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Multi-component gas mixture diffusion through porous media: A 1D analytical solution

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Abstract

In this paper, the equations governing the transport of gas mixtures through porous media in 1D geometry and in absence of mass sources are examined. When the mass fluxes are determined by external conditions, the transport equations can be solved to find the variations of gas composition through the media. For this class of problems, we show that the convective transport mechanism can be, in many cases, neglected, regardless of the physical properties of the porous media and of the flux intensities. An estimate of the maximum error made in neglecting the convective term is provided. A matrix analytical solution of the diffusion equations is given for the general case of *N*-components gas mixtures. Explicit analytical solutions are derived in two particular cases.

Keywords: Stefan–Maxwell; Knudsen; Dusty gas model; Fuel cells

1. Introduction

The transport of multi-component gas mixtures through porous media is a physical phenomenon that plays a fundamental role in many important applications. At present, for example, gas separation devices and fuel cell electrodes are the subject of a large number of experimental and modelling studies. The correct description of such phenomenon is, therefore, a living subject in the literature. Recently, Suvanwarangkul et al. [1] have compared different models commonly used in the description of gas transport inside porous fuel cells anodes: the Fick's model [2–4], the Dusty Gas Model (DGM) [5,6] and the Stefan Maxwell model [7,8]. As a conclusion, they find that the DGM is, in general, the most suitable model, but, since it requires a complex numerical solution they suggest its use only in case of necessity. However, their study is limited to a few specific gas mixtures and, therefore, it lacks of generality. Furthermore, they assume, without a rigorous justification, that the convective transport is negligible. This work aims to overcome these problems, as it provides (i) a general and rigorous analysis of the maximum error made in neglecting the convective term and (ii) a matrix analytical solution of the DGM diffusion equations.

The flux equations describing gas transport through a porous media can be derived by simple momentum transfer arguments [9]. There are three mechanisms by which a given species may loose momentum:

- Transfer to another species as a result of collisions between pairs of unlike molecules (Stefan–Maxwell).
- Direct transfer to the pores walls through particle-wall collisions (Knudsen).
- Indirect transfer to the wall via a sequence of molecule–molecule collisions terminating in a molecule–wall collision (Darcy).

1.1. Stefan–Maxwell

The Stefan–Maxwell equations [10,11] describe the diffusion in multi (n) component gas mixtures

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Nomenclature

a	average pore radius
$[\mathbf{a}]$	right eigenvectors of $[\boldsymbol{\varphi}]$
$(\mathbf{b})$	eigenvalues of $[\boldsymbol{\varphi}]$
B_0	Darcy law constant (pore characteristics)
D	dimensionless parameter depending on diffusion coefficients
D_i^{K}	Knudsen diffusion coefficient of species i
$D_{i,j}$	diffusion coefficient of the pair i–j in a gas mixture
F	Faraday constant
I	cell current density
M_i	molecular mass of component i
n	number of gas components
N	dimensionless parameter depending on molar fluxes
N_i	molar flux of gas species i
p	gas pressure
p_i	partial pressure of species i
R	gas constant
R_i	mass source of species i
T	temperature
x_i	molar fraction of species i
z	1D coordinate

Greek symbols

α	dimensionless parameter (Darcy versus Knudsen)
γ	dimensionless constant
δ	ratio between diffusive and convective terms
ε	porosity
$[\boldsymbol{\varphi}]$	Stefan–Maxwell equation matrix
μ_i	gas viscosity of species i
σ^2	molecular cross section
τ	tortuosity
$(\boldsymbol{\zeta})$, $(\boldsymbol{\xi})$	diffusion equation vectors
Ω	collision integral

Subscripts and superscripts

av	average
D	diffusive
i, j	chemical species
in	ingoing (at $z = 0$)
max	maximum
min	minimum
out	outgoing
ref	reference value
r, s	chemical species
V	convective

$$\nabla\left(\frac{p}{RT}x_i\right) = \sum_j \frac{N_j x_i - N_i x_j}{D_{i,j}}. \tag{1}$$

In Eq. (1), the indices i and j run over the n components of the gas mixture, x_i and N_i are the molar fraction and molar flux of species i. $D_{i,j}$ is the i and j pair diffusion coefficient, which can be expressed, by kinetic theory arguments, in terms of the molecular masses M_i and M_j and of the i and j molecular cross section $\sigma^2_{i,j}$, as [12]:

$$D_{i,j} \prec \frac{\sqrt{T^3 \frac{M_i+M_j}{2M_iM_j}}}{p\sigma^2_{i,j}}. \tag{2}$$

Eq. (1) is based on the hypothesis that each component of a gas mixture moves in a continuous medium, where it is subject to the friction forces caused by the other gas components.

