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Diffusive mass transfer with superimposed frictional flow

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Abstract

For the superimposing of the diffusive flows – ordinary diffusion and molecular motion – with a frictional, i.e. viscous flow, several models have been proposed. In the continuum region and in the Knudsen region the models are identical. They are different however in the transition region $1 < Kn < 0.01$. A description of the effects in this region has to take into account: pressure diffusion, slip flow and diffusion slip. It will be shown that only the model of parallel connection of ordinary and pressure diffusion on the one side and the concentration and the pressure term of molecular motion on the other side is physically plausible in the transition region. For this approach it is necessary to consider the convective compensation flow caused by the diffusion for a viscous frictional flow. On this basis an equation for the diffusive flow in the whole range of Knudsen-numbers will be derived, which includes the above-mentioned effects. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Diffusion in the continuum region

Within a porous structure in the continuum region – $Kn < 0.01$ – a gradient of concentration ∇y causes an ordinary diffusion. For binary gas mixtures the relative diffusion fluxes therefore, are described [1] by

$$\dot{j}_1^{(y)} = -D_{12}\left(\frac{c}{p}\right)p\nabla y, \quad \dot{j}_2^{(y)} = +D_{12}\left(\frac{c}{p}\right)p\nabla y, \quad (y = y_1) \tag{1}$$

with $(c/p) = 1/RT$ and the effective diffusion coefficient $D_{12} = D_{12}^{*}/\mu_{\mathrm{p}}$.

By diffusion with constant pressure a compensation flow is formed resulting in a bulk motion of the fluid because the velocities of diffusion for the components are different. The total diffusion fluxes can be written as the sum of the relative fluxes and the bulk flow [2]

$$\begin{aligned}\dot{N}^{(y)}_{\mathrm{dif},1} &= -D_{12}\left(\frac{c}{p}\right)p\nabla y + y(\dot{N}^{(y)}_{\mathrm{dif},1} + \dot{N}^{(y)}_{\mathrm{dif},2}) \\ &= -D_{12}\left(\frac{c}{p}\right)\frac{p\nabla y}{1 - y(1+\alpha)},\end{aligned}$$

$$\begin{aligned}\dot{N}^{(y)}_{\mathrm{dif},2} &= +D_{12}\left(\frac{c}{p}\right)p\nabla y + (1-y)(\dot{N}^{(y)}_{\mathrm{dif},1} + \dot{N}^{(y)}_{\mathrm{dif},2}) \\ &= +D_{12}\left(\frac{c}{p}\right)\frac{p\nabla y}{1 - (1-y)(1+1/\alpha)}.\end{aligned} \tag{2}$$

In these equations a separation factor is introduced, $\alpha = \dot{N}_{\mathrm{dif},2}/\dot{N}_{\mathrm{dif},1}$. It must be determined from the boundary conditions of the system, e.g. countercurrent diffusion, $\alpha = -D_{Kn,2}/D_{Kn,1}$ (Grahams law) or for diffusion through a stagnant film, $\alpha = 0$. Only for $\alpha = -1$ in case of equimolar diffusion in a closed system and $\nabla p = 0$, there is no bulk motion of the fluid (gas). However, if we describe the bulk motion in Eq. (2) $(\dot{N}^{(y)}_{\mathrm{dif},1} + \dot{N}^{(y)}_{\mathrm{dif},2})$ as a frictional viscous flow with Darcy's law [3]

$$\dot{N}^{y}_{\mathrm{dif},1} + \dot{N}^{(y)}_{\mathrm{dif},2} = -D_{\mathrm{vis}}\left(\frac{c}{p}\right)\nabla p \quad \text{with } D_{\mathrm{vis}} = \frac{kp}{\eta} \tag{3}$$

or by laminar flow in pores with a mean diameter d_{p} with $D_{\mathrm{vis}} = (d_{\mathrm{p}}^2 p/32\eta)$ we get a relation for the pressure gradient needed to dissipate the compensation flow

$$\nabla p = \frac{1+\alpha}{1 - y(1+\alpha)}p\nabla y\frac{D_{12}}{D_{\mathrm{vis}}} \tag{4}$$

or with a dimensionless ratio of the gradients

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Nomenclature

c	molar density (kmol/m^3)
d_p	pore diameter (m)
D^*	transport coefficient in the free space (m^2/s)
D_{12}	effective binary diffusion coefficient in the gas (m^2/s)
$D_{Kn,i}$	effective equivalent diffusion coefficient for molecular motion (m^2/s)
D_{vis}	effective equivalent diffusion coefficient for viscous flow (m^2/s)
$\dot{j}$	molar flux relative to the mass average velocity (kmol/(m^2 s))
k	permeability (m)
Kn	Knudsen number (Λ/d_p)
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)
R	gas constant (J/(kmol K))
s	length of diffusion path (m)
T	absolute temperature (K)
x	ordinate (m)
y	mole fraction

Greek symbols

α	separation factor $\dot{N}_2/\dot{N}_1$
Λ	mean free path of the gas molecules (m)
μ_i	ratio of relative mole masses, $M_{12} - Mi/M_{12}$
μ_p	tortuosity factor
η	dynamic viscosity (Pa s)

Indices

$i, 1, 2$	components
dif	flux due to ordinary diffusion
Kn	flux due to molecular motion
vis	flux due to viscous flow
0	by pressure p_0

Superscripts

p	flux due to pressure gradient
y	flux due to mole fraction gradient
$''$	by saturation or on $x = 0$
$'$	in the gas or on $x = s$

$$\vartheta = \frac{p\nabla y}{(1-y)\nabla p} \qquad (5)$$

$$\vartheta = \frac{1-y(1+\alpha)}{(1-y)(1+\alpha)}\frac{D_{vis}}{D_{12}}.$$

In the continuum region – $Kn \ll 0.01$ – the equivalent effective diffusion coefficient for the viscous flow, D_{vis}, is much greater than the ordinary diffusion coefficient D_{12} (cf. Fig. 2) so that a pressure gradient in the continuum region is to be neglected: $\nabla p \approx 0$.

