up-take measurements according to LERCH [5].
A: piston; B, B': metal bellows; C: volume adjusting unit; L: thermostat with vessels; D: difference pressure sensor; E, J: pressure sensors; H: cooling device; F, G: gas supply

Problems in the Evaluation of the Results of Up-take Experiments

While the experimental set-up is relatively simple in both cases, the evaluation of the results obtained can lead to some problems. In order to discuss them, let us focus our attention to a gas/solid system, first.

For measuring the adsorption rate a pressure jump is applied to the system. The following pressure decrease as a function of time, however,

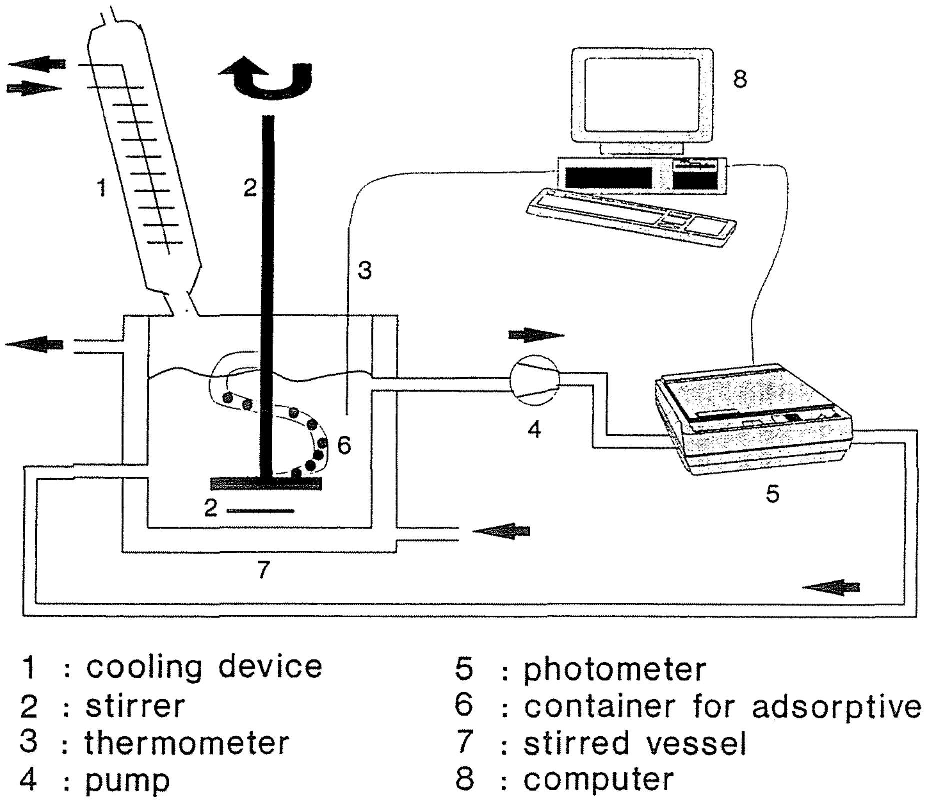

Fig. 3. Realization of a set-up for performing up-take experiments in liquid/solid systems

can only proceed by a diffusional mechanism in the pore space if Knudsen diffusion takes place. Otherwise, the $\Delta p(t)$-function will be markedly influenced by viscous Poiseuille flow. Thus, the diffusion experiments must be performed for sufficiently low gas pressure. In order to determine the desired D^{eff}-values, we, first of all, have to calculate from the $\Delta p(t)$-function the concentration change of the gas in the vessel containing the porous specimen, $c_g(t)$. Applying the material balance to a given porous particle, we have:

$$\varepsilon\left\{\frac{\partial c_1}{\partial t}+\frac{\partial c_1^a}{\partial t}\right\} = \operatorname{div}(D_K^{\text{eff}}\ \text{grad}\ c_1). \tag{3}$$

In this equation, ε stands for the particle's porosity. c_1 means the gas concentration in the pore space and c_1^a is the number of moles of the gas adsorbed on the inner surface of the pellet per unit pore volume. D_K^{eff} denotes the effective Knudsen diffusion coefficient.