The consequences of neglecting the friction forces of the gas molecules with any solid framework (i.e. no external force acts on the gas) are that there is no pressure gradient and that the diffusion equations are independent of the inertial reference frame (i.e. they contain no information about the global motion of the fluid).

The absence of a global pressure gradient can be easily verified: by summing the n Stefan–Maxwell equations (1), considering that, by definition, $\sum_i x_i = 1$, and using the symmetry of the pair diffusion coefficients, we get:

$$\nabla\left(\frac{p}{RT}\right) = 0.$$

As a consequence only $n - 1$ out of the n equations (1) are independent. By imposing mass conservation conditions:

$$\nabla \cdot N_i = R_i, \tag{3}$$

where R_i is the possible mass source of species i, we get n more scalar equations.

But, as we have n vector unknowns (N_i) and $n - 1$ independent scalar unknowns (x_i), there is one vector equation lacking and one scalar equation too much. This reflects the absence of information about the global motion of the flux mentioned above and a specific choice of inertial frame is required to close the system. If, for example, we choose the frame where the mean gas motion is zero, we can write:

$$\sum_i N_i = 0.$$

1.2. Knudsen

When the diffusion process occurs inside a porous medium, the friction forces between the gas species and the pores walls may not be negligible. In particular, when the mean pores diameter is much smaller than the mean free path of the gas molecules, the number of gas–solid collisions becomes much larger than the number of gas–gas collisions. In such conditions, the momentum transfer is dominated by the gas–solid friction force term and the fluxes are described by the Knudsen equations [13]:

$$\nabla\left(\frac{p}{RT}x_i\right) = -\frac{N_i}{D_i^{\mathrm{K}}}, \tag{4}$$

where the i species Knudsen diffusion coefficient D_i^{K} can be expressed in terms of the molecular mass and of the average pore radius a, as [9]:

$$D_i^{\mathrm{K}} \prec a\left(\frac{8RT}{\pi M_i}\right)^{\frac{1}{2}}. \tag{5}$$

When the mean pores diameter is comparable to the mean free path of the gas molecules, both the Stefan–Maxwell and Knudsen momentum loss mechanisms have to be considered, as the molecules of a given species exchange momentum both with molecules of different species and with walls.

$$\nabla\left(\frac{p}{RT}x_i\right) = \sum_j \frac{N_j x_i - N_i x_j}{D_{i,j}} - \frac{N_i}{D_i^{\mathrm{K}}}. \tag{6}$$

By summing the above equations, and considering that $\sum_i x_i = 1$, we get:

$$\nabla\left(\frac{p}{RT}\right) = -\sum_j \frac{N_j}{D_j^{\mathrm{K}}}. \tag{7}$$

We see that the gas–solid friction forces cause a global pressure gradient and provide as a reference frame the frame solid with the porous media.

Eq. (6) together with Eq. (3) forms a system of n vector and n scalar equations with n vector and n scalar unknowns. A more rigorous derivation of Eq. (6) can be found in the frame of the Dusty Gas Model [14].

1.3. Darcy

When the mean pore diameter is much larger than the molecular mean free path lengths, and for pure (single component) gases, the intra-molecular viscous friction forces dominate with respect to the friction forces caused by the collisions with the pore walls. In such conditions, the fluxes are described by the Darcy law [15]:

$$N_i = -\frac{x_i B_0 p}{\mu_i RT}\nabla p, \tag{8}$$

where μ_i is the gas viscosity of species i and B_0 is a factor, which characterizes the porous media. For cylindrical pores we have [9]:

$$B_0 = \frac{a^2}{8}. \tag{9}$$

When the mean pores diameter is comparable to the mean free path of the gas molecules, both the Knudsen and the Darcy mechanisms should be taken into account. Because molecules exchange momentum with the walls either directly or indirectly, the two mechanisms can be considered as occurring in parallel and the total flux can be considered as the sum of a viscous (convective) flux and a diffusive flux as:

$$N_i = N_i^{\mathrm{V}} + N_i^{\mathrm{D}}$$

with

$$N_i^{\mathrm{V}} = -\frac{x_i B_0 p}{\mu_i RT}\nabla p$$

and

$$\nabla\left(\frac{p x_i}{RT}\right) = \sum_j \frac{N_j^{\mathrm{D}} x_i - N_i^{\mathrm{D}} x_j}{D_{i,j}} - \frac{N_i^{\mathrm{D}}}{D_i^{\mathrm{K}}}.$$

The equations above, form a set of $2n$ vector equations for $2n$ unknown fluxes. In the limit where one of the three mechanisms dominates, this set reduces to the corresponding Eqs. (1) and (4) or (8). It has been shown [9] that it also provides a good description of the transport phenomena in intermediate situations, where all three mechanisms may be of comparable importance.

