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Mass transfer within the gas-phase of porous media

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Abstract

The laws of various transport modes—viscous flow, diffusion and Knudsen flow—can be caused by the gradients of concentration, total and partial pressure. Their combined transports are derived and proved by selected experiments in the continuum as well as in the Knudsen region. The combination of these transport modes leads to phenomena like pressure diffusion, slip flow and diffusive slip. The three transport coefficients—the permeability, the binary diffusion coefficient and the Knudsen coefficient—can be determined by steady-state permeability and diffusion measurements. Nonsteady-state measurements deliver additional information about the pore structure of the porous medium. The presented measurements were carried out at cylindrical samples of rock salt with low porosity. Hydrogen and nitrogen were used as nonadsorbing gases. The binary diffusion experiments confirm Graham's law with good accuracy. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

When isothermal conditions are assumed—T is the constant—in the pores of the porous medium the mass transfer can take place by viscous flow, Knudsen flow or ordinary diffusion. A transport of adsorbed molecules or atoms on solid surfaces—called surface diffusion—should be neglected. In the continuum region the mean free path of the gas is small compared with the pore diameter. Here molecule-molecule collisions predominate over molecule-wall collisions. The Knudsen number, the ratio of the mean free path of the gas to the pore diameter ($Kn=\lambda/d_{\mathrm{pore}}$), is less than 1 ($Kn \ll 1$). In a single gas a gradient of total pressure ∇p[1]) leads to a viscous flow. The flux can be described by Darcy's law [1]. In the Knudsen region the mean free path of the gas is large relative to the pore diameter ($Kn > 1$). Molecule-wall collisions predominate over molecule-molecule collisions [2]. The mass transport due to a pressure gradient can be described by Knudsen's law.

If the mean free path is small compared with the pore diameter (continuum region), in a gas mixture a concentration gradient ∇y_i leads to a mass transfer due to ordinary diffusion. If a gradient of total pressure additionally exists, the fluxes due to viscous flow must be added to the diffusive fluxes. The diffusive fluxes of a multicomponent mixture can be described by the Stephan–Maxwell equations. The diffusive fluxes of a binary mixture can be described by Fick's first law of diffusion, a special case of the Stephan–Maxwell equations and the viscous fluxes by Darcy's law. The viscous component of the flow is nonseparative. In the Knudsen region a gradient of concentration ∇y_i and total pressure ∇p leads to a mass transfer due to Knudsen flow. Here is no fundamental distinction between flow and diffusion and the molecules act

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[1] In the following the symbol ∇ designates the derivation in the z-direction, i.e. the direction of the flux.

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Nomenclature

c	molar density [kmol/m^3]
d_{pore}	pore diameter [m]
D	effective diffusion coefficient [m^2/s]
$\dot{J}$	molar flux relative to the mass-average velocity [kmol/(m^2 s)]
k	true permeability [m^2]
L	length of the sample [m]
M	molecular weight [kg/kmol]
$\dot{N}$	molar flux relative to stationary coordinates [kmol/(m^2 s)]
p	pressure [bar]
p_i	partial pressure of component i [bar]
$\mathcal{R}$	gas constant [J/(kmol K)]
t	time [s, h]
T	temperature [K]
$\dot{V}$	flow rate [m^3/s, ml/min]
V_a	volume of the vessel installed at the end of the sample [m^3, ml]
y	mole fraction

Greek letters

α	separation factor
δ	diffusion coefficient in the free space [m^2/s]
Λ	mean free path of the gas
ϵ_p	porosity
ϵ_a	accessible porosity
η	dynamic viscosity [Pa s]
μ_i	ratio of relative mole masses, $(M_{12}-M_i)/M_{12}$
μ_p	tortuosity factor
ρ	mass density [kg/m^3]

Indices

i, 1, 2	components
dif	flux due to ordinary diffusion
D	combined flux due to ordinary diffusion and Knudsen flow
kn	Knudsen
vis	viscous

Superscripts

p	flux due to a gradient of pressure
y	flux due to a gradient of mole fraction

entirely independently of each other. The fluxes are proportional to the gradient of the partial pressure of each component ∇p_i. Often Fick's first law is formed with the gradient of the partial pressure, too. We have to discuss whether Fick's first law of diffusion is related to the gradient of the partial pressure ∇p_i or to the gradient of the concentration ∇y_i. This is not of any importance in case of a vanishing pressure gradient ($\nabla p \approx 0$), however it is a basic problem in case of simultaneously existing diffusion and viscous flow. Additionally it should be discussed, whether in a gas mixture, which consists of two species with different molecular weights ($M_1 \neq M_2$), the ratio of the diffusion fluxes obeys Fick's law ($\sim M_2/M_1$) or Graham's law ($\sim \sqrt{M_1/M_2}$) [4] and under which conditions equimolar countercurrent diffusion can be assumed ($|\dot{N}_{1,\text{dif}}| = |\dot{N}_{2,\text{dif}}|$).

Special attention should be paid to the effects, which occur in the case of the combination of the various transport mechanisms: slip flow, diffusive slip and pressure diffusion. They only reach importance in the transition region ($0.01 < Kn < 1$) (Fig. 1). The different transport mechanisms are caused by different effective gradients—∇p, ∇p_i and ∇y_i. A direct addition is not automatically admissible.

The work 'The Dusty-Gas Model' from Meason and Malinauskas [10] gives a comprehensive survey of the gas transport in porous media. But the work cannot answer all the above asked questions. With regard to the combination of ordinary and pressure diffusion with viscous flow and Knudsen flow unanswered questions remain. For example in [10], Eq. (5), the diffusive flux is formed with the gradient of the molar concentration $\nabla n_i = \nabla(p_i/k_B T) \sim \nabla p_i$, which is certainly correct in case of constant pressure ($\nabla p = 0$). Ordinary

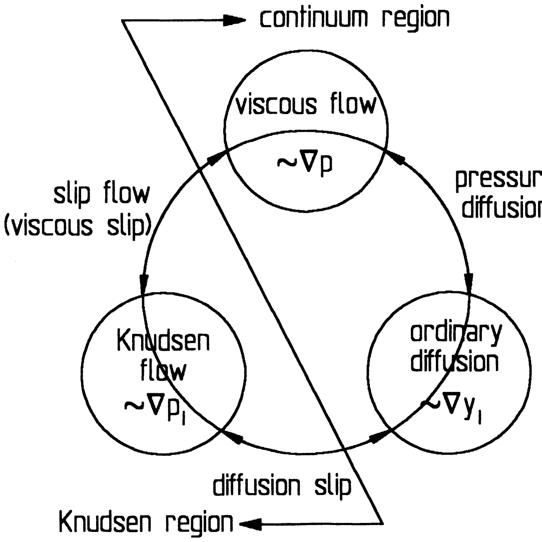

Fig. 1. Mass transport in the gas phase.

and Knudsen diffusion occur in series and at uniform pressure their combination is easily possible in this manner. This reflection fails in case of an additional pressure gradient ($\nabla p \neq 0$), Eqs. (25)–(32) in [10]. This is comprehensible when imagining that in a flowing gas mixture due to a pressure gradient ∇p the composition has to be constant, if therein is not any concentration gradient $\nabla y_i = 0$. But in the case of $\nabla y_i = 0$ and $\nabla p \neq 0$ the gradient of the partial pressure are not zero ($p_i \neq 0$). A diffusive flux should occur after this derivation. In [10], Eq. (60), this statement of the diffusive flux is justified by the effect of pressure diffusion. However there is a simplification that is not comprehensible: the dependence of the pressure diffusion from the molecular weights $(M_{12}-M_i)/M_{12}$ is neglected. It will be shown that this assumption is justified in many cases, however in some cases the influence of the molecular weights is directly provable. The correct consideration of pressure diffusion and the combination of ordinary and pressure diffusion with Knudsen flow leads to more complex dependencies of the molecular weights and the gradients of the various fluxes as shown in [10], Eq. (63) and (120). The transport phenomena have already been investigated in detail by Wicke et al. [5–9,24]. Until today these works have only recently been taken into account for technical applications. For use of microporous substances e.g. in adsorption techniques for gas purification or for use of waste disposal in salt mines, where radioactive gas components could permeate and diffuse through the porous rock salt, more detailed knowledge about the mass transport in porous media are demanded in order to enable safe drafts. For these purposes the presented work should give a comprehensive summary with regard to technical applications.

However until today we have not known any model to describe under consideration of the reciprocal effects stated above between the transport mechanisms, with chemical potential as the only driving force. Finally all efforts to describe the mass transport by means of models must be considered as approximation to the complex facts, including the presented paper.

In the presented paper the theoretical derivations are illustrated and confirmed by selected permeability and diffusion measurements. They are taken from a work where the permeability and diffusion behavior of hydrogen and nitrogen was investigated in core samples of rock salt [3].