In order to obtain the correct D_K^{eff}-value, the change of the concentration profile within each pellet has to be determined by solving equation (3) under the initial conditions:

$$\begin{array}{ll} c_1 = c_1^0 & \text{at the outer surface of the pellet'} \\ c_1 = c_1^{\infty} & \text{at the pellet's center} \end{array} \qquad (4)$$

and under the boundary conditions:

$$\begin{array}{ll} \text{grad } c_1 = 0 & \text{at the pellet's center,} \\ V_g \frac{dc_g}{dt} = \int_V \text{div}(\text{D}_K^{\text{eff}} \text{ grad } c_1)\ d\ V & \text{at the outer surface.} \end{array} \qquad (5)$$

In the last equation, the left hand side is obtained also from the $c_g(t)$-curve and the given volume V_g of the vessel containing the porous material.

The problem, thus, is to determine by trial and error that D_K^{eff}-value which leads to concentration profiles fulfilling not only the given differential equation but also the global balance expressed in *Eq.* (5). In solving it, let us assume the local adsorption equilibrium to be established within each pellet. In that case, we have the relation:

$$c_1^a = f(c_1) \qquad (6)$$

Denoting the derivative of the adsorption isotherm given in *Eq.* (6) by β, from *Eq.* (3), we obtain for constant D_K^{eff}-values the differential equation:

$$\frac{\partial c_1}{\partial t} = \frac{D_K^{\text{eff}}}{\varepsilon(1+\beta)} \Delta c_1 \qquad (7)$$

which has to be solved under the conditions given in the *Eq.* (4) and (5).

Taking the SiO_2 material AF 125 which is of spherical shape as the porous solid and n-butane as the measuring gas, V. LERCH [5] showed that the gas concentration as a function of time at the outer surface of the pellet, $c_1(R,t)$, can easily be calculated by solving *Eq.* (7) with the help of the *Cranck – Nicolson* method (see also [6]). As is demonstrated in *Fig. 4*, the calculated concentration values do agree sufficiently well with the measured $c_g(t)$-values for proper chosen D_K^{eff}-values. Since the adsorption isotherm is a straight line for a measuring temperature of 330 K up to a total pressure of 600 mbar, (*Fig. 5*), it can be shown [7] that the material transport within the pore space of the pellet proceeds by Knudsen diffusion since the D_K^{eff}-values are constant within the chosen pressure interval, (*Fig. 6*). Taking into account that the effective Knudsen diffusion coefficient follows the relation:

$$D_K^{\text{eff}} = \varepsilon \chi \frac{2}{3} \overline{r v}, \qquad (8)$$

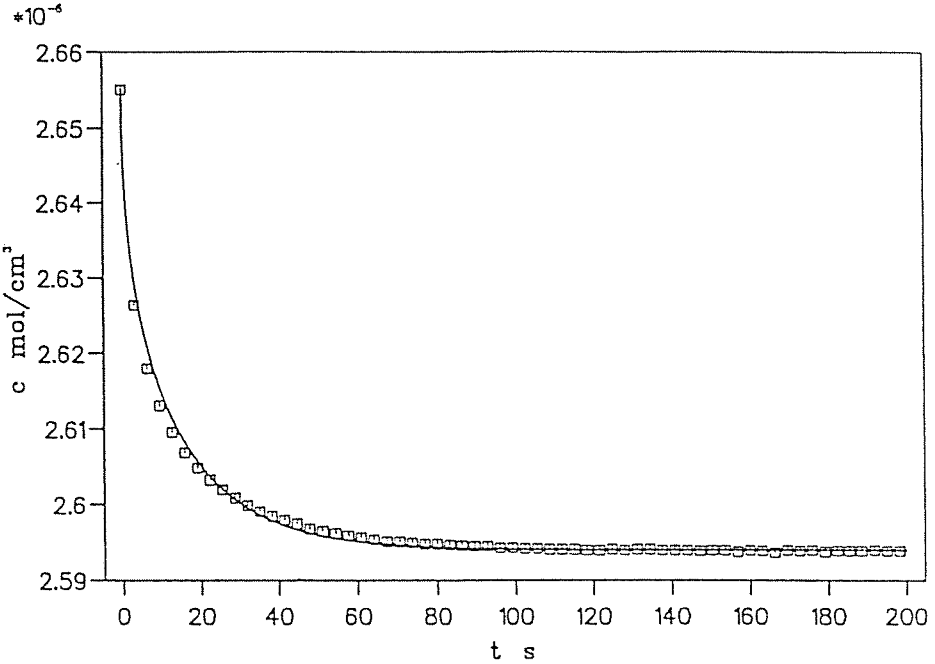

Fig. 4. Comparison of the measured $c_g(t)$-values (squares) to the calculated $c(R,t)$-function (curve)