In case of diffusion through a stagnant film (one-side diffusion) there is $\dot{N}^{(y)}_{dif,2} = 0$, resp., $\alpha = 0$ and we get from Eq. (5) for the ratio of the gradients

$$\vartheta = \frac{D_{vis}}{D_{12}}. \qquad (6)$$

The integration with the boundary conditions, Fig. 1,

$$x = 0 : y = y'' = \frac{p_1''}{p_{x=0}}, \quad x = s : y = y' = \frac{p_1'}{p_0}$$

results in the pressure $p_{x=0}$ on the place where the diffusion flux is generated, e.g. the surface area of the fluid by evaporation. This is an implicit equation

$$\frac{p_{x=0}}{p_0} = \left(\frac{1-y'}{1-y''}\right)^{1/\vartheta} = \left(\frac{p_0 - p_1'}{p_{x=0} - p_1''}\right)^{1/(\vartheta-1)}. \qquad (7)$$

If additionally the pressure dependence of the diffusion coefficients would be considered:

$$D_{vis} = D_{vis,0}\frac{p}{p_0}, \quad D_{12} = D_{12,0}\frac{p_0}{p},$$

$$\text{i.e. } \frac{D_{vis}}{D_{12}} = \left.\frac{D_{vis}}{D_{12}}\right|_0 \left(\frac{p}{p_0}\right)^2$$

the integration of Eq. (6) results in

$$\frac{p_{x=0}}{p_0} = \frac{p_{x=0} - p_1''}{p_0 - p_1'} \exp\left[\frac{1}{2}\vartheta_0\left(\left(\frac{p_{x=0}}{p_0}\right)^2 - 1\right)\right]. \qquad (8)$$

The numerical interpretation shows only a small effect of the pressure dependence (max −4%). In the following this influence will be neglected.

The diffusion flux of component 1 through a stagnant film – only this case will be considered afterwards in this

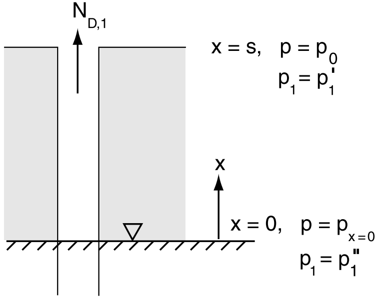

Fig. 1. Boundary conditions by diffusion through a stagnant film $\dot{N}_2 = 0$ – one-side diffusion.

paper – now can been calculated with the aid of Eqs. (3) and (6) to be:

$$\begin{aligned}\dot{N}^{(y)}_{\mathrm{dif},1} &= -D_{12}\left(\frac{c}{p}\right)p\nabla y - D_{\mathrm{vis}}\left(\frac{c}{p}\right)y\nabla p\\ &= -D_{12}\left(\frac{c}{p}\right)p\nabla y\left(1+\frac{D_{\mathrm{vis}}}{D_{12}}\frac{y}{1-y}\frac{1}{\vartheta}\right)\\ &= -D_{12}\left(\frac{c}{p}\right)\frac{p\nabla y}{1-y}. \qquad (9)\end{aligned}$$

For the integration of Eq. (9) the function $p = f(y)$ is to be determined. This can easily be done with the aid of Eq. (5) and Eq. (6)

$$\frac{1}{\vartheta}\int_{y'}^{y}\frac{\nabla y}{1-y} = \int_{p_0}^{p}\frac{\nabla p}{p} \quad \text{or} \quad \frac{p}{p_0} = \left(\frac{1-y'}{1-y}\right)^{1/\vartheta}. \qquad (10)$$

Eq. (10) introduced into Eq. (9) yields

$$\dot{N}^{(y)}_{\mathrm{dif},1} = -D_{12}\left(\frac{c}{p}\right)\frac{(1-y')^{1/\vartheta}}{(1-y)^{(\vartheta+1)/\vartheta}}p_0\nabla y$$

and after integrating we get

$$\dot{N}^{(y)}_{\mathrm{dif},1} = \frac{D_{12}}{s}c_0\vartheta\left[\left(\frac{1-y'}{1-y''}\right)^{1/\vartheta} - 1\right] \quad \text{with } c_0 = \frac{p_0}{RT}. \qquad (11)$$

The mol-fractions y' and y'' are given from Eq. (7) by

$$y' = \frac{p_1'}{p_0}, \quad y'' = \frac{p_1''}{p_{x=0}}.$$

In the limiting case of the continuum region the relation ϑ will be $\vartheta \to \infty$ and for the diffusion flux through a stagnant film (one-side diffusion) we get the well-known equation

$$\dot{N}^{(y)}_{\mathrm{dif},1} = \frac{D_{12}}{s}c_0\ln\frac{1-y'}{1-y_0''}. \qquad (12)$$

The ratio of the diffusing fluxes according to Eqs. (11) and (12) is shown in Table 1. One can see that the influence of the frictional viscous compensation flow is very small compared with the flow without friction. At first, caused by high vapor pressures p_1 and values of ϑ near the transition region ($\vartheta = 10$, $Kn = 0.035$ we are already in the transition region), the influence on the diffusion flux is remarkable.