1.4. Porous media

The presence of the solid media causes also a decrease of the volume free to gas diffusion and an extension of the path that the gas should walk to cross the tortuous media. These two effects can be described at a macroscopic level by using the porosity (ε) and the tortuosity (τ) parameters and by rescaling the pair and the Knudsen diffusion coefficients according to:

$$D = \frac{\varepsilon}{\tau} D^{\mathrm{void}},$$

where D^{void} is the corresponding parameter in the void space.

The same rescaling applies also to the Darcy parameter B_0.

1.5. 1D equations

When there is a preferential direction of flux motion and all the molar species flow along this direction, Eqs. (8) and (6) can be written in scalar form:

$$N_i = N_i^{\mathrm{V}} + N_i^{\mathrm{D}},$$

$$N_i^{\mathrm{V}} = -\frac{x_i B_0 p}{\mu_i RT}\frac{\partial p}{\partial z} \tag{10}$$

and

$$\frac{1}{RT}\frac{\partial (p x_i)}{\partial z} = \sum_j \frac{N_j^{\mathrm{D}} x_i - N_i^{\mathrm{D}} x_j}{D_{i,j}} - \frac{N_i^{\mathrm{D}}}{D_i^{\mathrm{K}}}, \tag{11}$$

where z is the coordinate along the flow direction.

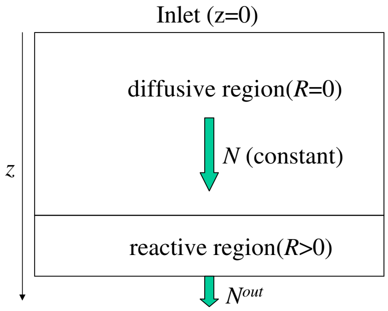

Fig. 1. Sketch of the diffusion media.

The conservation equations (3) become

$$\frac{\partial N_i}{\partial z} = R_i. \tag{12}$$

When the mass sources are absent or located in a well-defined portion of the porous media (the reactive region) in the remaining part of the porous media (the diffusive region) Eq. (12) implies constant fluxes along the z-direction. This situation is illustrated in Fig. 1.

In such case, following the boundary conditions, the transport problems can be divided into two main classes:

- when the gas composition is known at both sides of the porous media, the mass fluxes can be obtained by solving the transport equations;
- when the mass fluxes are determined by external conditions, the transport equations can be solved to find the variations of gas composition through the porous media.

In the following, we will consider only the problems belonging to the latter class. The problems of reactant transport toward (or from) the reaction sites often belong to the latter class. Indeed, the value of the reactant fluxes inside the diffusive region can be obtained by integrating the mass conservation equation inside the reactive region:

$$N_i = N_i^{\text{in}} = \int_{\text{reactive region}} R_i + N_i^{\text{out}}.$$

When the outgoing flux N_i^{out} is zero (for example when the reactive region is contiguous to a non permeable media or when the reactants are fully consumed by the reaction) the value of the fluxes in the diffusive region is determined by the integral of the mass sources. In a fuel cell, for example, the electrochemical reactions occur inside a thin reactive region located between the gas impermeable electrolyte and the electrode diffusive region. Inside the diffusive region, the molar fluxes are constant and proportional to the cell current density.

1.6. Paper summary

In the next section, we study how the convective term of the flux equations influences the gas composition profiles. It is seen that the convective term is very often negligible regardless of the physical properties of the porous medium and of the flux intensities. A rigorous quantitative estimate of the maximum error made in neglecting the convective term is provided for a two component gas mixture, together with a generalized estimate for multi-component mixtures. When this error is small, only the diffusive contributions to the flux equations should be considered to determine the variations of gas composition through the porous media. The simplified equations correspond to the Stefan–Maxwell–Knudsen equations (11).

In Section 3, a matrix analytical solution of the diffusion equations (11) is given.

In Section 4, the matrix procedure is used to find analytical solutions in the general two-component gas problem and in a particular three-component application concerning the anode of a solid oxide fuel cell. Finally, in Section 5, the results of this paper are discussed and conclusions are drawn.

2. Comparison between the convective and diffusive contribution to the molar fraction variations

When the molar fluxes are known, the set of flux equations (10) and (11) becomes a set of differential equations in the molar fractions, which, once a proper set of boundary conditions is provided, can be solved to get the molar fraction profiles.

In order to assess the possibility to simplify the flux equations by neglecting some of its composing terms, in this section we study how the different mechanisms contribute to the molar fraction variations. To reach this goal, we need first to rearrange suitably the flux equations.