2. Mass transfer of a single gas through porous media

The isothermal mass transport in a single gas takes place only by a pressure gradient ∇p. The flow rate through the porous medium due to the pressure gradient can be described by Darcy's law:

$$\dot{N}_{vis} = -\frac{k}{\eta} c \nabla p \tag{1}$$

where the gravity was neglected. The permeability only depends on the pore structure of the porous medium. Under consideration of an ideal gas and the following boundary conditions $p(z=0)=p_{\mathrm{e}}$; $p(z=L)=p_{\mathrm{a}}$ the integration gives

$$\dot{N}_{\mathrm{vis}} = \frac{k}{\eta}\frac{1}{\mathscr{R}T}\frac{p_{\mathrm{e}}^2 - p_{\mathrm{a}}^2}{2L} = \frac{k}{\eta}\frac{\bar{p}}{\mathscr{R}T}\frac{\Delta p}{L} \quad \text{with} \quad \bar{p} = \frac{p_{\mathrm{e}} + p_{\mathrm{a}}}{2}. \tag{2}$$

In the continuum region the flow through the pores of the porous medium can be assumed as laminar, which is justified under consideration of the dimensions of the pores. Darcy's law has the same form like the Poiseuille's law for laminar flow in a cylindrical tube. The following expression of the flow rate through a porous media can be found by applying Poiseuille's law:

$$\dot{N}_{\mathrm{vis}} = -\frac{\epsilon_{\mathrm{p}}}{\mu_{\mathrm{p,\,vis}}}\frac{\bar{d}^2_{\mathrm{pore}}}{32\eta} c \nabla p \tag{3}$$

where $\bar{d}_{\mathrm{pore}}$ describes a mean pore diameter and ϵ_{p} the porosity, which only takes into account the volume of the pores that go from one face of the porous medium right through to the other. The tortuosity factor $\mu_{\mathrm{p,vis}}$ takes account of the additional drag by the irregular shape and the actual length of the pores in comparison with a bundle of straight, parallel capillaries with constant diameter. The tortuosity factor μ_{p} can be divided into a path elongation factor μ_{L} and a shape factor μ_{F} ($\mu_{\mathrm{p}} = \mu_{\mathrm{L}}\mu_{\mathrm{F}}^2$). This fact should not be discussed in detail here. From the Poiseuille's law and Darcy's law the following relation of the permeability to the pore diameter can be found:

$$k = \frac{\epsilon_{\mathrm{p}}}{\mu_{\mathrm{p,\,vis}}}\frac{\bar{d}^2_{\mathrm{pore}}}{32\eta}. \tag{4}$$

2.1. Knudsen or free-molecule flow

In the Knudsen region ($Kn > 1$) the mass transfer of a gas occurs due to free-molecule flow [2]:

$$\dot{N}_{\mathrm{kn}} = -\frac{4}{3}\bar{d}_{\mathrm{pore}}\frac{\epsilon_{\mathrm{p}}}{\mu_{\mathrm{p,\,kn}}}\sqrt{\frac{1}{2\pi\mathscr{R}TM}}\nabla p \tag{5}$$

where ϵ_{p} describes again the porosity and $\mu_{\mathrm{p,kn}}$ the tortuosity factor, which however differs from the tortuosity factor $\mu_{\mathrm{p,\,vis}}$ [11]. It is possible to introduce an effective Knudsen coefficient D_{kn}:

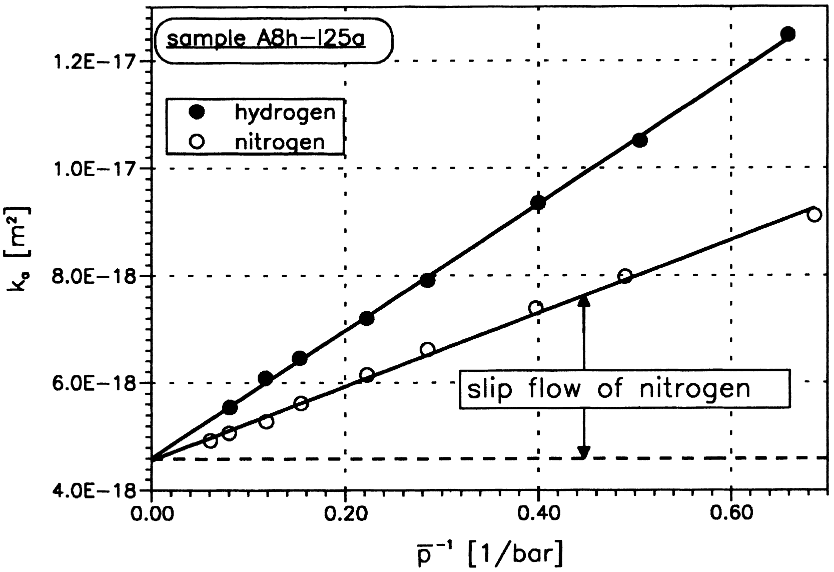

Fig. 2. Apparent permeability of hydrogen and nitrogen.

$$\dot{N}_{\mathrm{kn}} = -\frac{D_{\mathrm{kn}}}{\mathcal{R}T}\nabla p \tag{6}$$

with

$$D_{\mathrm{kn}} = \frac{4}{3}\bar{d}_{\mathrm{pore}}\frac{\epsilon_{\mathrm{p}}}{\mu_{\mathrm{p,\,kn}}}\sqrt{\frac{\mathcal{R}T}{2\pi M}}. \tag{7}$$

2.2. Transition region

In the transition region ($0.01 < Kn < 1$) the flux through a porous medium due to a pressure gradient can be described as the sum of the fluxes due to viscous flow and due to Knudsen flow [2]. The part of the Knudsen flow is called 'viscous slip' or 'slip flow', because the velocity at the solid walls is not zero. Considering the Eqs. (1), (3) and (6) the flux can be calculated:

$$\dot{N} = \dot{N}_{\mathrm{vis}} + \dot{N}_{\mathrm{kn}} = -\left(\frac{k}{\eta}p + D_{\mathrm{kn}}\right)\frac{1}{\mathcal{R}T}\nabla p. \tag{8}$$

For analysis and evaluation of the measurements an apparent permeability k_a should be introduced[2]

$$\dot{N} = \frac{k_{\mathrm{a}}}{\eta}\frac{\bar{p}}{\mathcal{R}T}\nabla p \tag{9}$$

$$k_{\mathrm{a}} = k\left(1 + \frac{D_{\mathrm{kn}}\eta}{k\bar{p}}\right) \tag{10}$$

The apparent permeability is a linear function of the reciprocal mean pressure (Fig. 2). The part of slip flow is also called Klinkenberg-part [12]. This part is for hydrogen greater than for nitrogen, because for a given mean pressure the mean free path of hydrogen is greater than for nitrogen. Hence the slope of the apparent permeability vs. the reciprocal mean pressure is steeper for hydrogen than for nitrogen as used gas.

The Knudsen coefficient was introduced as a pressure independent value. However at very low pressure Knudsen [12] found a weak pressure dependence, that can be neglected in nearly all technical applications. The apparent permeability k_{a} extrapolated to infinite pressure ($\bar{p}^{-1} = 0$) gives the true permeability, which only depends on the pore structure of the porous medium. With the knowledge of the viscosity of the used gas the Knudsen coefficient is obtained from the slope of the apparent permeability. With use of a second gas, e.g. hydrogen instead of nitrogen, the measured values of the true permeability and of the Knudsen coefficient can be confirmed. The Knudsen coefficients of two gases behave inversely proportional to the square root of the molecular weight ratio:

$$\frac{D_{\mathrm{kn,\,1}}}{D_{\mathrm{kn,\,2}}} = \sqrt{\frac{M_2}{M_1}}. \tag{11}$$

2.3. Nonsteady-state permeability measurements

The goal of the nonsteady-state methods is the de-

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[2] Instead of the apparent permeability k_{a} acc. to Eq. (10) an apparent permeability coefficient $K = \bar{p}k_{\mathrm{a}}/\eta = \bar{p}k/\eta + D_{\mathrm{kn}}$ is also possible [10], whose application vs the mean pressure $\bar{p}$ is a straight line of equivalent meaning.

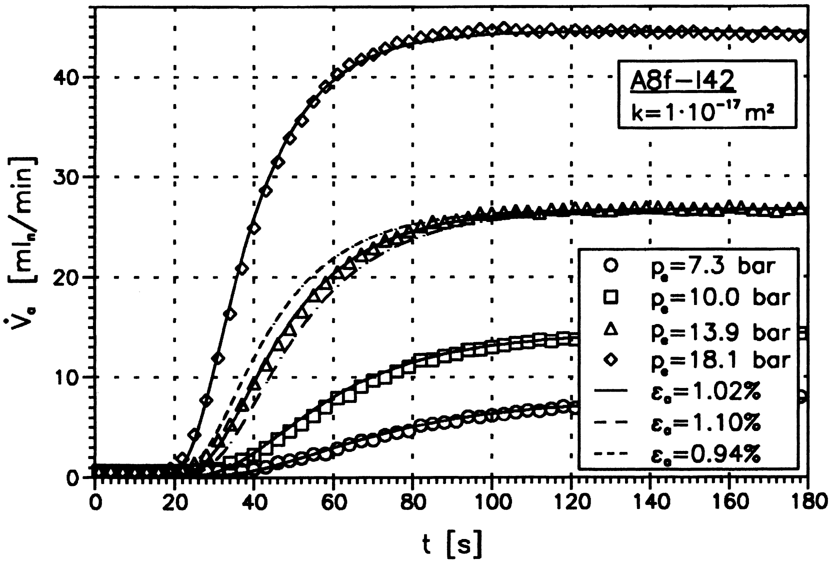

Fig. 3. Volume rate of flow at the end of the sample after a suddenly increased injection pressure at time $t = 0$ (observed and calculated flows at different injection pressures in the open system).

termination of the accessible porosity, the ratio of the accessible void space inside the porous medium, that can be reached from the external surface, to the total volume of the porous medium [13]. The accessible porosity is normally smaller than the total porosity of a system, because the total porosity contains all parts of the void space, regardless of whether they can be reached. At time $t = 0$ the pressure in front of the upstream end face of the core sample is suddenly increased from atmospheric pressure up to the pressure p_e and then it is maintained constant. In the open system the pressure p_a is kept at atmospheric pressure. Some time after the pressure jump a slowly increasing flow is measured at the end of the sample. After some time the flow reaches steady state (Fig. 3). In the half-open system a closed vessel is installed at the end of the sample. The pressure in the vessel is measured as a function of time from $t \geq 0$, Fig. 4.