By a pressure gradient ∇p in a gas- or fluid-mixture in a porous structure beyond the viscous flow, a pressure diffusion becomes possible. For ideal gases the rate of the diffusion flux [1,6] can be written

$$\dot{N}^{(p)}_{\mathrm{dif},i} = -\mu_1 D_{12}\left(\frac{c}{p}\right)y_i\nabla p \qquad (13)$$

with μ_i being the ratio of the molecular weights of the components in the mixture

$$\mu_1 = \frac{M_{12}-M_1}{M_{12}} = \frac{(1-y)(M_2-M_1)}{M_{12}},$$

$$\mu_2 = \frac{M_{12}-M_2}{M_{12}} = \frac{-y(M_2-M_1)}{M_{12}}.$$

In the foregoing section it was shown that the pressure gradient generated by the ordinary diffusion in the continuum region is very small. Therefore, a flux by pressure diffusion is to be neglected, too. By the pressure increase in the transition region, however, the pressure diffusion will get remarkable. In the Knudsen region the pressure diffusion turns into the pressure term of the molecular motion $\dot{N}^{(p)}_{Kn,i}$, just like all other terms change over to the corresponding terms of the molecular motion (see below). Certainly, if an external pressure gradient is imposed, like centrifugal forces in a gas-centrifuge, e.g., only then the pressure diffusion is the dominating transport mechanism.

The fluxes by ordinary diffusion, by pressure diffusion and viscous flow are allowed to be directly added. Effects of linkages are not relevant, because the various flows are proportional to gradients (linear laws), and these quantities of different tensorial character do not couple in the linear approximation in isotropic systems (Curie's theorem) [2].

Table 1
Influences of p_1''/p_0 and ϑ, resp. Kn_0 at the pressure rise $p_{x=0}/p_0$ and diffusion flux $\dot{N}_{\mathrm{dif},1}$ in the continuum region

$$\left(\vartheta = \frac{p\nabla y}{(1-y)\nabla p},\ \frac{\dot{N}_{\mathrm{dif},1}}{\dot{N}_{\mathrm{dif},1|0}} = \vartheta\left[\left(\frac{1-y'}{1-y''}\right)^{1/\vartheta} - 1\right]\left[\ln\frac{1-y'}{1-y_0''}\right]^{-1}\right)$$

	p_1''/p_0	0.1	0.3	0.5	0.7	0.9
$\vartheta = 1000;\ Kn_0 = 3\times10^{-3}$	$p_{x=0}/p_0$	1.0001	1.0004	1.0007	1.0012	1.0023
	$\dot{N}_{\mathrm{dif},1}/\dot{N}_{\mathrm{dif},1\vert0}$	1.0000	0.9997	0.9994	0.9983	0.9923
$\vartheta = 100;\ Kn_0 = 1\times10^{-2}$	$p_{x=0}/p_0$	1.0011	1.0036	1.0069	1.0118	1.0215
	$\dot{N}_{\mathrm{dif},1}/\dot{N}_{\mathrm{dif},1\vert0}$	1.0000	0.9974	0.9936	0.9834	0.9345
$\vartheta = 10;\ Kn_0 = 3.5\times10^{-2}$	$p_{x=0}/p_0$	1.0105	1.0348	1.0654	1.1055	1.1610
	$\dot{N}_{\mathrm{dif},1}/\dot{N}_{\mathrm{dif},1\vert0}$	0.9939	0.9764	0.9437	0.8762	0.6991

2. Molecular motion in the Knudsen region

In the Knudsen region $Kn > 1$ only the impulse of the gas- or vapor-molecules against the wall of the pores dispose of the mass transfer. Diffusion and bulk flow turn into the molecular motion. Fig. 2 shows the true equivalent diffusion coefficients (without tortuosity factors) as function of the pore diameter and of the Knudsen-number $Kn = \Lambda/d_\mathrm{p}$, resp. With the equivalent diffusion coefficient for the molecular motion

$$D_{Kn,i} = \frac{4}{3}\frac{d_\mathrm{p}}{\mu_\mathrm{p}}\sqrt{\frac{RT}{2\pi M_i}} \tag{14}$$

the mass transfer occurs due to the free molecule flow:

$$\begin{aligned}\dot{N}_{Kn,1} &= -D_{Kn,1}\left(\frac{c}{p}\right)p\nabla y - D_{Kn,1}\left(\frac{c}{p}\right)y\nabla p\\ &= -D_{Kn,1}\left(\frac{c}{p}\right)\nabla p_1,\\ \dot{N}_{Kn,2} &= +D_{Kn,2}\left(\frac{c}{p}\right)p\nabla y - D_{Kn,2}\left(\frac{c}{p}\right)(1-y)\nabla p\\ &= -D_{Kn,2}\left(\frac{c}{p}\right)\nabla p_2.\end{aligned} \tag{15}$$

The partial-pressure gradients in Eq. (15) are defined by

$$\nabla p_1 = p\nabla y + y\nabla p, \quad \nabla p_2 = -p\nabla y + (1-y)\nabla p$$

Eq. (15) reveals that the fluxes $\dot{N}_{Kn,i}$ consist of the parts $\dot{N}^{(y)}_{Kn,i} \sim \nabla y$ and $\dot{N}^{(p)}_{Kn,i} \sim \nabla p$. A superimposed bulk-flow, like the compensation flow by diffusion, is impossible.

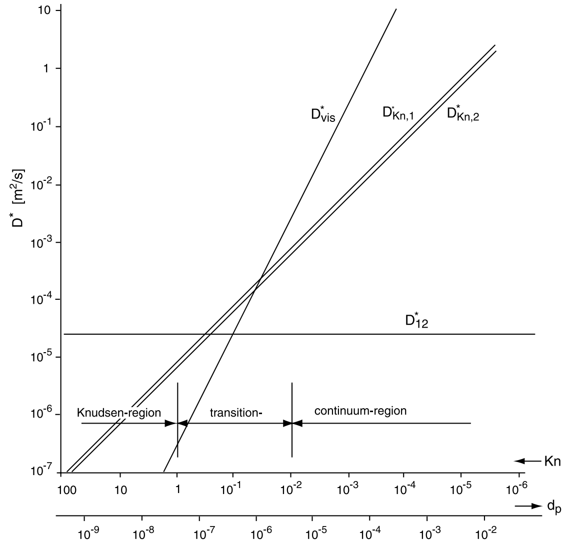

Fig. 2. Equivalent diffusion coefficients for H_2O-vapor–air in a stagnant film ($\alpha = 0$); ordinary diffusion D_{12}, molecular motion $D_{Kn,i}$ viscous flow D_vis, without tortuosity, for $p_0 = 1$ bar.