wherein $\overline{r}$ denote the mean pore radius and $\overline{v}$ the mean thermal velocity, we obtain with the data given in *Table 1* a χ-value of 0.633. Since we can expect the porous solid to be an agglomeration of spherical particles this result is, indeed, realistic. The proposed measuring technique, thus, seems to be useful.

This statement is further confirmed by experiments performed with ethene as the measuring gas, see *Fig. 7*. We obtain a χ-value of 0.689 showing that the labyrinth factor is independent oF the chosen gaseous component.

Taking the porous SiO_2 material T 1571 as the solid and n-butane as the measuring gas the experiments lead to a χ-value of 0.7 for a measuring temperature of 333 K. Lowering the temperature to 268 K, however, gives the unrealistic value: $\chi \approx 1.3$. In addition, it is observed that the calculated D_K^{eff}-values increase with increasing pressure.

In order interpret these findings, let us assume that the material transport within the pore space of the solid proceeds not only by Knudsen dif-

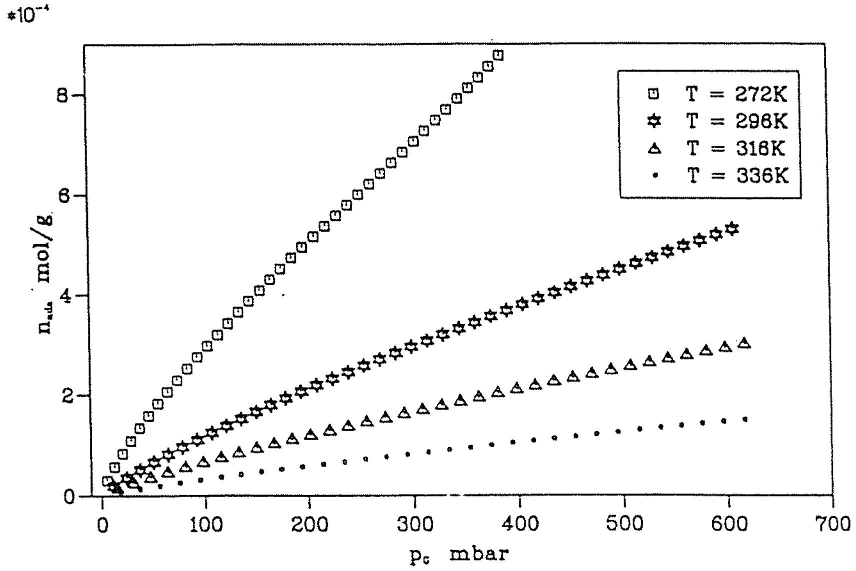

Fig. 5. Adsorption isotherms of the n-butane/AF 125-system

fusion, but also by surface diffusion. In that case, the material balance equation states:

$$\varepsilon\left(\frac{\partial c_1}{\partial t}+\frac{\partial c_1^a}{\partial t}\right)=\operatorname{div} D_K^{\text{eff}}\ \operatorname{grad} c_1+D_s\ \operatorname{grad} c_1^a, \tag{9}$$

wherein D_s is the surface diffusion coefficient. Assuming the local adsorption equilibrium to be established, *Eq.* (9) leads to the differential equation:

$$\frac{\partial c_1}{\partial t}=\frac{D_K^{\text{eff}}}{\varepsilon(1+\beta)}\operatorname{div}\left[\left\{1+\frac{D_s}{D_K^{\text{eff}}}\varepsilon\beta\right\}\operatorname{grad} c_1\right]. \tag{10}$$