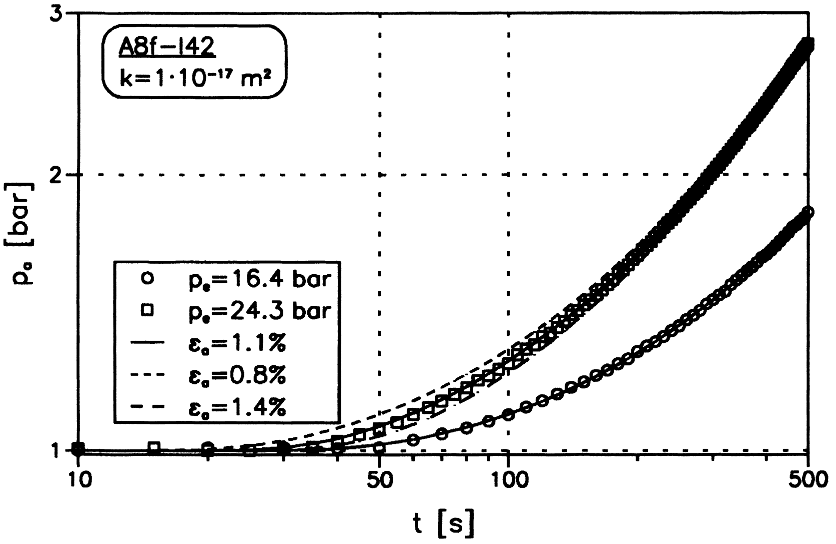

Fig. 4. Pressure in a closed vessel installed at the end of the sample after a jump of the injection pressure (observed and calculated pressures in the half-open system).

For the determination of the accessible porosity ϵ_a the equation of continuity must be solved within the sample ($0 < z < L$):

$$\epsilon_a \frac{\partial c}{\partial t} = -\nabla \dot{N} \tag{12}$$

with the following boundary conditions:

open system

$$p(z=0,\ t \geq 0) = p_e = \text{const.}$$

$$p(z=L,\ t \geq 0) = p_a = \text{const.}$$

half-open system

$$p(z=0,\ t \geq 0) = p_e = \text{const.}$$

$$p(z=L,\ t=0) = p_a = p_e$$

$$\left.\frac{\partial p}{\partial t}\right|_{z=L} = \frac{A}{V_a}\left(\frac{k}{\eta}p + D_{kn}\right)\left.\frac{\partial p}{\partial z}\right|_{z=L} \rightarrow p_a = f(t).$$

The flux $\dot{N}$ is calculated by Eq. (8), where the permeability k and the Knudsen coefficient D_{kn} are already known from the steady-state measurements. Consequently in Eq. (12) the accessible porosity remains as the only unknown. In the numerical solution the accessible porosity is chosen in the way that measurement (symbol) well agrees with calculation (solid line), Figs. 3 and 4. The calculated solution reacts very sensitively to various values of the accessible porosity; compare solid and dashed curves.

3. Mass transport in a binary gas mixture

In a gas mixture the gradient of concentration ∇y_i leads to a mass transfer due to ordinary diffusion and Knudsen flow. An additional pressure gradient ∇p leads to a mass transfer due to viscous flow, Knudsen flow and pressure diffusion.

3.1. Ordinary diffusion and viscous flow in the continuum region

In the continuum region ($Kn < 0.01$) the fluxes due to diffusion and due to viscous flow may be added:

$$\dot{N}_1 = \dot{N}_{1,\,\text{dif}} + \dot{N}_{1,\,\text{vis}}. \tag{13}$$

The reason for this additivity follows from the kinetic theory of gases, in that there are no viscous terms in the Stephan–Maxwell equations, and no diffusion terms in the Navier–Stokes equations [10]. The viscous part of the flow is nonseparative. It can be described by Darcy's law:

$$\dot{N}_{1,\,\text{vis}} = y_1 \dot{N}_{\text{vis}} = -y_1 \frac{k}{\eta_{12}} c \nabla p \tag{14}$$

In an isothermal system the total diffusive flux consists of three contributions associated with the following mechanical driving forces:

1. Driving force due to gradients of mole fractions—concentration diffusion.
2. Driving force due to a pressure gradient—pressure diffusion.
3. Driving force due to an external force—forced diffusion.

The total diffusive flux $\dot{N}_{1,\text{dif}}$ can be written as the sum of the terms describing ordinary (concentration) diffusion, pressure diffusion and forced diffusion:

$$\dot{N}_{1,\,\text{dif}} = \dot{N}^{(y)}_{1,\,\text{dif}} + \dot{N}^{(p)}_{1,\,\text{dif}} + \dot{N}^{(F)}_{1,\,\text{dif}} \tag{15}$$

The diffusive flux due to an external force $\dot{N}^{(F)}_{1,\,\text{dif}}$, e.g. the electric field on an ion, is not considered in this paper. The tendency for a mixture to separate under a pressure gradient is very small, but use is made of this effect in centrifuge separation in which tremendous pressure gradients may be established. The flux due to concentration diffusion consists of two contributions: a flux resulting from the diffusion superimposed on the bulk fluid and a flux resulting from the bulk motion on the fluid:

$$\dot{N}^{(y)}_{1,\,\text{dif}} = \dot{J}^{(y)}_1 + y_1\left(\dot{N}^{(y)}_{1,\,\text{dif}} + \dot{N}^{(y)}_{2,\,\text{dif}}\right) \quad \text{with}$$

$$\dot{J}^{(y)}_1 = -D_{12} c \nabla y_1$$

$$\dot{N}^{(y)}_{2,\,\text{dif}} = \dot{J}^{(y)}_2 + (1 - y_1)\left(\dot{N}^{(y)}_{1,\,\text{dif}} + \dot{N}^{(y)}_{2,\,\text{dif}}\right) \quad \text{with}$$

$$\dot{J}^{(y)}_2 = -D_{12} c \nabla y_1 \tag{16}$$

The effective binary diffusion coefficient D_{12} comprises the binary diffusion coefficient δ_{12} in the free space and the additional resistance due to the impeding of the transport in the porous medium by tortuosity and porosity:

$$D_{12} = \frac{\epsilon_p \delta_{12}}{\mu_{p,\,\text{dif}}}. \tag{17}$$

The binary diffusion coefficient behaves reciprocally to the pressure ($p\delta_{12} = \text{const.}$). It is not possible to calculate both the diffusive fluxes from Eq. (16) without any additional assumptions. Therefore a separation factor shall be introduced

$$\alpha = \frac{\dot{N}^{(y)}_{2,\,\mathrm{dif}}}{\dot{N}^{(y)}_{1,\,\mathrm{dif}}} \tag{18}$$

It must be determined from the boundary conditions of the system or by experiment. Generally the diffusive fluxes can be expressed[3]

$$\dot{N}^{(y)}_{1,\,\mathrm{dif}} = \frac{-D_{12}c}{1-y_1(1+\alpha)}\nabla y_1,$$

$$\dot{N}^{(y)}_{2,\,\mathrm{dif}} = \frac{D_{12}c}{1-(1-y_1)(1+1/\alpha)}\nabla y_1.$$

The following values of the separation factor are physically found in a binary gas mixture, which is composed of species with different molecular weights ($M_1 \neq M_2$):

Equimolar diffusion (it can be assumed in a closed system, when a pressure gradient can be neglected):

$$\dot{N}^{(y)}_{1,\,\mathrm{dif}} = -\dot{N}^{(y)}_{2,\,\mathrm{dif}} \quad \rightarrow \alpha = -1.$$

No relative mass flow ($\nabla p = 0$):

$$\dot{m}^{(y)}_{1,\,\mathrm{dif}} = -\dot{m}^{(y)}_{2,\,\mathrm{dif}} \quad \rightarrow \alpha = -M_1/M_2.$$

The net axial momentum transferred to the walls of the pores by all the molecular collisions is zero:

$$\dot{m}^{(y)}_{1,\,\mathrm{dif}}v_1 = -\dot{m}^{(y)}_{2,\,\mathrm{dif}}v_2 \quad \rightarrow \alpha = -\sqrt{M_1/M_2}.$$

Diffusion through a stagnant gas film:

$$\dot{N}^{(y)}_{2,\,\mathrm{dif}} = 0 \quad \rightarrow \alpha = 0.$$

In case of countercurrent diffusion in an open system existing experimental results show according to Graham's law:

$$\rightarrow \alpha = -\sqrt{M_1/M_2}.$$

Therefore a general expression of the separation factor α is not possible. In order to make all further considerations on a basis of general applicability, the separation factor should be maintained.

The flux due to pressure diffusion is composed of a part resulting from the diffusion superimposed on the bulk fluid and a part resulting from the bulk motion of the fluid:

$$\dot{N}^{(p)}_{1,\,\mathrm{dif}} = -D_{12}\frac{M_{12}-M_1}{M_{12}}\frac{y_1}{\mathcal{R}T}\nabla p + y_1\left(\dot{N}^{(p)}_{1,\,\mathrm{dif}} + \dot{N}^{(p)}_{2,\,\mathrm{dif}}\right) \tag{20}$$

$$\dot{N}^{(p)}_{1,\,\mathrm{dif}} = -D_{12}\frac{c}{p}\frac{y_1\mu_1}{1-y_1(1+\alpha^{\mathrm{p}})}\nabla p \quad \text{with} \quad \mu_1 = \frac{M_{12}-M_1}{M_{12}}. \tag{21}$$

Similar to the ordinary diffusion a separation factor α^{p} was introduced. It cannot be determined from the Eqs. (20) and (21). The separation factor for pressure diffusion α^{p} does not have to be equal to the separation factor of ordinary diffusion α^{y}.