The separation factor α

$$\alpha = \frac{\dot{N}_{Kn,2}}{\dot{N}_{Kn,1}} = +\frac{D_{Kn,2}}{D_{Kn,1}}\frac{\nabla p_2}{\nabla p_1} = -\frac{D_{Kn,2}}{D_{Kn,1}}\frac{p\nabla y - (1-y)\nabla p}{p\nabla y + y\nabla p} \tag{16}$$

is valid in the continuum region as well as in the Knudsen region, as shown by other theoretical and experimental investigations [2,5].

From Eq. (16) the pressure gradient ∇p created in the Knudsen region and the appropriate ratio ϑ, resp., is calculated by

$$\vartheta = \frac{p\nabla y}{(1-y)\nabla p} = \frac{(1-y)(D_{Kn,2}/D_{Kn,1}) - y\alpha}{(1-y)(D_{Kn,2}/D_{Kn,1} + \alpha)}. \tag{17}$$

One-side transfer, i.e. evaporation, through a porous medium requires a pressure gradient, corresponding to Eq. (15) for $\dot{N}_{Kn,2} = 0$ or to Eq. (17) for $\alpha = 0$

$$\nabla p_2 = -p\nabla y + (1-y)\nabla p = 0 \rightarrow \vartheta = \frac{p\nabla y}{(1-y)\nabla p} = 1. \tag{18}$$

This result already can be derived from Eq. (6), if the flow and the diffusion change over to the molecular-motion in the Knudsen region: $D_\mathrm{vis}, D_{12} \rightarrow D_{Kn,i}$. The molecular flux by one-side transfer $\dot{N}_{Kn,1}$ now can be calculated with Eq. (15) and the condition following from Eq. (18):

$$\begin{aligned}\dot{N}_{Kn,1} &= -D_{Kn,1}\left(\frac{c}{p}\right)(p\nabla y + y\nabla p)\\ &= -D_{Kn,1}\left(\frac{c}{p}\right)p\nabla y\left(1 + \frac{y}{1-y}\,\frac{1}{\vartheta}\right)\\ &= -D_{Kn,1}\left(\frac{c}{p}\right)\frac{p\nabla y}{1-y}.\end{aligned} \tag{19}$$

The function $p = f(y)$ is to be calculated by an integration of Eq. (17) for $\alpha = 0$

$$\frac{p}{p_0} = \frac{1-y'}{1-y} = \frac{p}{p_0}\,\frac{p_0 - p_1'}{p - p_1} \quad \text{or } p = p_0 + (p_1 - p_1'). \tag{20}$$

For the pressure at $x = 0$ it follows

$$p_{x=0} = p_0 + (p_1'' - p_1') \quad \text{or} \quad \frac{p_{x=0}}{p_0} = 1 + \frac{p_1'' - p_1'}{p_0}, \tag{21}$$

which is a relation independent of ϑ and valid in the whole Knudsen region. Inserting Eq. (20) into Eq. (19) we can write

$$\dot{N}_{Kn,1} = -D_{Kn,1}\left(\frac{c}{p}\right)p_0\frac{(1-y')\nabla y}{(1-y)^2}$$

and after integrating between the boundary conditions (cf. Fig. 1)

$$x = 0 : y = y'' = \frac{p_1''/p_0}{p_{x=0}/p_0}, \quad x = s : y' = p_1'/p_0$$

one gets

$$\dot N_{Kn,1} = \frac{D_{Kn,1}}{s} c_0 \frac{y'' - y'}{1 - y''}. \tag{22}$$

It must be pointed out that by a transfer through a stagnant film in the Knudsen region there must be an increase of the pressure at $x = 0$ to neutralize the flux $\dot N_{Kn,2}$ which is a fundamental fact. Then this gradient is taken into account by the integration, too. The result of Eq. (22) holds the form of a known approximation for ordinary diffusion, but the principal origin is different (see Section 6, too).

3. Mass transfer in the transition region

In the transition region diffusion (ordinary and pressure diffusion) and molecular motion superimpose. The formal disposition is known [2]. Beyond the indicated concentration gradient, a pressure gradient will be formed, like it was shown in the foregoing section for the molecular motion and for the boundary between continuum- and transition region. This fact imposes that beyond the fluxes on account of the concentration gradient – $\dot N^{(y)}_{\mathrm{dif},i}$ (ordinary diffusion) and $\dot N^{(y)}_{Kn,i}$ (molecular motion term $\sim \nabla y$) – fluxes on account of the pressure gradient – $\dot N^{(p)}_{\mathrm{dif},i}$ (pressure diffusion) and $\dot N^{(p)}_{Kn,i}$ (molecular motion term $\sim \nabla p$) are generated. Moreover the viscous flow $\dot N_{\mathrm{vis}}$ is to be superimposed. For this case two model-concepts have the same chance to be correct. They are identical in the continuum region and in the Knudsen region, but they are different in the transition region [4,5]. It is to prove which one is able to describe the effects in the transition region correctly.