Taking the initial pressure change sufficiently small, we can assume the value of the sum:

$$1+\frac{D_s}{D_K^{\text{eff}}}\varepsilon\beta \tag{11}$$

to be a constant during the experiments. Thus we do not determine pure D_K^{eff}-values in this case but D^{eff}-values given by the relation:

$$D^{\text{eff}}=D_K^{\text{eff}}+\beta D_s. \tag{12}$$

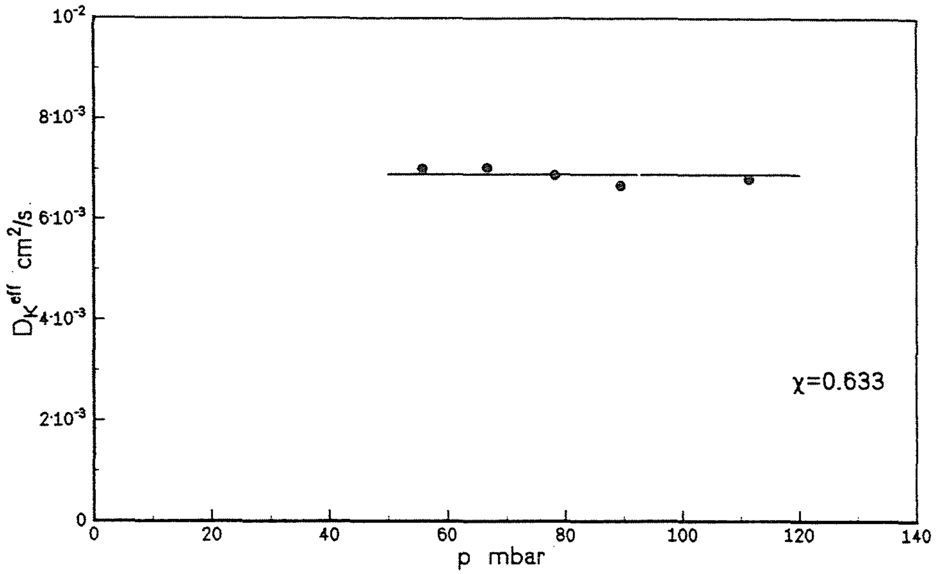

Fig. 6. Effective Knudsen diffusion coefficient as a function of pressure; temperature 333 K; systeme: *n*-butane/AF 125

Since the β-values increase with increasing pressure for the system in question (see *Fig. 8*, we, indeed, have pressure dependent D^{eff}-values. Assuming the surface coverage by n-butane to be sufficiently small, the D_s-values are constant. In that case, we expect the D^{eff}-values to increase linearly with increasing β-values. As it is shown in *Fig. 9* this is, indeed, the case.

These experiment have an interesting consequence. If we take a gas strongly adsorbed on the solid surface, the main transport mechanism for establishing the adsorption equilibrium can be surface diffusion. Such a situation is realized in the system clay/water. In that case the β-values are in the order of several thousand. Assuming the adsorption equilibrium to follow the Langmuir concept and the surface diffusion process to obey the model of HIGASHI, ITO and OISHI [8] we have the relations:

$$D_s = \frac{D_s^\circ}{1-\Theta}, \tag{13}$$

$$\Theta = \frac{bp}{1+bp}$$

i.e.

$$D_s = D_s^\circ(1+bp). \tag{14}$$

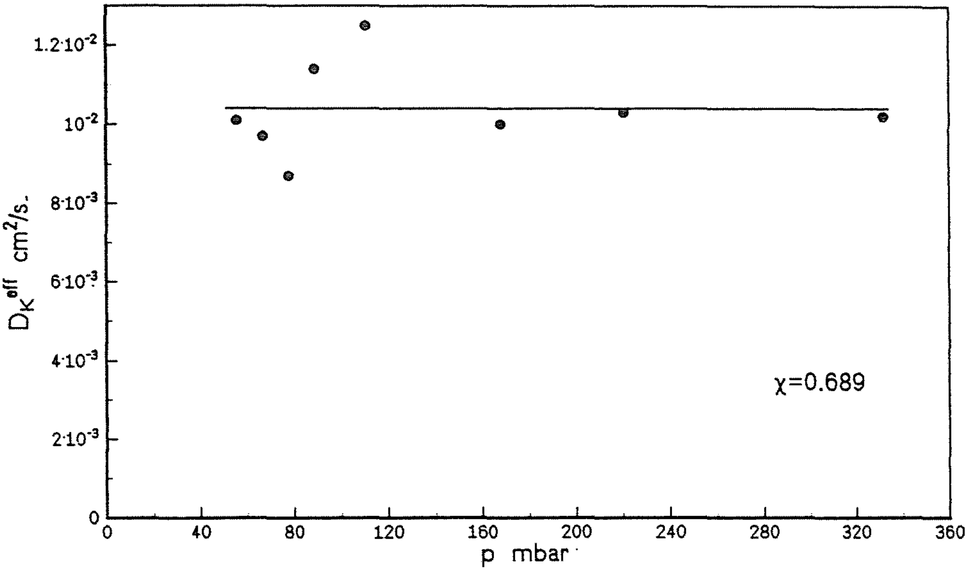

Fig. 7. Effective Knudsen diffusion coefficient as a function of pressure, temperature 272 K; system: ethene/AF 125