The fluxes due to viscous flow, ordinary and pressure diffusion can be added. This additivity yields the following result for the total flux of component 1:

$$\dot{N}_1 = \dot{N}_{1,\,\mathrm{vis}} + \dot{N}^{(y)}_{1,\,\mathrm{dif}} + \dot{N}^{(p)}_{1,\,\mathrm{dif}} \tag{22}$$

$$\dot{N}_1 = -y_1\frac{k}{\eta_{12}}c\nabla p - \frac{D_{12}c}{1-y_1(1+\alpha^{\mathrm{y}})}\nabla y_1 - \frac{D_{12}(c/p)y_1\mu_1}{1-y_1(1+\alpha^{\mathrm{p}})}\nabla p \tag{23}$$

and in case of $\alpha^{\mathrm{y}} = \alpha^{\mathrm{p}} = \alpha$

$$\dot{N}_1 = -y_1\frac{k}{\eta_{12}}c\nabla p - \frac{D_{12}(c\nabla y_1 + (c/p)y_1\mu_1\nabla p)}{1-y_1(1+\alpha)}. \tag{24}$$

In order to estimate the maximum influence of the pressure diffusion to the diffusive flux, the following assumptions shall be made:

$$\mu_1 = 1 \quad \text{i.e.} \quad y_1M_1 << (1-y_1)M_2 \quad \text{and} \quad \alpha^{\mathrm{y}} = \alpha^{\mathrm{p}} = \alpha.$$

Under this assumptions the ratio of the flux due to pressure diffusion to the flux due to ordinary diffusion simplifies to:

$$\frac{\dot{N}^{(p)}_{1,\,\mathrm{dif}}}{\dot{N}^{(y)}_{1,\,\mathrm{dif}}} = \frac{y_1\nabla p}{p\nabla y_1} \tag{25}$$

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[3] Eqs. (16)–(19): Eq. (16) can also be represented in the way in which the diffusive convective flux, induced by the diffusion, a viscous flow acc. to Eq. (14) is taken as basis [15]:

$$\dot{N}^{(y)}_{1,\,\mathrm{dif}} = -D_{12}c\nabla y_1 - D_{\mathrm{vis}}(c/p)y_1\nabla p$$

$$\dot{N}^{(y)}_{2,\,\mathrm{dif}} = D_{12}c\nabla y_1 - D_{\mathrm{vis}}(c/p)(1-y_1)\nabla p. \tag{19}$$

On the basis of the relation from Eq. (18)—$\alpha = \dot{N}^{(y)}_{2,\,\mathrm{dif}}/\dot{N}^{(y)}_{2,\,\mathrm{dif}}$—we get a relation between the gradient of pressure and concentration consequently to the diffusive convective flux:

$$(1+\alpha)D_{12}\nabla y_1 = (1-y_1(1+\alpha))D_{\mathrm{vis}}\nabla p.$$

When using the correlation in Eq. (54), we will have Eq. (19) in identical manner. In case of a superposition of the gradient of total pressure, there will be an additional viscous flow acc. to Eq. (14), which must be added. The gradient of pressure due to the diffusive convective flow and due to this additional flow must be added. This type of derivation shows the viscous character of the diffusive convective flow clearly.

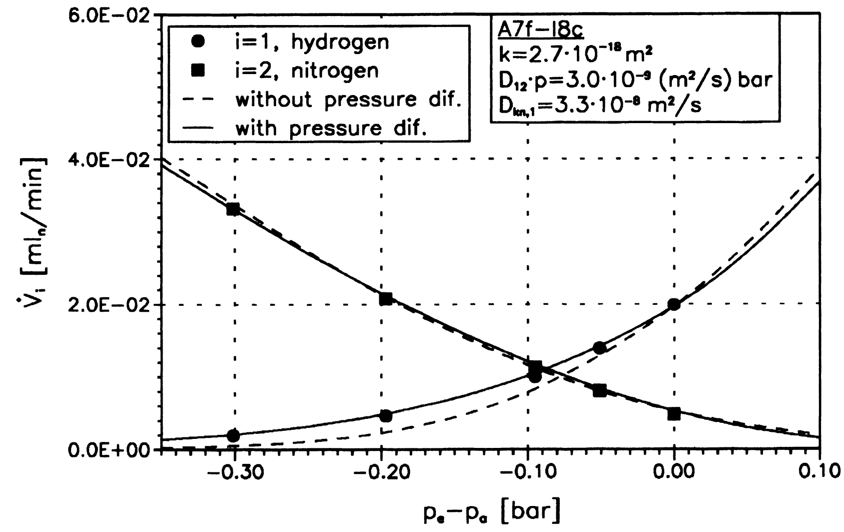

Fig. 5. Calculated and observed flows of hydrogen and nitrogen under combined gradients of pressure and concentration.

i.e. in case of an increasing pressure gradient and a small concentration gradient the contribution of pressure diffusion to the diffusive flux is appreciable. In case of a small pressure gradient it is negligible. Under the same assumptions the following result is obtained for the diffusive flux:

$$\dot{N}^{(y)}_{1,\,\text{dif}} + \dot{N}^{(p)}_{1,\,\text{dif}} = -D_{12}(c\nabla y_1 + (c/p)y_1\nabla p). \tag{26}$$

Only under these assumptions the total diffusive flux may be derived with the gradient of the partial pressure ∇p_1:

$$\dot{N}_{1,\,\text{dif}} = \dot{N}^{(y)}_{1,\,\text{dif}} + \dot{N}^{(p)}_{1,\,\text{dif}} = -D_{12}(c/p)\nabla p_1. \tag{27}$$

But in the continuum region the contribution of the viscous flow to the total flux must be still taken into account. It is considerably greater than the flux due to pressure diffusion. Only in the transition region, when the part of the viscous flow to the total flux decreases, an appreciable influence of the pressure diffusion is observed. Indeed a separation of a mixture in a tube flow by pressure diffusion has not yet been observed. The small but observable influence of pressure diffusion is shown in Fig. 5. The calculated fluxes which take into account the pressure diffusion (solid line), fit the measured values better than the calculated fluxes where the pressure diffusion was neglected (dashed line).

3.2. Knudsen flow

In the free-molecule region ($Kn > 1$) the Knudsen flow determines the mass transfer [14]. The flux of component i can be derived from the kinetic theory of gases[4]:

$$\begin{aligned} \dot{N}_{i,\,\text{kn}} &= -\frac{D_{\text{kn},\,i}}{\mathcal{R}T}\nabla p_i = -\frac{D_{\text{kn},\,i}}{\mathcal{R}T}(p\nabla y_i + y_i\nabla p) \\ &= \dot{N}^{(y)}_{i,\,\text{kn}} + \dot{N}^{(p)}_{i,\,\text{kn}} \end{aligned} \tag{28}$$

with $i = 1, 2$.

Here the gradient of the partial pressure ∇p_i is the driving force. The division of the flux into a part proportional to the pressure gradient ∇p, called slip flow, and into another part proportional to the gradient of the mole fraction ∇y_i, called Knudsen diffusion, occurs in analogous manner with regard to the transport mechanisms in the continuum region—ordinary diffusion ($\sim\nabla y_i$), pressure diffusion and viscous flow ($\sim\nabla p$). The division is not required but it simplifies the comparison of those fluxes that are induced by equivalent gradients and the estimation which mechanism mainly influences the mass transfer at a given gradient of concentration and pressure.

The effective Knudsen coefficient of component i is:

$$D_{\text{kn},\,i} = \frac{\epsilon_\text{p}}{\mu_{\text{p},\,\text{kn}}}\delta_{\text{kn},\,i} \quad \text{with} \quad \delta_{\text{kn},\,i} = \frac{4}{3}\bar{d}_{\text{pore}}\sqrt{\frac{\mathcal{R}T}{2\pi M_i}}. \tag{29}$$

The tortuosity $\mu_{\text{p,kn}}$ takes account of the additional re-

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[4] Eq. (28): Within the Knudsen regime, there is no fundamental distinction between flow and diffusion as there is in the continuum region. Here only free-molecular flow (Knudsen flow) is possible. This leads to the fact, that at a given gradient of concentration an appreciable gradient of pressure could be built up in a closed system.

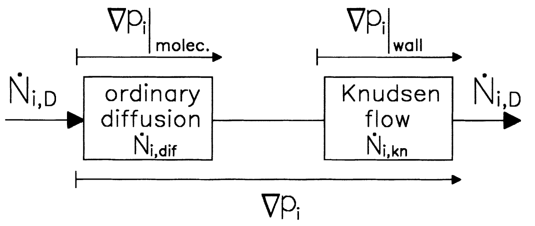

Fig. 6. Electrical analogue circuit according to [10] at $\nabla p = 0$.

sistances in pores by path elongation, reversing and pore geometry. In case of two different gases ($M_1 \neq M_2$) at a uniform pressure in an open system the following ratio of the fluxes can be found:

$$\frac{\dot{N}_{2,\,\mathrm{kn}}}{\dot{N}_{1,\,\mathrm{kn}}} = -\sqrt{\frac{M_1}{M_2}}. \tag{30}$$

3.3. Transition region

In the transition region there are gas/gas impacts as well as gas/wall impacts. The free path of the gas is of the size of the pore diameter. Mass transfer takes places due to a gradient of mole fraction by ordinary diffusion and Knudsen flow and due to a pressure gradient by pressure diffusion, Knudsen flow and viscous flow. The flux due to a viscous flow may be added to the diffusive flux [10,16]:

$$\dot{N}_1 = \dot{N}_{1,\,\mathrm{D}} + \dot{N}_{1,\,\mathrm{vis}} \tag{31}$$

3.3.1. Mass transport in the transition region at a uniform pressure

The combination of ordinary diffusion and Knudsen flow shall be derived at a uniform total pressure in an open system. In an open system both end faces of the cylindrical sample are continuously swept by gases at uniform pressure. The method is to consider a momentum balance on species i, which includes momentum transferred by i to the wall as well as to other molecules in the gas phase. The partial pressure difference expressed as momentum loss between the end of a capillary for a given component is considered to be the sum of the momentum transferred to the wall plus the momentum transferred to other molecules:

$$\nabla p_1 = \nabla p_1 \mid_{\mathrm{wall}} + \nabla p_1 \mid_{\mathrm{molecule}}. \tag{32}$$