(1) The fluxes $\dot N^{(y)}_{\mathrm{dif},i}$ and $\dot N^{(y)}_{Kn,i}$ are serially connected as well as the fluxes $\dot N^{(p)}_{\mathrm{dif},i}$ and $\dot N^{(p)}_{Kn,i}$. The two compensation fluxes in both ways are connected parallel, cf. Fig. 3. The total fluxes in this connection are given by

$$\begin{aligned}\dot N_{D,1} &= \dot N^{(y)}_{D,1} + \dot N^{(p)}_{D,1}\\ &= -\left[\frac{1 - y(1+\alpha^{(y)})}{D_{12}} + \frac{1}{D_{Kn,1}}\right]^{-1}\left(\frac{c}{p}\right)p\nabla y\\ &\quad -\left[\frac{1 - y(1+\alpha^{(p)})}{\mu_1 D_{12}} + \frac{1}{D_{Kn,1}}\right]^{-1}\left(\frac{c}{p}\right)y\nabla p\end{aligned} \tag{23}$$

with

$$\alpha^{(y)} = \frac{\dot N_{D,2}}{\dot N_{D,1}} = \frac{-D_{Kn,2}}{D_{Kn,1}}, \quad \alpha^{(p)} = \frac{\dot N_{D,2}}{\dot N_{D,1}} = -\left(\frac{\mu_1}{\mu_2}\right)\left(\frac{D_{Kn,2}}{D_{Kn,1}}\right)$$

and in an analogous manner for component 2.

If viscous, i.e. frictional compensation flows are introduced like Eq. (3) in both diffusion flows:

$$\dot N^{(y)}_{\mathrm{vis}} = \dot N^{(y)}_{D,1} + \dot N^{(y)}_{D,2} = \dot N^{(y)}_{D,1}(1+\alpha^{(y)}) = -D_{\mathrm{vis}}\left(\frac{c}{p}\right)\nabla p^{(y)}$$

$$\dot N^{(p)}_{\mathrm{vis}} = \dot N^{(p)}_{D,1} + \dot N^{(p)}_{D,2} = \dot N^{(p)}_{D,1}(1+\alpha^{(p)}) = -D_{\mathrm{vis}}\left(\frac{c}{p}\right)\nabla p^{(p)}$$

then a pressure gradient ∇p^y is generated in the flow of the ordinary diffusion $\dot N^{(y)}_{\mathrm{dif},i} \sim \nabla y$. But this pressure gradient cannot be disintegrated because this model does not provide a flow $\sim \nabla p$ for this kind of ordinary diffusion. The serial connection of the fluxes $\dot N^{(y)}_{\mathrm{dif},i}$ and $\dot N^{(y)}_{Kn,i}$, as well as of the fluxes $\dot N^{(p)}_{\mathrm{dif},i}$ and $\dot N^{(p)}_{Kn,i}$ seems plausible, because only the fluxes with the same gradient are superimposed in the well-known manner. Nevertheless, this consideration by introduction of a viscous compensation flow shows that this model of serial connection is unable to describe the effects in a physically correct way.

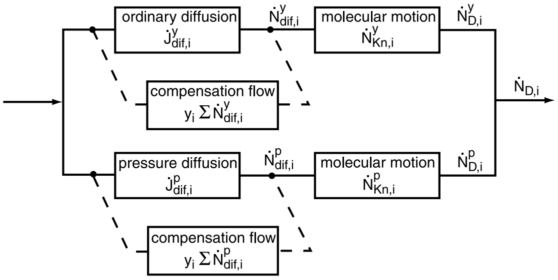

Fig. 3. Model for the diffusive fluxes in serial connection.

(2) In the second model the diffusion fluxes $\dot N^{(y)}_{\mathrm{dif},i}$ and $\dot N^{(p)}_{\mathrm{dif},i}$ are connected parallel, as well as the fluxes $\dot N^{(y)}_{Kn,i}$ and $\dot N^{(p)}_{Kn,i}$ of the molecular motion, cf. Fig. 4. The mass transfer by this connection is described by the equations

$$\begin{aligned}\dot N_{D,1} &= \left[\frac{1}{\dot N_{\mathrm{dif},1}} + \frac{1}{\dot N_{Kn,1}}\right]^{-1}\\ &= -\left(\frac{c}{p}\right)\left[\frac{1 - y(1+\alpha)}{D_{12}p\nabla y + D_{12}\mu_1 y\nabla p}\right.\\ &\quad \left. + \frac{1}{D_{Kn,1}(p\nabla y + y\nabla p)}\right]^{-1}\end{aligned} \tag{24}$$

with

$$\alpha = \frac{D_{Kn,2}}{D_{Kn,1}}\frac{\nabla p_2}{\nabla p_1} = -\frac{D_{Kn,2}}{D_{Kn,1}}\frac{p\nabla y - (1-y)\nabla p}{p\nabla y + y\nabla p}$$

and analogous for component 2.

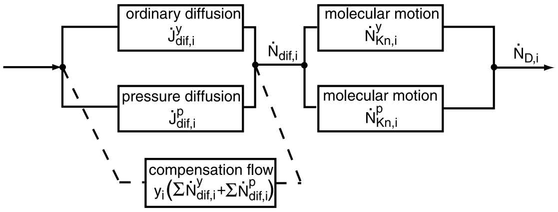

Fig. 4. Model for the diffusive fluxes in parallel connection.

In the continuum region, $Kn \ll 0.01$, the pressure gradient is to be neglected, as shown above. But in the transition – and in the Knudsen region there arises a pressure gradient, which results in a viscous flow, a molecular motion and a pressure diffusion. At first the pressure gradient is unknown and is to be calculated for the conditions of the different systems, e.g. for an open or closed system, for countercurrent diffusion or for diffusion through a stagnant film.