Table 1
Characteristic data of the porous materials

	AF 125	T 1571
shape	spherical	spherical
diameter [mm]	2.5	4.5
g [m^2/g]	300	113
V_p [cm^3/g]	0.91	0.91
ϵ	0.64	0.64
ρ_p [g/cm^3]	0.79	0.79
ρ_s [g/cm^3]	2.2	2.2
mean pore radius [Å]	50	90

Wherein D_s° is the surface diffusion coefficient for a vanishing surface coverage Θ. b denotes the adsorption coefficient. Plotting the measured D_s-values as a function of pressure, we obtain the relationship depicted in *Fig. 10*. From the interept with the ordinate and the slope of the line, we get the values:

$$\begin{aligned} D_s^\circ &= 1.05 \cdot 10^{-3}\ \mathrm{cm}^2/\mathrm{sec} \\ b &= 0.16\ \mathrm{mbar}^{-1} \end{aligned} \tag{15}$$

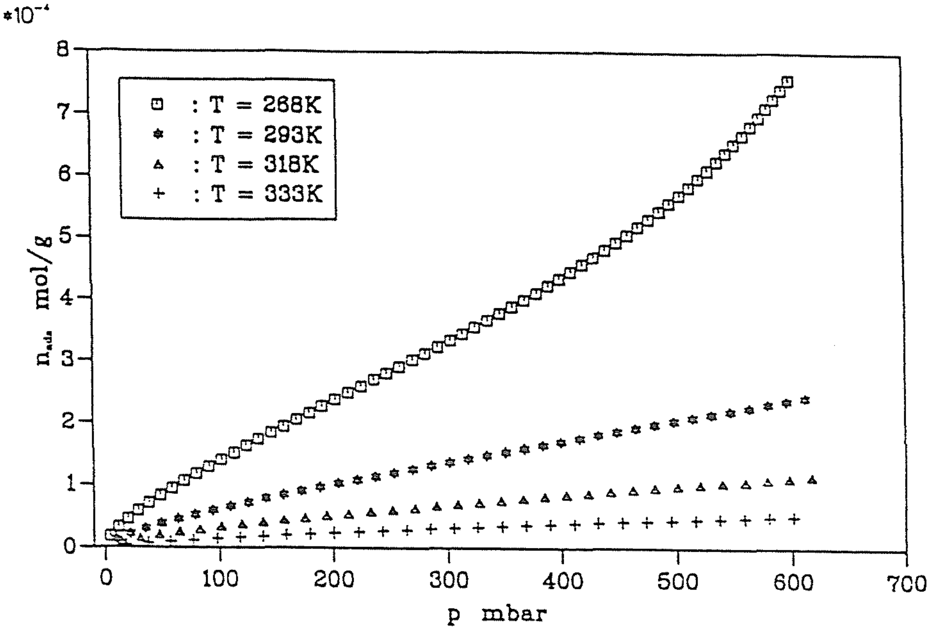

Fig. 8. Adsorption isotherms of the *n*-butane/T 1571 system

for a temperature of 297 K. Although the adsorption isotherm leads to a b-value of 0.25 mbar^{-1} the agreement is sufficiently good. We, thus, have to conclude that the proposed technique can also be used to investigate the main influences on surface diffusion processes, provided, the temperature is taken low enough to allow for large β-values. If we are interested in χ-values, the temperature must be chosen so that the rate determining step for establishing the adsorption equilibrium is Knudsen diffusion.

The question now arises if similar particuliarities occur in liquid/solid systems. In discussing it, we investigated the diffusion process of dimethylthionine dissolved in water in the pore space of the SiO_2 material AF 125. The experiments were performed in that way that preloaded porous material was added to the solution of the dye in the experimental set-up depicted in *Fig. 3*. The dye concentration in the solution was chosen so that the total concentration change due to the dimethylthionine adsorption on the preloaded pellets was relatively small.