For better comprehension an electric analogous circuit comprising two resistors in series shall be introduced [10], Fig. 6. The diffusive fluxes $\dot{N}^{(y)}_{1,\mathrm{kn}}$ and $\dot{N}^{(y)}_{1,\mathrm{dif}}$ are identical. They shall be designated $\dot{N}^{(y)}_{1,\mathrm{D}}$. In a binary gas mixture we obtain the following expression for the diffusive flux of the component 1

$$\dot{N}^{(y)}_{1,\,\mathrm{D}} = -\left(\frac{1}{D_{12}} + \frac{1}{D_{\mathrm{kn},\,1}}\right)^{-1} c\nabla y_1 + \frac{y_1 D_{\mathrm{kn},\,1}}{D_{\mathrm{kn},\,1} + D_{12}}\left(\dot{N}^{(y)}_{1,\,\mathrm{D}} + \dot{N}^{(y)}_{2,\,\mathrm{D}}\right). \tag{33}$$

In case of equimolar diffusion ($M_1 = M_2$) the diffusive fluxes are of equal magnitude but oppositely directed ($\alpha = -1$). We get the Bosanquest formulation of the diffusion coefficient in the transition region [18]. However we must generally suppose that in a mixture, which is composed of species with different molecular weights ($M_1 \neq M_2$), a non-equimolar countercurrent diffusion occurs. The diffusive flux of component 2 may be derived in the same manner as Eq. (33) by exchanging of the indices 1 with 2 and 2 with 1. The two independent equations permit the calculation of the diffusive flux of component 1:

$$\dot{N}^{(y)}_{1,\,\mathrm{D}} = -\left(\frac{1 - y_1\left(1 - \sqrt{M_1/M_2}\right)}{D_{12}} + \frac{1}{D_{\mathrm{kn},\,1}}\right)^{-1} c\nabla y_1. \tag{34}$$

The diffusive flux of component 2 is calculated correspondingly. The ratio of the two fluxes obeys the inverse square root molecular weight relationship:

$$\frac{\dot{N}^{(y)}_{2,\,\mathrm{D}}}{\dot{N}^{(y)}_{1,\,\mathrm{D}}} = -\sqrt{\frac{M_1}{M_2}} = \alpha^{y} \tag{35}$$

This ratio maintains over the entire pressure range from pure Knudsen to pure molecular diffusion. In order to obtain a general applicable statement of the diffusive flux in the transition region, Eq. (34) may be written as[5]:

$$\dot{N}^{(y)}_{1,\,\mathrm{D}} = -\left(\frac{1 - y_1(1 + \alpha^{y})}{D_{12}} + \frac{1}{D_{\mathrm{kn},\,1}}\right)^{-1} c\nabla y_1. \tag{36}$$

In the limiting case of low pressure or small pore radii ($Kn \gg 1$; $D_{12} \gg D_{\mathrm{kn},i}$) Eq. (36) changes over to Eq. (28). At high pressure or great pore radii ($Kn \ll 1$; $D_{12} \ll D_{\mathrm{kn},i}$) the flux of component 1 due to a mole fraction is described by the following equation:

$$\dot{N}^{(y)}_{1,\,\mathrm{D}} = \frac{-D_{12}}{1 - y_1\left(1 - \sqrt{M_1/M_2}\right)} c\nabla y_1. \tag{37}$$

This equation differs from Eq. (19), which described

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[5] Eq. (36): The derivation in the Eqs. (32) to (34) may be compared with an electrical analogy of a serial connection of two resistors, Fig. 6. In analogy to an electric current I: $1/I = 1/I_1 + 1/I_2$, we find: $1/\dot{N}^{(y)}_{1,\mathrm{D}} = 1/\dot{N}^{(y)}_{1,\mathrm{dif}} + 1/\dot{N}^{(y)}_{1,\mathrm{kn}}$, where the currents, resp. flows induced by the global driving potentials. For reasons of clarification of the physical relation the more detailed derivation above was chosen.

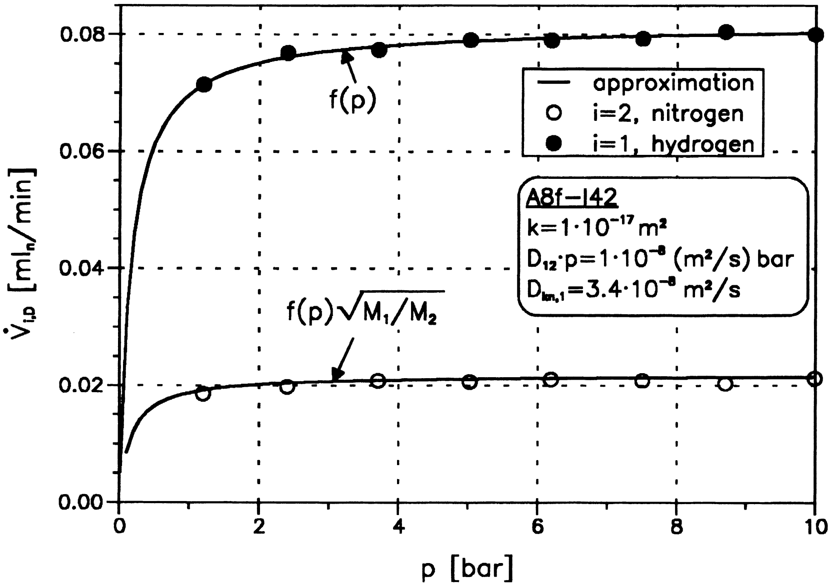

Fig. 7. Measured diffusion flows (●, ○) and approximation with the theoretical value for the molecular flow ratio according to Graham's law.

the diffusive flux of component 1 in the continuum region, in the way that the separation factor can be directly calculated without any additional assumption. Various measurements confirm the inverse square root molecular weight relationship of α^y, Eq. (35), in the entire pressure range from pure Knudsen to pure molecular diffusion [17–22]. The relationship is theoretically verified, too [23]. In 1829 Thomas Graham was the first who discovered the inverse square root molecular weight relationship of the diffusive fluxes in the continuum region by experiment. Therefore the ratio of the diffusive fluxes is designated Graham's law.

The mass average velocity v differs in the limiting case $Kn \ll 1$ from zero[6]):

$$\rho v = \dot m_1 + \dot m_2 = \dot N^{(y)}_{1,\mathrm{D}} M_1 + \dot N^{(y)}_{2,\mathrm{D}} M_2 = D_{12}\frac{\sqrt{M_1}(\sqrt{M_2}-\sqrt{M_1})}{1-y_1(1-\sqrt{M_1/M_2})} c\nabla y_1. \tag{38}$$

Despite a constant total pressure ($\nabla p = 0$) a measurable flow exists. It was observed in porous bodies as well as in capillaries [20]. This phenomena is called *diffusive slip* [24]. The mass flux due to diffusive slip tends towards the concentration gradient of the heavier gas component.

In steady state the flux of component 1 can be calculated by integration of Eq. (36):

$$\dot N^{(y)}_{1,\mathrm{D}} = \frac{D_{12}c}{(1+\alpha^y)L} \ln\left(\frac{1-y_{1,\mathrm{a}}(1+\alpha^y)+D_{12}/D_{\mathrm{kn},1}}{1-y_{1,\mathrm{e}}(1+\alpha^y)+D_{12}/D_{\mathrm{kn},1}}\right). \tag{39}$$

For analysing and evaluation of the diffusion measurements an effective diffusion coefficient D_e shall be introduced:

$$\dot N^{(y)}_{1,\mathrm{D}} = -D_\mathrm{e}c\nabla y_1 + y_1(\dot N^{(y)}_{1,\mathrm{D}} + \dot N^{(y)}_{2,\mathrm{D}}) = -D_\mathrm{e}c\nabla y_1 + y_1(1+\alpha^y)\dot N^{(y)}_{1,\mathrm{D}}. \tag{40}$$

The effective diffusion coefficient is the same for both components. Under steady-state conditions we get:

$$\dot N^{(y)}_{1,\mathrm{D}} = \frac{D_\mathrm{e}c}{(1+\alpha^y)L} \ln\left(\frac{1-y_{1,\mathrm{a}}(1+\alpha^y)}{1-y_{1,\mathrm{e}}(1+\alpha^y)}\right). \tag{41}$$

The theoretical value of the effective diffusion coefficient can be calculated from Eqs. (39) and (41):

$$D_\mathrm{e} = D_{12}\left(\ln\left[\frac{1-y_{1,\mathrm{a}}(1+\alpha^y)}{1-y_{1,\mathrm{e}}(1+\alpha^y)}\right]\right)^{-1} \ln\left(\frac{1-y_{1,\mathrm{a}}(1+\alpha^y)+D_{12}/D_{\mathrm{kn},1}}{1-y_{1,\mathrm{e}}(1+\alpha^y)+D_{12}/D_{\mathrm{kn},1}}\right). \tag{42}$$

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[6] Eq. (38): If $\dot m_1 = -\dot m_2$, i.e. $\alpha = -M_1/M_2$, there would be no diffusion slip. Therefore Graham's law $\alpha = -\sqrt{M_1/M_2}$ is a direct consequence of the diffusion slip.