The frictional compensation flow $\dot{N}_{\text{vis}}$ in this model also includes the compensation flow of the ordinary and the pressure diffusion. This flow will be calculated with Eq. (3) again

$$\dot{N}_{\text{vis}} = \dot{N}^{(y)}_{\text{dif},1} + \dot{N}^{(y)}_{\text{dif},2} + \dot{N}^{(p)}_{\text{dif},1} + \dot{N}^{(p)}_{\text{dif},2} = -D_{\text{vis}}\left(\frac{c}{p}\right)\nabla p. \tag{25}$$

With Eq. (25) we can write for Eq. (24):

$$\dot{N}_{D,1} = -\left(\frac{c}{p}\right)\left[\frac{1}{D_{12}p\nabla y + \mu_1 D_{12} y\nabla p + D_{\text{vis}} y\nabla p} + \frac{1}{D_{Kn,1}(p\nabla y + y\nabla p)}\right]^{-1}. \tag{26}$$

It is easy to prove the compatibility of the Eqs. (24) and (26).

The gradient ∇p can be determinated as follows: The concentration gradient can be considered as the sum of the gradient owning to the collisions of the molecules with each other and to the collisions of the molecules with the wall of the pores

$$\nabla y = \nabla y|_{\text{molec}} + \nabla y|_{\text{wall}}.$$

In the continuum region the mass transfer $\dot{N}^{y}_{\text{dif},i}$ is produced by $\nabla y|_{\text{molec}}$, in the Knudsen region $\dot{N}^{y}_{Kn,i}$ by $\nabla y|_{\text{wall}}$. In the continuum region the gradient ∇p causes the pressure diffusion and the viscous flow, in the Knudsen region the molecular motion term $\dot{N}^{p}_{Kn,I}$:

$$\dot{N}_{\text{dif},1} = -D_{12}\left(\frac{c}{p}\right)p\nabla y|_{\text{molec}} - (\mu_1 D_{12} + D_{\text{vis}})\left(\frac{c}{p}\right)y\nabla p, \tag{27}$$

$$\dot{N}_{Kn,1} = -D_{Kn,1}\left(\frac{c}{p}\right)p\nabla y|_{\text{wall}} - D_{Kn,1}\left(\frac{c}{p}\right)y\nabla p. \tag{28}$$

With the ratio of the gradient $\vartheta = (p\nabla y/(1-y)\nabla p)$ i.e. for the continuum region $\vartheta = \vartheta|_{\text{molec}}$ due Eq. (5) and for the Knudsen region $\vartheta = \vartheta|_{\text{wall}}$ due Eq. (17) the Eqs. (27) and (28) can be resolved for $\nabla y|_{\text{molec}}$, and for $\nabla y|_{\text{wall}}$, resp.:

$$\left(\frac{c}{p}\right)p\nabla y|_{\text{molec}} = \frac{-\dot{N}_{\text{dif},1}}{D_{12} + (\mu_1 D_{12} + D_{\text{vis}})\frac{y}{1-y}\frac{1}{\vartheta|_{\text{molec}}}}, \tag{29}$$

$$\left(\frac{c}{p}\right)p\nabla y|_{\text{wall}} = \frac{-\dot{N}_{Kn,1}}{D_{Kn,1}\left(1 + \frac{y}{1-y}\frac{1}{\vartheta|_{\text{wall}}}\right)}. \tag{30}$$

The addition of the both gradients results in the total gradient of the concentration [2]:

$$\left(\frac{c}{p}\right)p\nabla y = \left(\frac{c}{p}\right)\left(p\nabla y|_{\text{molec}} + p\nabla y|_{\text{wall}}\right) \tag{31}$$

In this addition it has to be regarded, that the fluxes $\dot{N}_{\text{dif},1}$ and $\dot{N}_{Kn,1}$ must be identical (as by a serial connection): $\dot{N}_{\text{dif},i} = \dot{N}_{Kn,i} = \dot{N}_{D,i}$. So we get

$$\left(\frac{c}{p}\right)p\nabla y = -\dot{N}_{D,1}\left[\frac{1}{D_{12} + (\mu_1 D_{12} + D_{\text{vis}})\frac{y}{1-y}\frac{1}{\vartheta|_{\text{molec}}}} + \frac{1}{D_{Kn,1}\left(1 + \frac{y}{1-y}\frac{1}{\vartheta|_{\text{wall}}}\right)}\right] \tag{32}$$

Eq. (32) is an universal equation to calculate the diffusive flux $\dot{N}_{D,i}$ by different values of ϑ due to the Eq. (5) and (17), respectively, of the separation factor α in these equations.

For the mass transfer through a stagnant film (one-side diffusion) it is to set $\dot{N}_{D,2} = 0$, $\alpha = 0$. We get

$$\left(\frac{c}{p}\right)\frac{p\nabla y}{1-y} = -\dot{N}_{D,1}\left(\frac{1}{D_{12}}\frac{D_{\text{vis}}}{\mu_1 y D_{12} + D_{\text{vis}}} + \frac{1}{D_{Kn,1}}\right). \tag{33}$$

In the case of a compensation flow without friction there is $D_{\text{vis}} \to \infty$ and we obtain the known equation (note: because $\nabla p = 0$, $p = p_0 : \vartheta_{\text{wall}} = \infty$, $\vartheta_{\text{molec}}/D_{\text{vis}} = 1/D_{12}$)

$$\left(\frac{c}{p}\right)p\nabla y = -\dot{N}_{D,1}\left(\frac{1-y}{D_{12}} + \frac{1}{D_{Kn,1}}\right). \tag{34}$$

The ratio of the gradient for the whole range of Knudsen-numbers will be formed by superimposing $\vartheta|_{\text{molec}}$ due to Eq. (5) and $\vartheta|_{\text{wall}}$ due to Eq. (17):

$$\vartheta = \vartheta|_{\text{molec}} + \vartheta|_{\text{wall}} = \frac{p\nabla y}{(1-y)\nabla p} = \frac{D_{\text{vis}}}{D_{12}}\frac{1-y(1+\alpha)}{(1-y)(1+\alpha)} + \frac{(1-y)\frac{D_{Kn,2}}{D_{Kn,1}} - y\alpha}{(1-y)\left(\frac{D_{Kn,2}}{D_{Kn,1}} + \alpha\right)}. \tag{35}$$