Since we know from the investigations described above that for the taken material the Ψ-value equals 0.66, we were able to estimate the expected D_F^{eff}-value by using the equation of WILKE and CHANG [9]:

$$D_F = 7.4 \cdot 10^{-8}\ (2.6\ M_L)^{1/2} \frac{T}{\eta_L V_F^{0.6}} \qquad [\text{cm}^2/\text{sec}]. \tag{16}$$

Herein, M_L is the molecular mass of the solvents, η_L its viscosity and T the temperature. V_F means the molecular volume of the diffusing component. Inserting the appropriate parameter values into *Eq.* (16), we obtain:

$$D_F = 4.6 \cdot 10^{-6}\ \text{cm}^2/\text{sec}, \quad \text{i.e.} \quad D_F^{\text{eff}} = 3.0 \cdot 10^{-6}\ \text{cm}^2/\text{sec}. \tag{17}$$

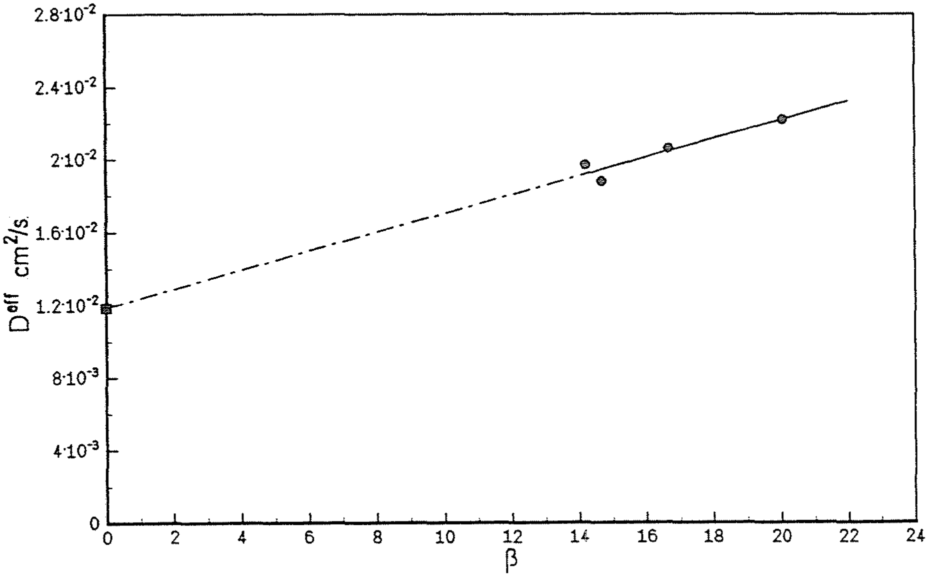

Fig. 9. Effective diffusion coefficient as a function of b; temperature 268 K; system: *n*-butane/T 1571

In *Fig. 11*, the experimentally determined D_F^{eff}-values are plotted as a function of the number of moles of the dye, n, adsorbed per gram of solid. While the values for low surface coverage agree relatively well with the expected values, large deviations are obtained for higher n-values. Since dimethylthionine is a relatively large molecule of rectangular shape, see *Fig. 12*, it is not useful to assume that surface diffusion processes can cause such a behaviour. The reason for this peculiarity seems to come from the fact that the dye molecules exist as ions when dissolved in water,