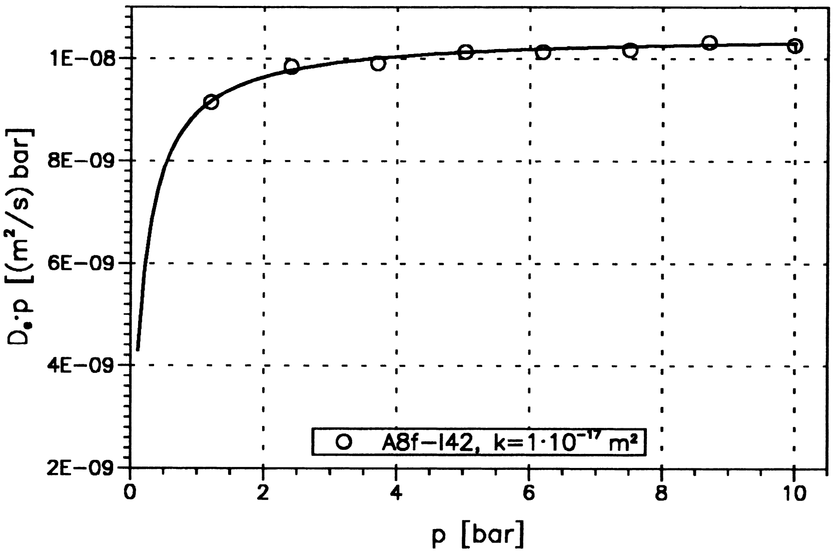

Fig. 8. Effective diffusion coefficient D_e multiplied by the global pressure.

The binary diffusion coefficient may be obtained from Eq. (39) and measurements at high pressure, the Knudsen coefficient from measurements at low pressure. Then the effective diffusion coefficient may be calculated by Eq. (42). This requires the variation of the total pressure over several orders of magnitude. In the experimental apparatus described in [3] diffusion measurements were carried out with hydrogen and nitrogen as nonadsorbing gases at total pressures from 1.2 to 10.0 bar. Rock salt cores were employed as porous samples. The Knudsen coefficient was obtained from permeability measurements. Under the knowledge of the Knudsen coefficient only a single diffusion experiment at constant pressure is necessary to determine the binary diffusion coefficient. If several diffusion measurements at several total pressures were carried out, the binary diffusion coefficient may be determined from an approximation function. In the function $\dot{N}_{1,\mathrm{D}} = f(p)$, Eq. (39), the pressure independent value $D_{12}p$ is chosen in the way that calculation well fits measurement. Fig. 7 shows the measured diffusion fluxes of hydrogen and nitrogen through a porous salt core. Under the assumption of Graham's law the calculated diffusive fluxes of hydrogen and nitrogen well fit the measured values. With increasing total pressure the diffusive flux varies only weakly. The mass transport mainly occurs due to ordinary diffusion in the continuum region. At low gas pressure the mass transfer takes place due to Knudsen flow. Here the flux is directly proportional to the pressure. Fig. 8 shows the calculated and measured effective diffusion coefficient multiplied by the total pressure. At high pressure the effective diffusion coefficient D_e turns into the binary diffusion coefficient D_{12}. It behaves reciprocally to the total pressure. Therefore at small Knudsen numbers the effective diffusion coefficient multiplied by the total pressure $D_e p$ is a constant value.

3.3.2. *Mass transport in the transition region under combined gradients of concentration and pressure*

If additionally to the concentration gradient ∇y_i a pressure gradient ∇p is imposed on the porous medium, a flux due to viscous flow, slip flow and pressure diffusion will occur. Hence the total flux has to be a combination of:

viscous flow $\dot{N}_{i,\,\mathrm{vis}} = -D_{\mathrm{vis}}(c/p)y_i\nabla p;\quad D_{\mathrm{vis}} = kp/\eta$

ordinary diffusion $\dot{N}^{(\mathrm{y})}_{i,\,\mathrm{dif}} = -D_{12}c\nabla y_i + y_i\Sigma\dot{N}^{(\mathrm{y})}_{j,\,\mathrm{dif}}$

pressure diffusion $\dot{N}^{(\mathrm{p})}_{i,\,\mathrm{dif}} = -D_{12}(c/p)\mu_i y_i\nabla p + y_i\Sigma\dot{N}^{(\mathrm{p})}_{j,\,\mathrm{dif}}$

Knudsen flow $\dot{N}_{i,\,\mathrm{kn}} = -D_{\mathrm{kn},\,i}(c/p)\nabla p_i.$

The flux due to viscous flow may be added to the diffusive flux (compare Eq. (31)). Several possibilities exist in order to combine the diffusive fluxes caused by different gradients—∇y_i, ∇p, ∇p_i.

3.3.2.1. *(a) Maximum influence of pressure diffusion,* $\mu_i = 1$. As shown above the pressure diffusion has to be only taken into account in the transition region. The contribution of the pressure diffusion is small compared to the fluxes due to ordinary diffusion and vis-

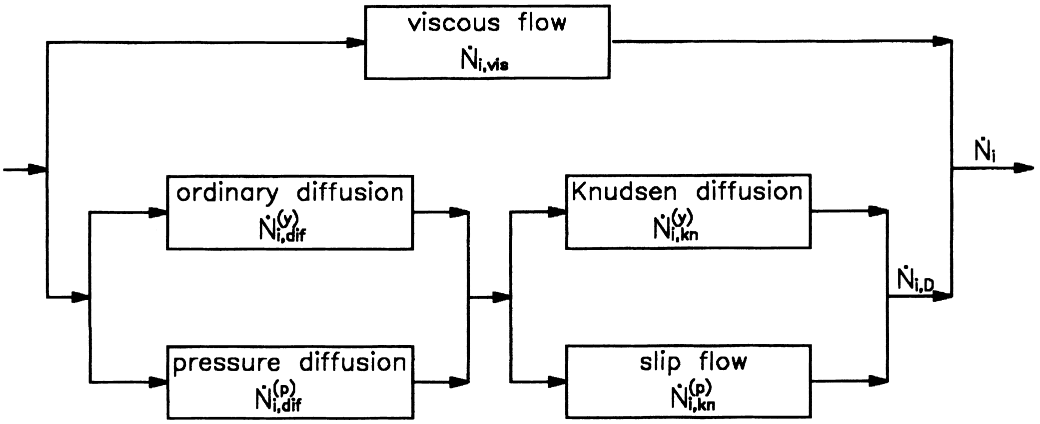

Fig. 9. Extended analogous model—diffusion fluxes in parallel connection.

cous flow. Therefore it is allowed to assume $\mu_i = 1$ for every component in the gas mixture in order to take account of a maximum value of the pressure diffusion. This agrees to the Dusty-Gas model under the assumption that all external forces, including the clamping force, which act on the dust particles in the porous medium, must be equal to the drag force due to viscous flow. Hence the effect of μ_i is suppressed.

Under this assumption the gradient of the partial pressure is the driving force of the sum of ordinary and pressure diffusion. In that case the combination of diffusion and Knudsen flow shall be calculated as shown in the scheme of Eqs. (32)–(34). We obtain the Stefan–Maxwell form of the diffusion equation in the transition region [25]:

$$\begin{aligned}\nabla p_1 &= p\nabla y_1 + y_1\nabla p \\ &= \frac{-1}{D_{12}c/p}\{(1-y_1)\dot N_{1,\mathrm{D}} - y_1\dot N_{1,\mathrm{D}}\} \\ &\quad - \frac{1}{D_{\mathrm{kn},1}c/p}\dot N_{1,\mathrm{D}}.\end{aligned} \tag{43}$$

In comparison with the upper considered case, here the gradient of pressure is not zero. After some algebra we obtain the following result for the diffusive flux of component 1:

$$\begin{aligned}\dot N_{1,\mathrm{D}} = -&\left(\frac{1-y_1(1-\sqrt{M_1/M_2})}{D_{12}}\right. \\ &\left.+\frac{1}{D_{\mathrm{kn},1}}\right)^{-1}\left[c\nabla y_1 + \left(1+\frac{D_{\mathrm{kn},2}}{D_{12}}\right)\frac{c}{p}y_1\nabla p\right].\end{aligned} \tag{44}$$

In Eq. (44) the first term on the right side ($\sim\nabla y_1$) may be considered as a combination of ordinary diffusion and Knudsen diffusion, the second term ($\sim\nabla p$) as a combination of pressure diffusion and slip flow. The equation satisfies the limiting cases in the continuum and in the Knudsen region. In the Knudsen region the Knudsen coefficient is considerably smaller than the binary diffusion coefficient ($D_{\mathrm{kn},i} \ll D_{12}$), whereas in the continuum region the flux due to pressure diffusion is small compared to the viscous flux ($D_{12} \ll D_{\mathrm{vis}}$). In a binary gas mixture, which consists of species with the same molecular weights ($M_1 = M_2$), there is no pressure diffusion. Under this condition the combination of viscous flow and Knudsen flow reduces to the following expression:

$$\dot N_i^{(\mathrm{p})} = -(D_{\mathrm{vis}} + D_{\mathrm{kn},i})y_i(c/p)\nabla p.$$

However the physical meaning of the factor $(1 + D_{\mathrm{kn},2}/D_{12})$ in the flux of component 1 is difficult to explain. It has to vanish in the continuum region. The discrepancy arises due to the derivation of Eq. (44) by the assumption of $\mu_i = 1$; $i = 1, 2$. The assumption was made in order to enable the addition of the partial pressure drops due to molecule–wall collisions $\nabla p_i|_{\mathrm{wall}}$ and molecule–molecule collisions $\nabla p_i|_{\mathrm{molecule}}$. This is not correct because the definition of μ_i (Eq. (21)) leads to $y_1\mu_1 = -(1-y_1)\mu_2$.