Eqs. (10) and (11) can be written in compact form in terms of the total fluxes:

$$\begin{aligned}\frac{p}{RT}\nabla x_r + \frac{x_r}{RT}\left(1+\frac{B_0 p}{\mu D_r^{\mathrm{K}}}\right)\nabla p \\ = -\sum_{s\neq r}\frac{x_s N_r - x_r N_s}{D_{r,s}} - \frac{N_r}{D_r^{\mathrm{K}}}.\end{aligned} \tag{13}$$

By defining an average Knudsen diffusion coefficient as:

$$\frac{1}{D_{\text{av}}^{\mathrm{K}}} = \sum_s \frac{x_s}{D_s^{\mathrm{K}}}$$

and the dimensionless parameter α as:

$$\alpha = \frac{B_0 p}{\mu D_{\text{av}}^{\mathrm{K}}} \tag{14}$$

and by summing Eq. (13) on the index r, we obtain an expression for the pressure gradient:

$$\nabla p = -\frac{RT}{1+\alpha}\sum_s \frac{N_s}{D_s^{\mathrm{K}}}. \tag{15}$$

By combining Eqs. (13) and (15), we get:

$$\frac{p}{RT}\nabla x_r = \underbrace{\overbrace{\sum\nolimits_{s\neq r}\frac{x_rN_s - x_sN_r}{D_{r,s}}}^{\text{Stefan–Maxwell}} + \overbrace{x_r\sum\nolimits_{s}\frac{N_s}{D_s^{\mathrm{K}}} - \frac{N_r}{D_r^{\mathrm{K}}}}^{\text{Knudsen}}}_{\text{diffusive terms}} + \underbrace{\frac{\alpha}{1+\alpha}\sum\nolimits_{s}\frac{N_s}{D_s^{\mathrm{K}}}x_r\left(\frac{D_{\mathrm{av}}^{\mathrm{K}}}{D_r^{\mathrm{K}}}-1\right)}_{\text{convective term}}. \quad (16)$$

In Eq. (16), the contributions of the different momentum transfer mechanisms to the molar fraction variations have been emphasized.

In the following, we first study the limiting conditions of very small and very large pore radius, and then, we analyze the relative importance of the convective mechanism in the whole range of pore radii.

The parameter α (see Eq. (14)) gives a measure of the relative importance of the Darcy mechanism with respect to the Knudsen one. By substituting Eqs. (5) and (9) in Eq. (14), we see that α is proportional to the average pore radius a. Therefore, in the limit of very small pore radius, α becomes very small and the convective term in Eq. (16) can be neglected. Moreover, in the limit of very small a, the Stefan–Maxwell term in Eq. (16) can be neglected as well and Eq. (16) reduces to the Knudsen equation (4).

In the opposite limit of very large pore radius, α becomes very large and Eq. (16) becomes:

$$\lim_{\alpha\to\infty}\left(\frac{p}{RT}\nabla x_r\right) = -\sum_{s\neq r}\frac{x_sN_r - x_rN_s}{D_{r,s}} - \frac{N_r}{D_r^{\mathrm{K}}} + x_r\frac{D_{\mathrm{av}}^{\mathrm{K}}}{D_r^{\mathrm{K}}}\sum_s\frac{N_s}{D_s^{\mathrm{K}}}. \quad (17)$$

In the limit of large a, the Knudsen diffusion coefficients become very large and the last two terms in Eq. (17) becomes negligible, and Eq. (17) reduces to the Stefan–Maxwell Eq. (1).

Here above, we have seen that in both limits of very large and very small pore radius, the convective term in Eq. (16) is negligible. To see if and in which conditions the convective term of Eq. (16) is still negligible in the intermediate pore radius range, the simple case of a two-component gas is examined in Appendix A. The value of the ratio δ between the diffusive and the convective contributions to the molar fraction variation is found to be larger than a minimum value $\delta_{\min}$:

$$\delta \geqslant \delta_{\min} = \frac{\left(\frac{N}{\sqrt{\gamma}}\sqrt{1-D^2} - D\sqrt{1-N^2} + N + D\right)^2}{2D\left(1-\sqrt{1-N^2}\right)(N+D)}, \quad (18)$$

where

$$\gamma = \frac{B_0pD_{1,2}}{\mu D_1^{\mathrm{K}}D_2^{\mathrm{K}}}, \quad N = \frac{N_1+N_2}{N_1-N_2},$$
$$D = \frac{D_2^{\mathrm{K}} - D_1^{\mathrm{K}}}{D_2^{\mathrm{K}} + D_1^{\mathrm{K}}} = \frac{\sqrt{M_1}-\sqrt{M_2}}{\sqrt{M_1}+\sqrt{M_2}} \quad (19)$$

are dimensionless variables: γ is evaluated in Appendix B, and it is seen to be approximately constant around the value of 0.13. N depends on the molar fluxes. When we are dealing with reactive flows, one of the two species is the reactant and the other is the product. In such case, the fluxes N_1 and N_2 have opposite signs and N is comprised between -1 and 1. The presence of the term $\sqrt{1-N^2}$ in Eq. (18) indicates that such condition is necessary in order to have a minimum value of δ.[1]