In the case of the diffusion through a stagnant film there is $\alpha = 0$

$$\vartheta = \frac{D_{\text{vis}}}{D_{12}} + 1. \tag{36}$$

The development of the pressure along the diffusion path will be received by integration of Eq. (35) (cf. Eq. (10)):

$$\frac{p}{p_0} = \left(\frac{1-y'}{1-y}\right)^{1/\vartheta} = \left(\frac{p_0 - p'_1}{p - p_1}\right)^{1/(\vartheta-1)}. \tag{37}$$

For the pressure on the side of the generation of the diffusive flux, e.g. by evaporation, drying – $x = 0$, $p = p_{x=0}$, $p_1 = p''_1$ – we get

$$\frac{p_{x=0}}{p_0} = \left(\frac{p_0 - p'_1}{p_{x=0} - p''_1}\right)^{D_{12}/D_{\mathrm{vis}}}. \tag{38}$$

By integration of Eq. (33) for the diffusive flux the relation $p = f(y)$ according to Eq. (37) has to be taken into account. This equation can be integrated only numerically. However the error by the integration will be small, if we regard the term $y\mu_1$ to be a constant with a mean value $\bar{y} = \frac{1}{2}(y' + y'')$. Then for the flux by diffusive mass transfer through a stagnant film with ϑ according to Eq. (36) we obtain

$$\dot{N}_{D,1} = \frac{D_{12}c_0}{s}\vartheta\left[\left(\frac{1-y'}{1-y''}\right)^{1/\vartheta} - 1\right] \times \left[\frac{D_{\mathrm{vis}}}{D_{\mathrm{vis}} + \overline{\mu_1 y} D_{12}} + \frac{D_{12}}{D_{Kn,1}}\right]^{-1}. \tag{39}$$

The limiting values of Eq. (39) in the continuum region ($D_{\mathrm{vis}} \gg D_{Kn,i} \gg D_{12}, \vartheta \to \infty$) are

$$\dot{N}_{D,1} = \frac{D_{12}c_0}{s}\ln\frac{1-y'}{1-y''_0} \quad \text{(cf. Eq. (13))} \tag{40}$$

and in the Knudsen region ($D_{\mathrm{vis}} \ll D_{Kn,i} \ll D_{12}, \vartheta = 1$)

$$\dot{N}_{D,1} = \frac{D_{Kn,1}c_0}{s}\frac{y'' - y'}{1-y''} \quad \text{(cf. Eq. (22))}. \tag{41}$$

The concentrations y' and y'' are to be set $y' = p'_1/p_0, y'' = p''_1/p_{x=0}$ i.e. at first the pressure rise $p_{x=0}$ by Eq. (38) must be calculated.

For the diffusive flux without a viscous compensation flow, i.e. frictionless, we get $\dot{N}_{D,1|0}$ by integration of Eq. (34)

$$\dot{N}_{D,1|0} = \frac{D_{12}c_0}{s}\ln\frac{1 + (D_{Kn,1}/D_{12})(1-y')}{1 + (D_{Kn,1}/D_{12})(1-y''_0)}. \tag{42}$$

This equation includes only the diffusion slip in the transition region. In Fig. 5 the diffusive flux $\dot{N}_{D,1}$, in a dimensionless form $(\dot{N}_{D,1}s/D_{12}c_0)\,(1/y''_0 - y')$ for different vapor pressures p''_1, and the ratio ϑ are represented. Fig. 6 shows the pressure rise $p_{x=0}$ in the dimensionless form $p_{x=0} - p_0/p''_1 - p'_1$.

In the transition region there is a continuous changeover from the frictionless compensation flow of the continuum region ($\nabla p \approx 0$) to the basically given pressure rise in the Knudsen region as illustrated in Figs. 5 and 6.

With these considerations on one-side mass transfer through a stagnant film – as it occurs in evaporation, drying, adsorption, catalytically processes and so on – it is demonstrated that only the so-called model with parallel connection, Fig. 4, is able to give physically plausible results.

Eqs. (26), (32), (33) and their integration – numerical or analytical (Eq. (39)) – include the effects of pressure diffusion, diffusion slip and slip flow in an implicate but distinct manner.

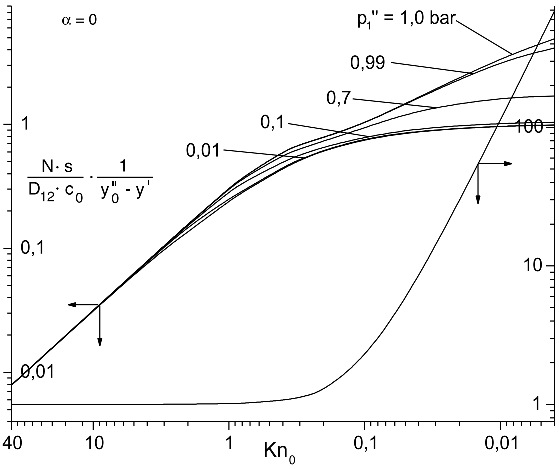

Fig. 5. Dimensionless ratio of the gradients $\vartheta = (p\nabla y/(1-y)\nabla p)$, dimensionless diffusion flux $(\dot{N}_{D,1}s/D_{12}c_0)\,(1/y''_0 - y')$ as function of the Knudsen number Kn_0 for the diffusion H_2O-vapor in a stagnant film ($\alpha = 0$) ($p_0 = 1$ bar, $p'_1 = 0$, $D_{\mathrm{vis}} = 172 \times 10^6 d_p^2 (p/p_0)$ m²/s, $D_{12} = 25,1 \times 10^6 (p_0/p)$ m²/s, $D_{Kn,1} = 198 \cdot d_p$ (m²/s), $D_{Kn,2} = 156 \cdot d_p$ (m²/s), $\Lambda_0 = 40 \times 10^{-9}$ m).