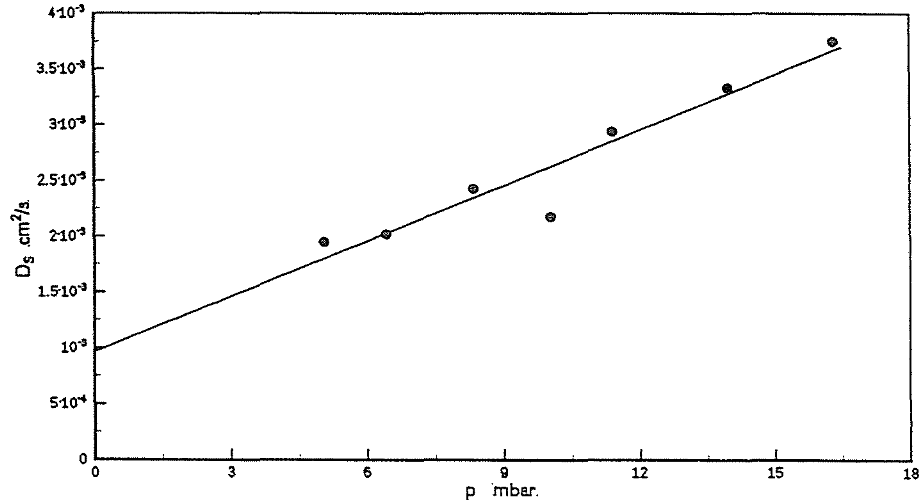

Fig. 10. Surface diffusion coefficient as a function of gas pressure; temperature 297 K; system: clay/water

see *Fig. 12.*These ions are bounded to the surface for low surface coverage in a flat form while they erect for higher coverage. This behaviour can easily be recognized in the form of the adsorption isotherm of the system shown in *Fig. 13*. Since the area of an adsorption site for the first adsorption state is much larger than for the other one, the monomolecular coverage is lower in the former. Taking into account, that the mean pore radius is nearly 5 nm for the SiO_2-material AF 125, the adsorption state for higher surface coverage, i.e. for n-values larger than 0.04, can lead to pore blocking processes in the narrow parts of the pore space. Since these processes can reduce the χ-value dramatically, it is not surprising that the measured values for the diffusion coefficients of the dye molecules are so small for higher n-values. As a consequence, the time needed to reach the new adsorption equilibrium in the porous sample will become dramatically long, e.g. several hundred hours. Simultaneously, the change in the dye concentration of the solution as a function of time will become relatively small. In that case, we will reach the limits of this measuring technique since the equilibrium state is hard to determine.

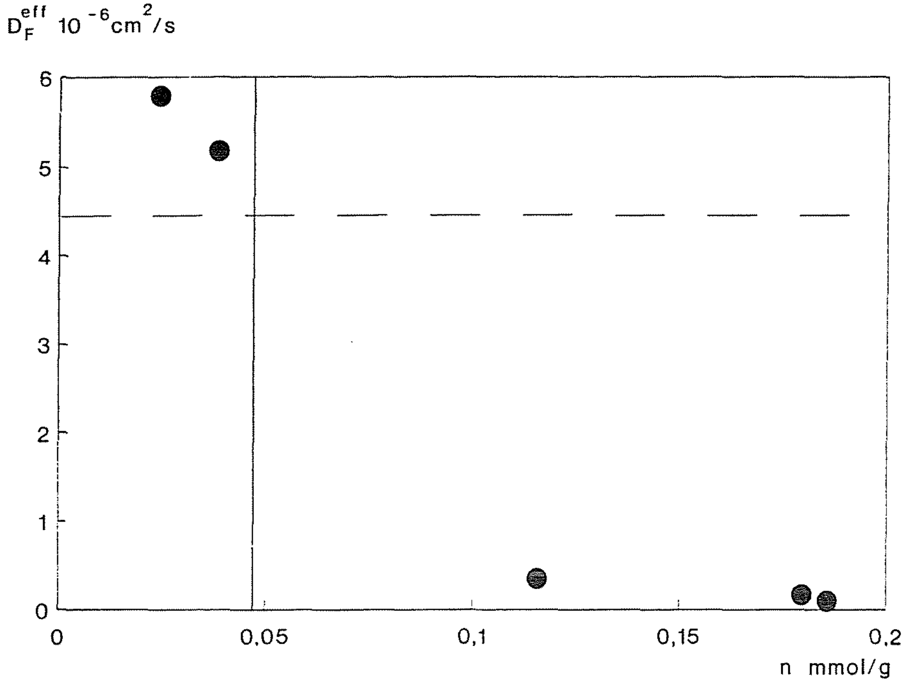

Fig. 11. Effective diffusion coefficient as a function of adsorbed moles of the dye, n; system : dimethylthionine dissolved in water/AF 125