3.3.2.2. (b) Extended analogous model—diffusive flows in parallel connection. The fluxes due to ordinary and pressure diffusion with regard to the factor μ_i are directly added (parallel connected) as shown in the Fig. 9. In consideration of the Eqs. (19) and (21) we obtain:

$$\begin{aligned}\dot N_{i,\mathrm{dif}} &= \dot N^{(\mathrm{y})}_{i,\mathrm{dif}} + \dot N^{(\mathrm{p})}_{i,\mathrm{dif}} \\ &= -\frac{D_{12}(c\nabla y_i + (c/p)\mu_i y_i\nabla p}{1-y_i(1+\alpha)}.\end{aligned}$$

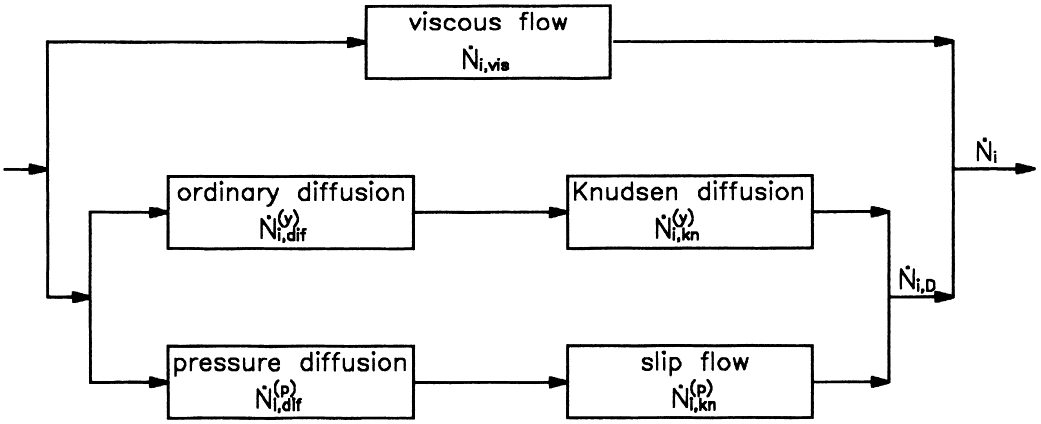

Fig. 10. Extended analogous model—diffusion fluxes in serial connection.

The flux due to Knudsen flow may be calculated by Eq. (28):

$$\dot N_{i,\,\mathrm{kn}} = -\frac{D_{\mathrm{kn},\,i}}{\mathcal{R}T}\nabla p_i.$$

The diffusive fluxes $\dot N_{i,\mathrm{dif}}$ and $\dot N_{i,\mathrm{kn}}$ shall connect in series as shown in the sketched model, Fig. 9. The combination of the diffusive fluxes leads to the following result (see footnote 5):

$$\frac{1}{\dot N_{i,\,\mathrm{D}}} = \frac{1}{\dot N_{i,\,\mathrm{dif}}} + \frac{1}{\dot N_{i,\,\mathrm{kn}}}. \tag{45}$$

In a binary gas mixture we obtain the following expression for the flux of component 1:

$$\dot N_{1,\,\mathrm{D}} = -\left[\frac{1-y_1(1+\alpha)}{D_{12}(c\nabla y_1 + (c/p)\mu_1 y_1\nabla p)} + \frac{1}{D_{\mathrm{kn},\,1}(c\nabla y_1 + (c/p)y_1\nabla p)}\right]^{-1} \tag{46}$$

and the flux of component 2, respectively:

$$\dot N_{2,\,\mathrm{D}} = -\left[\frac{1-(1-y_1)(1+1/\alpha)}{D_{12}(-c\nabla y_1 + (c/p)\mu_2(1-y_1)\nabla p)} + \frac{1}{D_{\mathrm{kn},\,2}(-c\nabla y_1 + (c/p)(1-y_1)\nabla p)}\right]^{-1}. \tag{47}$$

The separation factor $\alpha = \dot N_{2,\mathrm{D}}/\dot N_{1,\mathrm{D}}$ can be calculated by means of the two equations. The following relations are helpful:

$$\mu_1 y_1 = -\mu_2(1-y_1)$$

$$1-(1-y_1)(1+1/\alpha) = -(1-y_1(1+\alpha))/\alpha$$

$$p^{-1}\nabla p_1 = \nabla y_1 + y_1 p^{-1}\nabla p$$

$$p^{-1}\nabla p_2 = -\nabla y_1 + (1-y_1)p^{-1}\nabla p.$$

We obtain the following expression for the separation factor

$$\alpha = \frac{D_{\mathrm{kn},\,2}}{D_{\mathrm{kn},\,1}}\frac{\nabla p_2}{\nabla p_1} = -\sqrt{\frac{M_1}{M_2}}\frac{p\nabla y_1 - (1-y_1)\nabla p}{p\nabla y_1 + y_1\nabla p}. \tag{48}$$

In the case of a vanishing pressure gradient ($\nabla p = 0$) Eq. (48) changes over to Graham's law (Eq. (35)). In order to consider the limiting cases, model (b) should be written in the Stefan–Maxwell form:

$$\frac{1}{D_{12}c}\{(1-y_1)\dot N_{1,\,\mathrm{D}} - y_1\dot N_{2,\,\mathrm{D}}\} + \frac{\dot N_{1,\,\mathrm{D}}}{D_{\mathrm{kn},\,1}c} = -\left(\frac{1-y_1(1+\alpha)}{D_{12}} + \frac{1}{D_{\mathrm{kn},\,1}}\right)\left[\frac{1-y_1(1+\alpha)}{D_{12}(\nabla y_1 + \mu_1 y_1 p^{-1}\nabla p)} + \frac{1}{D_{\mathrm{kn},\,1}(\nabla y_1 + y_1 p^{-1}\nabla p)}\right]^{-1}. \tag{49}$$

Model (b) describes the mass transfer in the both limiting cases—Knudsen region ($D_{\mathrm{kn}} \ll D_{12}$) and continuum region ($D_{\mathrm{kn}} \gg D_{12}$)—exactly. In the continuum region the driving forces are—($\nabla y_i + \mu_i y_i/p\nabla p_i$); in the Knudsen region the driving force is the partial pressure of each component—($\nabla y_i + y_i/p\nabla p_i$) $= -1/p\nabla p_i$. The difference between the two driving forces is only small but of fundamentally physical importance. In the continuum region a pressure diffusion $\sim \mu_i y_i/p\nabla p_i$ can superimpose the ordinary diffusion. The pressure diffusion is the consequence of the difference between the molar-average velocity and the mass-average velocity of each species $\mu_i y_i = y_i - \omega_i$ with $\omega_i = \rho_i/\rho$. Model (b) Eq. (49) describes the transition region between the continuum and the Knudsen region.

3.3.2.3. (c) Extended analogous model—diffusive fluxes in serial connection. It is possible to connect the diffusive fluxes in a manner as sketched in Fig. 10. The serial connection of ordinary diffusion $\dot{N}^{(y)}_{1,\mathrm{dif}}$ and Knudsen diffusion $\dot{N}^{(y)}_{1,\mathrm{kn}}$ to a flux $\dot{N}^{(y)}_{1,\mathrm{D}}$ and pressure diffusion $\dot{N}^{(p)}_{1,\mathrm{dif}}$ and slip flow $\dot{N}^{(p)}_{1,\mathrm{kn}}$ to a flux $\dot{N}^{(p)}_{1,\mathrm{D}}$ yields the following result[7]:

$$\dot{N}^{(y)}_{1,\mathrm{D}} = -\left(\frac{1-y_1(1+\alpha^{y})}{D_{12}} + \frac{1}{D_{\mathrm{kn},1}}\right)^{-1} c\nabla y_1 - \left(\frac{1-y_1(1+\alpha^{p})}{D_{12}\mu_1} + \frac{1}{D_{\mathrm{kn},1}}\right)^{-1} (c/p)y_1\nabla p$$

$$\dot{N}^{(y)}_{2,\mathrm{D}} = \left(\frac{1-(1-y_1)(1+1/\alpha^{y})}{D_{12}} + \frac{1}{D_{\mathrm{kn},2}}\right)^{-1} c\nabla y_1 - \left(\frac{1-(1-y_1)(1+1/\alpha^{p})}{D_{12}\mu_2} + \frac{1}{D_{\mathrm{kn},2}}\right)^{-1} \times (c/p)(1-y_1)\nabla p. \tag{50}$$

In these equations two separation factors have to be distinguished[8]:

$$\frac{\dot{N}^{(y)}_{2,\mathrm{D}}}{\dot{N}^{(y)}_{1,\mathrm{D}}} = \alpha^{y} = -\sqrt{\frac{M_1}{M_2}};\quad \frac{\dot{N}^{(p)}_{2,\mathrm{D}}}{\dot{N}^{(p)}_{1,\mathrm{D}}} = \alpha^{p} = [-\frac{\mu_1}{\mu_2}\sqrt{\frac{M_1}{M_2}} = -\frac{M_{12}-M_1}{M_{12}-M_2}\sqrt{\frac{M_1}{M_2}}. \tag{51}$$

In order to consider the limiting cases, model (c) should be written in the Stefan–Maxwell form:

$$\frac{1}{D_{12}c}\{(1-y_1)\dot{N}_{1,\mathrm{D}} - y_1\dot{N}_{2,\mathrm{D}}\} + \frac{\dot{N}_{1,\mathrm{D}}}{D_{\mathrm{kn},1}c} = -\frac{D_{\mathrm{kn},1}(1-y_1(1+\alpha^{p})) + D_{12}}{D_{\mathrm{kn},1}(1-y_1(1+\alpha^{p})) + \mu_1 D_{12}}\mu_1 y_1 p^{-1}\nabla p - \nabla y_1. \tag{52}$$

The mass transfer in the both limiting cases—Knudsen and continuum region—is exactly described by model (c) and also by model (b).

The three presented models (a), (b) and (c) are identical in the case of isobaric counterdiffusion ($\nabla p = 0$). In the Knudsen regime ($D_{\mathrm{kn}} \ll D_{12}$) they describe the mass transfer for all gradients of pressure exactly, too. However in the limiting case $D_{\mathrm{kn}} \gg D_{12}$—continuum regime—the three models differ in the separation factor α. The essential difference between the models is the treatment of the pressure diffusion. The pressure diffusion is only observed in the transition region. Hence the discussion of this question is secondary. Nevertheless it is a fundamental question. More important is the question, which gradient is the driving force of ordinary diffusion. Only in the case of a binary gas mixture, which consists of species with the same molecular weights ($\mu_i = 1$), the gradient of the partial pressure ∇p_i is the driving force. In general the driving force of ordinary diffusion is the gradient of the mole fraction ∇y_i. It is superposed by a pressure diffusion in the transition region, which obeys the gradient $\sim\mu_i\nabla p_i$. This should be taken into account on the left side of the Maxwell's Eq. (43).