Without loss of generality, we can suppose $D > 0$, (otherwise it is sufficient to exchange the 1 and 2 indices). In such conditions, it can be seen that the minimum value of $\delta_{\min}$ is obtained when N is worth one. Then we get:

$$\delta_{\min}(N=1) = \frac{\left(\sqrt{(1-D)} + \sqrt{(1+D)\gamma}\right)^2}{2D\gamma} \quad (20)$$

or, by using the definition of D given in Eq. (19),

$$\delta_{\min}(N=1) = \frac{\left(1+\sqrt{\gamma\sqrt{\frac{M_1}{M_2}}}\right)^2}{\gamma\sqrt{\frac{M_1}{M_2}}-\gamma}.$$

Another interesting case is $N = 0$ which corresponds to a reaction transforming species 1 into species 2. In this case we get:

$$\delta_{\min}(N=0) = \frac{\left(\sqrt{1-D^2}+\sqrt{\gamma}\right)^2}{D^2\gamma} = \left(1+\frac{2}{\sqrt{\gamma}}\,\frac{\left(\frac{M_1}{M_2}\right)^{\frac{1}{4}}+\sqrt{\gamma}}{\sqrt{\frac{M_1}{M_2}}-1}\right)^2.$$

In Fig. 2, we plot $\delta_{\min}$ versus the mass ratio for both $N = 1$ and $N = 0$.

It is seen that the value of the ratio between the particle masses can provide a sufficient criteria to neglect the convective term of the flux equations. When the masses of species 1 and 2 are very close, $\delta_{\min}$ goes to infinity meaning that the convective term is negligible. In the opposite limit of very different masses, $\delta_{\min}$ goes to 1. Clearly, in this limit, the convective term can not be neglected.

For example, in the case of a hydrogen–water (mixture) counter diffusion (anode of a solid oxide fuel cell), we get $N = 0$, $M_1/M_2 = 9$, $D = 0.5$, $\gamma = 0.13$ and $\delta_{\min} = 46.3$. We see that, in this case, by neglecting the convective term, we make an error, at worse, around 2%.

The general case of a multi-component gas mixture is, of course, more complicated and it is difficult to provide a rigorous estimate of the error made when neglecting the con-

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[1] When the two fluxes have the same direction ($N^2 > 1$), it exists a particular value of the molar fractions $x_1 = N_1/(N_1+N_2)$ that cancels the Stefan–Maxwell contribution. In such conditions and for very large pores (the Knudsen term become negligible as well), the whole diffusive term becomes very small and $\delta_{\min}$ becomes zero.

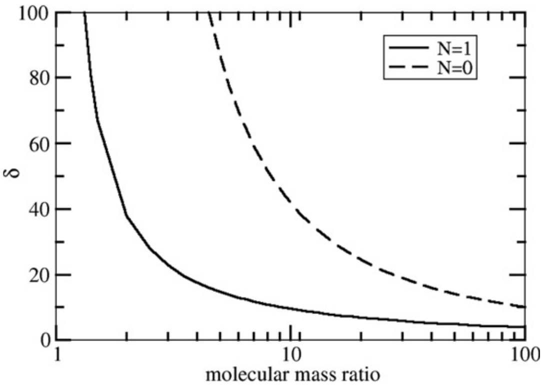

Fig. 2. Minimum value of the ratio δ between the diffusive and convective contribution to the mass fraction variations as a function of the molecular mass ratio. The full line has been obtained for $N = 1$ while the dashed line for $N = 0$.

vective term. It is, in particular, difficult to generalize the condition $N^2 < 1$, necessary in order to have a minimum value of δ (see footnote at page 10). To overcome this limitation, we can consider the comparison problem in a broader sense: for a given gas mixture composition and porous media, we compare the maximum diffusive contribution to the molar fraction variations with the maximum convective contribution, obtainable by keeping the molar fluxes under a fixed threshold value.

In Appendix C, the ratio between the maximum diffusive and convective contributions to the molar fraction variation is calculated for the particular porous media which maximize the convective contribution. It is found:

$$\delta = \frac{D}{2}\,\frac{(1+D)\sqrt{\gamma}+\sqrt{1-D^2}}{\sqrt{1-D^2}+\sqrt{\gamma}-\sqrt{(1-D^2)(1+\gamma)+2\sqrt{(1-D^2)\gamma}}}. \tag{21}$$

In Fig. 3, we plot δ from Eq. (21) versus the mass ratio.