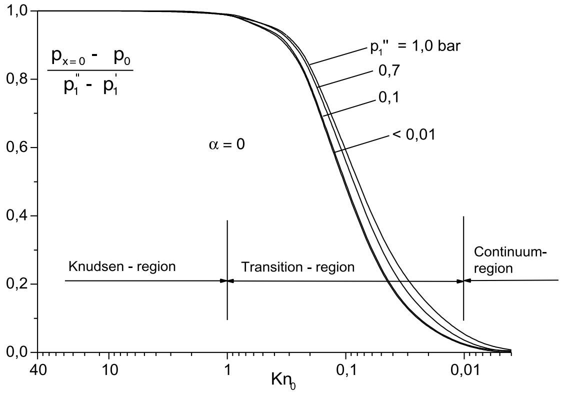

Fig. 6. Dimensionless pressure rise $p_{x=0} - p_0/p''_1 - p'_1$ as function of Kn_0 for the example in Fig. 5.

4. The influence of pressure diffusion

The influence of pressure diffusion in the transition region on the pressure rise $p_{x=0}$ and on the diffusive flux

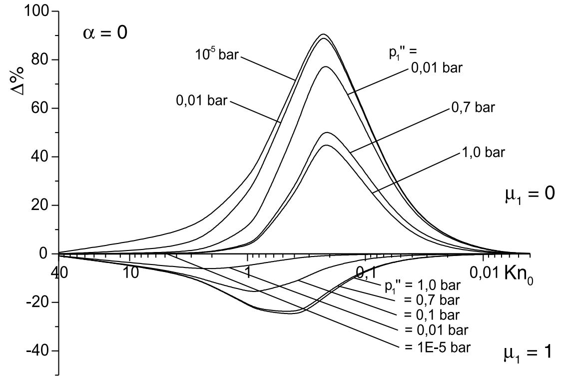

Fig. 7. Influence of the pressure diffusion on the diffusive flux in the transition region for the limiting cases $\mu_1 = 1$ and $\mu_1 = 0$ compared with the numerical integration of Eq. (33):

$$\Delta\% = \left(\frac{\dot{N}_{D1|\mu_1=1 \text{ or}=0}}{\dot{N}_{D1|\mu_i}} - 1 \right) \times 100.$$

$\dot{N}_{D,1}$ can easily be derived if we set 1. $\mu_1 = 0$, i.e. the pressure diffusion is neglected, and 2. $\mu_1 = 1$, i.e. the pressure diffusion is taken into account with its maximal value. The deviations of these limiting cases from the exact values gained by the numerical integration of Eq. (33) are calculated for the example of Fig. 5 and showed in Fig. 7. As one can see the pressure diffusion is only to be taken into consideration in the transition region, but in this region its influence is significant in certain cases.

5. Comparison of the frictional and the frictionless disposition

Without a viscous compensation flow, i.e. $\nabla p = 0$, in case of $\alpha = 0$, we have obtained for the diffusive flux $\dot{N}_{D,1|0}$, Eq. (42) with the limiting equation of the continuum region

$$\dot{N}_{D,1|0} = \frac{D_{12} c_0}{s} \ln \frac{1 - y'}{1 - y''_0} \quad \text{with } y''_0 = \frac{p''_1}{p_0} \tag{43}$$

identical Eq. (40), and for the Knudsen region

$$\dot{N}_{D,1|0} = \frac{D_{Kn,1} c_0}{s} (y''_0 - y'). \tag{44}$$

Eq. (44) is identical Eq. (41), too. This can be proved, if we set $y'' = p''_1 / p_{x=0}$ and $p_{x=0} = p_0 + p''_1 - p'_1$ (Eq. (21)):

$$y''_0 - y' = \frac{y'' - y'}{1 - y''}. \tag{45}$$

This identity must be demanded for the Knudsen region, because there is only molecular motion and not any other flow.

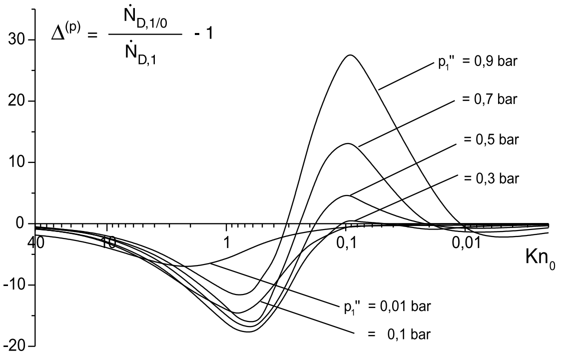

Fig. 8. Deviations between the description of the diffusive fluxes by a viscous frictional flow and by a frictionless flow.

In Fig. 8 the deviations of $\dot{N}_{D,1|0}$, Eq. (42), to $\dot{N}_{D,1}$, by numerical integration of Eq. (33) with Eq. (37), in the form $\dot{N}_{D,1|0} / \dot{N}_{D,1} - 1$ are shown. In the continuum and Knudsen region there are no deviations, like it has to be. Only in the transition region deviations will be formed. Positive, if the reduction effect of the viscous flow on $\dot{N}_{D,1}$ is more considerable than the increasing effect of pressure diffusion. Negative, if the effect of the missing pressure diffusion $\dot{N}_{D,1|0}$ is more intense than the effect of the frictionless flow.

6. Final remarks

It has to be pointed out that the model discussed in this paper is only a concept to calculate certain effects of mass transfer and not the absolute physical reality – like all models for physical and other processes.

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