3.3.3. Comparison of the transport coefficients

In order to evaluate which transport mechanisms predominate under simultaneously existing gradients of mole fraction and pressure, a comparison of the transport coefficient is often sufficient, Fig 11. For this purpose the pressure diffusion shall be neglected. This is not only justified for large pore diameters, but also, as shown above, for a lot of binary gas mixtures, which consist of species with nearly the same molecular weights. Hence the transport due to a pressure gradient takes place by viscous flow and Knudsen flow. They are added directly.

For the double-logarithmic application of the transport coefficients vs the pore radius R_{pore}, the permeability coefficient D_{vis} is drawn as a straight line with the slope 2, the Knudsen coefficient as a straight line with the slope 1. The diffusion coefficient, here calculated on the basis of the Bosanquet formulation, changes over from the Knudsen coefficient to the binary diffusion coefficient with increasing pore radius. The binary diffusion coefficient D_{12} is independent of the pore radius and behaves reciprocally to the pressure. The Knudsen coefficient is independent of the gas

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[7] As shown in footnote (3) a viscous flow can substitute the diffusive convective flow of ordinary diffusion. If we calculate here in the same way due to the ordinary and pressure diffusion:

$$y_1(\dot{N}^{(y)}_{1,\mathrm{dif}} + \dot{N}^{(y)}_{2,\mathrm{dif}} + \dot{N}^{(p)}_{1,\mathrm{dif}} + \dot{N}^{(y)}_{2,\mathrm{dif}}) = -D_{\mathrm{vis}}(c/p)y_1\nabla p$$

we obtain

$$\dot{N}_{1,\mathrm{dif}} = -\frac{D_{12}c}{1-y_1(1+\alpha^{y})}\nabla y_1 - \frac{D_{12}(c/p)y_1\mu_1}{1-y_1(1+\alpha^{p})}\nabla p.$$

The separation factors α^{y} and α^{p} are unknown and must be calculated by further considerations. The form of the above derived equation is confirmed to Eq. (50).

[8] In case of consideration of the limiting case $\mu_1 = \mu_2$ the mean molecular weight M_{12} is considered as a constant value and the molecular weights M_1 and M_2 as variables. If M_{12} is also considered as a function of the molecular weights of the single species M_1 and M_2 ($M_{12} = f(M_1, M_2)$), we obtain $\dot{N}_{1,\mathrm{D}} \sim 2D_{12}$. This is physically meaningless.

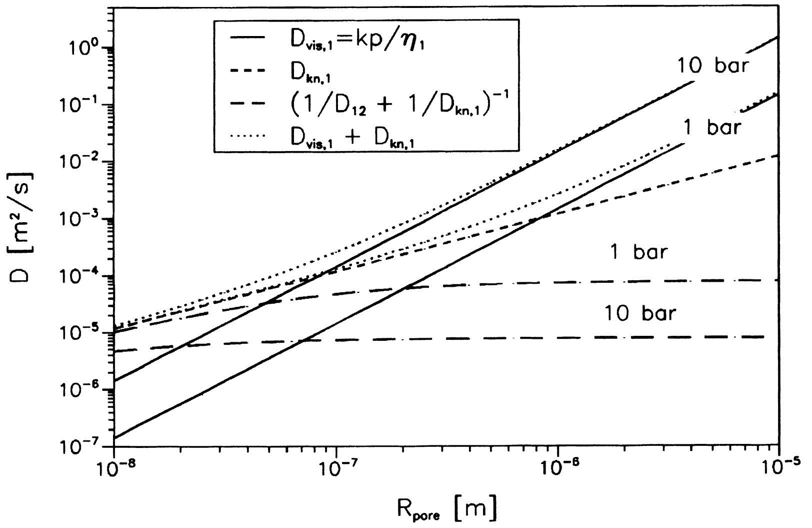

Fig. 11. Transport coefficients of hydrogen depending on the pore radius and on the total pressure in a capillary tube at 21°C.

pressure and the permeability coefficient behaves proportionally to the pressure.

If porous media possess large pores ($R_{\text{pore}} \approx 10^{-5}$ m), only a small gradient of pressure will be necessary for the flux due to viscous flow to predominate the flux due to Fick's diffusion ($D_{\text{vis}} \ll D_{12}$). With decreasing pore radii an increasing gradient of pressure must be imposed on the porous medium, so that the flux induced by a gradient of pressure predominates the diffusive flux. With decreasing pore radius the Knudsen coefficient is the transport coefficient, which determines the flux due to a gradient of pressure. It takes a greater value than the permeability coefficient. The reason is its simple dependence on the pore radius ($D_{\text{kn}} \sim R_{\text{pore}}$) in comparison to the square dependence of the permeability coefficient on the pore radius ($D_{\text{vis}} \sim R^2_{\text{pore}}$). With decreasing pore radius the binary diffusion coefficient changes over to the Knudsen coefficient. Hence in a porous medium with very small pores there is no distinction between a flux due to a gradient of pressure and concentration.

When comparing the transport coefficients we can see, that for the mass transfer due to a gradient of pressure the transition from the continuum region to the Knudsen region takes place at larger pores than for the diffusion. In case of a Knudsen number of $Kn \approx 1/13$ the parts of viscous and slip flow are of the same magnitude. By using hydrogen at an absolute pressure of 1 bar and a porous medium with pore radii of $R_{\text{pore}} \approx 8 \times 10^{-7}$ m the Knudsen coefficient takes the same value as the permeability coefficient. Only for a pore radius of $R_{\text{pore}} \approx 6 \times 10^{-8}$ m the binary diffusion coefficient and the Knudsen coefficient have approximately the same value.

3.4. Non-steady diffusion measurements

The goal of the nonsteady-state diffusion measurements is the determination of the accessible porosity. The accessible porosity obtained by the nonsteady-state diffusion measurements may be compared with the accessible porosity obtained by the nonsteady-state permeability measurements. They should be equal. At the beginning of the experiment the void space inside the porous medium is entirely saturated with nitrogen. Until $t = 0$ both end faces of the sample are swept with nitrogen at uniform and equal pressure. From $t \geq 0$ one end face of the sample ($z = 0$) is swept with hydrogen instead of nitrogen and the other end face ($z = L$) is still swept with nitrogen at the same total pressure ($\nabla p = 0$). After some time a slowly increasing hydrogen concentration can be measured in the nitrogen stream ($z = L$).

For the determination of the accessible porosity the equations of continuity for the both species 1 and 2 have to be solved within the sample ($0 < z < L$):

$$\epsilon_a \frac{\partial c_i}{\partial t} = \epsilon_a \left(y_i \frac{\partial c}{\partial t} + c \frac{\partial y_i}{\partial t} \right) = -\nabla \dot{N}_i \quad \text{with} \qquad \dot{N}_i = \dot{N}_{i,\,\mathrm{D}} + \dot{N}_{i,\,\mathrm{vis}}, \quad i = 1, 2 \tag{53}$$

with the following boundary conditions:

$$y_1(z = 0,\ t \geq 0) = y_{1,\,\mathrm{e}} = 1$$

$$p(z = 0,\ t \geq 0) = p_{\mathrm{e}}$$

$$y_1(z = L,\ t \geq 0) = y_{1,\,\mathrm{a}} = 0$$

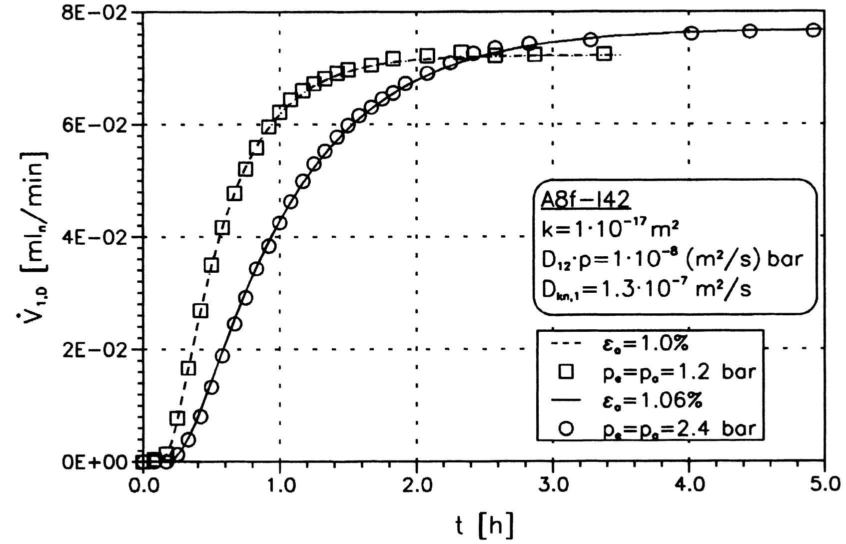

Fig. 12. Nonsteady-state diffusion measurements at different total pressures.

$$p(z = L, t \geq 0) = p_a = p_e.$$

The fluxes of both the species 1 and 2 are calculated by the Eq. (31) and (44), where the three transport coefficients are already known from the steady-state experiments. In Eq. (53) the accessible porosity remains as the only unknown. The accessible porosity is chosen in the way that calculation (solid curve) well fits the measured data (symbols), Fig. 12. In the figure the fluxes of hydrogen through the sample are drawn as a function of time at different total pressures (1.2 bar and 2.4 bar). Under the chosen conditions ($p_e = p_a$) the gradient of pressure ∇p within the sample will be very small and the three models (a), (b) and (c) are equivalent. A distinction is not necessary.

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