We see that, unless the molecular masses are very different, the maximum convective contribution is limited to a few percent of the maximum diffusive contribution.

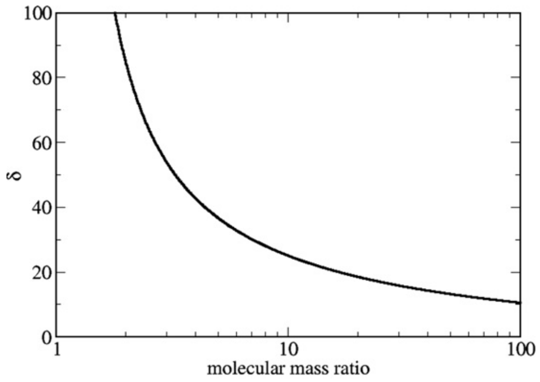

Fig. 3. Value of the ratio δ (from Eq. (21)) between the maximum diffusive and convective contribution to the mass fraction variations as a function of the molecular mass ratio.

For a multi-component mixture, it is easy to rationalize that a conservative estimate of δ can be done by using Eq. (21) but with a different expression for D:

$$D = \frac{\sqrt{M_{\max}}-\sqrt{M_{\min}}}{\sqrt{M_{\max}}+\sqrt{M_{\min}}},$$

where $M_{\max}$ and $M_{\min}$ are the maximum and minimum molecular masses between the species composing the gas mixture.

3. Matrix solution of the Stefan–Maxwell–Knudsen equations

In the last section we have shown that, in most of the cases, only the diffusive terms of the flux equations contribute to the variations of gas composition through the porous media. The simplified equations correspond to the Stefan–Maxwell–Knudsen equations (11).

In this section, a matrix analytical solution of the diffusion equations (11) is given.

Since the total pressure is not constant, it can be preferable to rewrite Eq. (11) in terms of partial pressures instead of molar fractions ($p_i = px_i$):

$$\nabla\left(\frac{p_i}{RT}\right) = \sum_j \frac{N_j p_i - N_i p_j}{pD_{i,j}} - \frac{N_i}{D_i^{\mathrm{K}}}. \tag{22}$$

Because the pair diffusion coefficients (2) are proportional to the inverse of the pressure, the product $pD_{i,j}$ is constant.

By summing and integrating Eq. (22), we get:

$$p = p^{\mathrm{in}} - \sum_j \frac{N_j}{D_j^{\mathrm{K}}} RTz, \tag{23}$$

where p^{in} is the pressure at $z = 0$.

To get a matrix solution of the system it is convenient, to avoid degeneracy, to use Eq. (23) to eliminate one out of the equations (11). By substituting

$$p_n = p - \sum_{j=1}^{n-1} p_j \tag{24}$$

in Eq. (22) and using Eq. (23) we get:

$$\begin{aligned}\frac{1}{RT}\frac{\partial p_i}{\partial z} &= \sum_{j=1}^{n}\frac{N_j p_i}{pD_{i,j}} - \sum_{j=1}^{n-1}\frac{N_i p_j}{pD_{i,j}} \\ &\quad - \frac{N_i}{pD_{i,n}}\left(p^{\mathrm{in}} - \sum_{j=1}^{n}\frac{N_j}{D_j^{\mathrm{K}}}RTz - \sum_{j=1}^{n-1}p_j\right) \\ &\quad - \frac{N_i}{D_i^{\mathrm{K}}}, \quad i = 1,\ldots,n-1,\end{aligned} \tag{25}$$

which is a system of $n-1$ independent Eq. (25) in $n-1$ independent unknowns (p_i).

To solve analytically the above system of equations, we write it in matrix form:

$$\frac{1}{RT}\frac{\partial(\mathbf{p})}{\partial z} = [\boldsymbol{\varphi}](\mathbf{p}) + (\boldsymbol{\zeta}) + (\boldsymbol{\xi})RTz, \tag{26}$$

where the elements of the $n-1\mathrm{X}n-1$ matrix $[\boldsymbol{\varphi}]$ are given by:

$$\varphi_{i,j} = -\frac{N_i}{pD_{i,j}} + \frac{N_i}{pD_{i,n}}, \quad i \neq j$$

$$\varphi_{i,i} = \sum_{k=1}^{n} \frac{N_k}{pD_{i,k}} + \frac{N_i}{pD_{i,n}}.$$

The $n-1$ components of vectors $(\boldsymbol{\zeta})$ and $(\boldsymbol{\xi})$ are given by:

$$\zeta_i = -\frac{N_i}{D_i^{\mathrm{K}}} - \frac{N_i p^{\mathrm{in}}}{pD_{i,n}},$$

and

$$\xi_i = \frac{N_i}{pD_{i,n}} \sum_{k=1}^{n} \frac{N_k}{D_k^{\mathrm{K}}}.$$

The differential matrix equation (26) can be solved formally as a scalar equation. By imposing the boundary conditions:

$$(\mathbf{p}(z)) = (\mathbf{p}^{\mathrm{in}}), \quad z = 0,$$

the solution is:

$$(\mathbf{p}) - (\mathbf{p}^{\mathrm{in}}) = [\exp([\boldsymbol{\varphi}]RTz) - [\mathbf{1}]][(\mathbf{p}^{\mathrm{in}}) + [\boldsymbol{\varphi}]^{-1}(\boldsymbol{\zeta}) + [\boldsymbol{\varphi}]^{-2}(\boldsymbol{\xi})] - [\boldsymbol{\varphi}]^{-1}(\boldsymbol{\xi})RTz. \tag{27}$$

Here above, $[\mathbf{1}]$ is the identity matrix. As usual, the exponential of the $[\boldsymbol{\varphi}]$ matrix should be intended as its polynomial expansion and can be expressed in terms of the eigenvalues $(\mathbf{b})$ and the right eigenvectors $[\mathbf{a}]$ of $[\boldsymbol{\varphi}]$ as:

$$\exp([\boldsymbol{\varphi}]) = [\mathbf{a}]\exp(\mathbf{b})[\mathbf{a}]^{-1}.$$

Notice that, as the matrix $[\boldsymbol{\varphi}]$ is real but non symmetric, its eigenvalues can be complex numbers. It is possible to demonstrate that when the sum of all molar fluxes is zero, the matrix $[\boldsymbol{\varphi}]$ has a zero eigenvalue and it is not possible to define its inverse. Because such condition can be easily verified (as in the example of a methane-free SOFC anode shown in the previous section) it is important to find a way to circumvent the problem. At this scope, we can rewrite Eq. (27) as:

$$(\mathbf{p}) = [\mathbf{a}](\boldsymbol{\theta})[\mathbf{a}]^{-1}(\mathbf{p}^{\mathrm{in}}) + [\mathbf{a}](\boldsymbol{\chi})[\mathbf{a}]^{-1}(\boldsymbol{\zeta}) + [\mathbf{a}](\boldsymbol{\omega})[\mathbf{a}]^{-1}(\boldsymbol{\xi}), \tag{28}$$

where the vectors $(\boldsymbol{\theta})$, $(\boldsymbol{\chi})$ and $(\boldsymbol{\omega})$ are defined by

$$\theta_i = \exp(b_i RTz), \quad \chi_i = \frac{\exp(b_i RTz) - 1}{b_i},$$

$$\omega_i = \frac{\exp(b_i RTz) - 1 - b_i RTz}{b_i^2}, \quad \text{for } b_i \neq 0$$

and

$$\theta_i = 1, \quad \chi_i = RTz, \quad \omega_i = \frac{1}{2}(RTz)^2, \quad \text{for } b_i = 0.$$

4. Results

In the previous section, we have shown that the problem of solving the n coupled differential equations (11) can be reduced to the problem of finding eigenvalues and eigenvectors of the $n-1\mathrm{X}n-1$ matrix $[\boldsymbol{\varphi}]$. This matrix problem is equivalent to a $n-1$th degree polynomial equation and, therefore, has explicit solutions for n up to 4. However, the general solutions for $n > 2$ have very complicated expressions and it is not worth to show them. In such conditions, it is preferable to use a numerical matrix solver to find the matrix $[\mathbf{a}]$ and vector $(\mathbf{b})$ to be inserted in Eq. (28).

In this section, we first present the general solution of the two-component gas diffusion problem. Then, as an example of numerical matrix solution, we describe a particular three-component case.