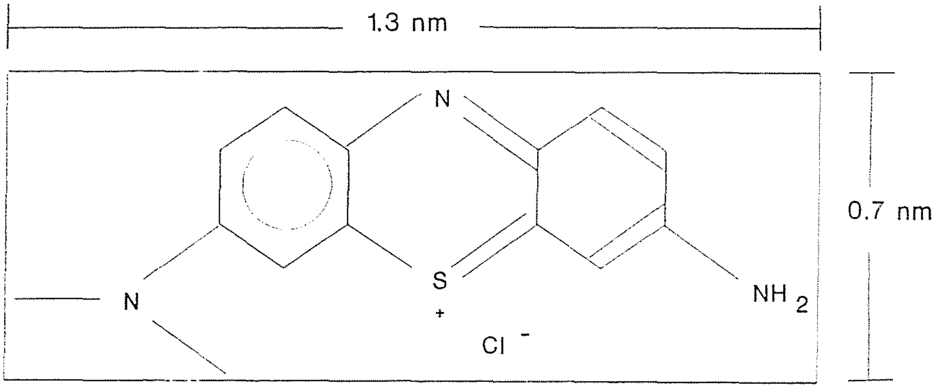

Fig. 12. Geometrical shape of a dimethylthionine molecule

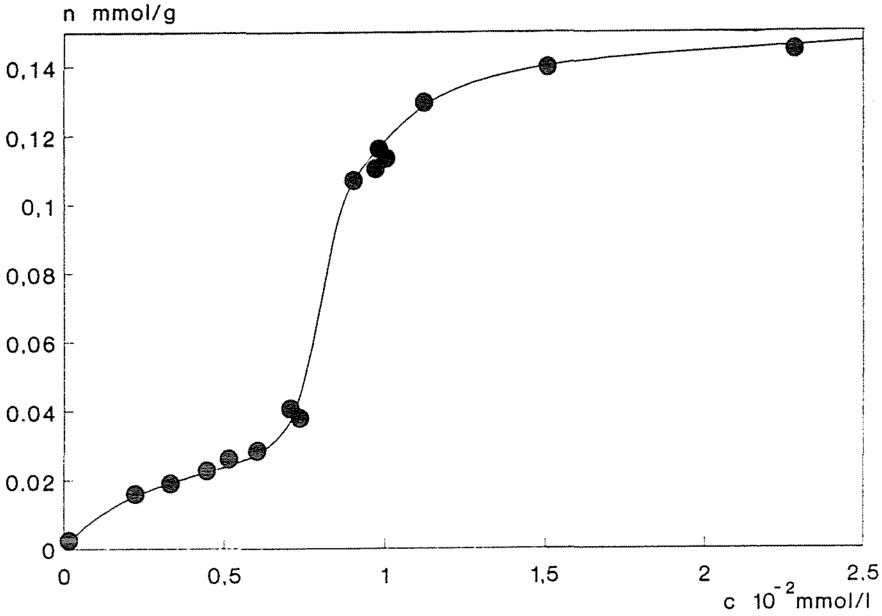

Fig. 13. Adsorption isotherm of the system dimethylthionine/water/AF 125; temperature 295 K

Conclusion

In summing up, we have to state that the Up-Take Technique can, indeed, be used to set up a routine procedure for the investigation of the diffusional transport in the pore space of a porous material. The evaluation of the experimental results, however, requires a detailed knowledge of the adsorption behaviour of the system. Since the measurements can be performed in that way that the adsorption isotherm is obtained as an additional result of the experiments, thus, this requirement leads to no disadvantage. Mathematical problems, however, can arise for those cases in which the porous specimen is of cylindrical shape and/or the effective transport coefficients depend on the local concentration of the migrating component. In order to circumvent these difficulties in a set-up for routine measurements much more work has to be done in this field.

List of symbols

b	adsorption coefficient
c_D	dye concentration in the solution
c_g	gas concentration
c_1	concentration in the gas phase
c_1^a	concentration of the adsorption phase
D^{eff}	effective diffusion coefficient
D_K^{eff}	effective Knudsen diffusion coefficient
D_F	diffusion coefficient of a liquid
D_F^{eff}	effective diffusion coefficient of a liquid
D_s	surface diffusion coefficient
M_L	molecular mass of the solvent
p	pressure
T	temperature
V_g	volume of the vessel
V_F	molecular volume of the diffusing component
β	derivative of the adsorption isotherm
ε	porosity
η_L	viscosity of the solvent
χ	labyrinth factor
Ψ	permeability

Acknowledgement

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