4.1. Example 1: two components Stefan–Maxwell–Knudsen

When $n = 2$, all the vectors and matrices, which are of dimension $n-1$, become scalars. In particular, we have:

$$\boldsymbol{\varphi} = \frac{N_1 + N_2}{pD_{1,2}},$$

$$\boldsymbol{\zeta} = -\frac{N_1}{D_1^{\mathrm{K}}} - \frac{N_1 p^{\mathrm{in}}}{pD_{1,2}},$$

$$\boldsymbol{\xi} = -\frac{N_1}{pD_{1,2}}\left(\frac{N_1}{D_1^{\mathrm{K}}} + \frac{N_2}{D_2^{\mathrm{K}}}\right).$$

By using these values, Eq. (27) becomes:

$$p_1(z) = p_1^{\mathrm{in}} + \left[\exp\left(\frac{N_1 + N_2}{pD_{1,2}}RTz\right) - 1\right] \times \left[\frac{p_1^{\mathrm{in}}N_2 - p_2^{\mathrm{in}}N_1}{N_1 + N_2} - \frac{N_1 pD_{1,2}}{(N_1 + N_2)^2}\left(\frac{2N_1 + N_2}{D_1^{\mathrm{K}}} + \frac{N_2}{D_2^{\mathrm{K}}}\right)\right] + \frac{N_1 RTz}{(N_1 + N_2)}\left(\frac{N_1}{D_1^{\mathrm{K}}} + \frac{N_2}{D_2^{\mathrm{K}}}\right).$$

The case $N_1 + N_2 = 0$, corresponds to a zero eigenvalue of $[\boldsymbol{\varphi}]$. In this case we must use Eq. (28) and obtain:

$$p_1(z, N_1 + N_2 = 0) = p_1^{\mathrm{in}} - N_1\left(\frac{p^{\mathrm{in}}}{pD_{1,2}} + \frac{1}{D_1^{\mathrm{K}}}\right)RTz - \frac{1}{2}\frac{N_1^2}{pD_{1,2}}\left(\frac{1}{D_1^{\mathrm{K}}} - \frac{1}{D_2^{\mathrm{K}}}\right)(RTz)^2.$$

4.2. Example 2: a methane fed solid oxide fuel cell anode

The anode of methane fed SOFC, in general contains a five-component gas mixture of H_2,CO, CH_4, CO_2 and H_2O.

It can be easily demonstrated that, when the methane steam reforming reaction is fast and irreversible, the shift reaction is at equilibrium and methane is present, water and carbon dioxide are fully consumed. In such conditions, the molar fluxes of the three remaining species are simply related to the cell current density I through the Faraday constant F as follows:

$$N_{\mathrm{H_2}} = -\frac{I}{F}, \quad N_{\mathrm{CO}} = -\frac{I}{2F}, \quad N_{\mathrm{CH_4}} = \frac{I}{2F}.$$

For this gas mixture we have $D = .578$ and, by inserting this value in Eq. (21), we obtain $\delta_{\min} = 21.5$. This means that, by neglecting the convective terms, we make an error of only about 5%. Therefore, this is a simple and physically meaningful case of a three component Stefan–Maxwell–Knudsen diffusion problem, which can be solved by the above procedure.

To keep the results as general as possible, we rewrite Eq. (26) in dimensionless form:

$$\frac{\partial(\tilde{\mathbf{p}})}{\partial\tilde{z}} = [\tilde{\boldsymbol{\varphi}}](\tilde{\mathbf{p}}) + (\tilde{\boldsymbol{\zeta}}) + (\tilde{\boldsymbol{\xi}})\tilde{z},$$

where

$$\tilde{z} = \frac{N_{\mathrm{ref}}}{D_{\mathrm{ref}}}\frac{RT}{p_{\mathrm{ref}}}z, \quad (\tilde{\mathbf{p}}) = \frac{1}{p_{\mathrm{ref}}}(\mathbf{p}), \quad [\tilde{\boldsymbol{\varphi}}] = \frac{p_{\mathrm{ref}}D_{\mathrm{ref}}}{N_{\mathrm{ref}}}[\boldsymbol{\varphi}],$$
$$(\tilde{\boldsymbol{\zeta}}) = \frac{D_{\mathrm{ref}}}{N_{\mathrm{ref}}}(\boldsymbol{\zeta}), \quad (\tilde{\boldsymbol{\xi}}) = \frac{p_{\mathrm{ref}}D^2_{\mathrm{ref}}}{N^2_{\mathrm{ref}}}(\boldsymbol{\xi})$$

and we have defined:

$$N_{\mathrm{ref}} = \frac{I}{2F}, \quad p_{\mathrm{ref}} = 1\ \mathrm{atm}, \quad D_{\mathrm{ref}} = \frac{\varepsilon}{\tau}\ \mathrm{cm^2\ s^{-1}}.$$

In Table 1, the binary and Knudsen diffusion coefficients corresponding to a temperature of 800 °C, atmospheric pressure, and a mean pore diameter of one micrometer are reported.

By assigning the indices 1, 2 and 3, to the species H_2, CO and CH_4, the matrix $[\tilde{\varphi}]$ and vectors $(\tilde{\zeta})$ and $(\tilde{\xi})$ corresponding to these values are:

$$[\tilde{\boldsymbol{\varphi}}] = \begin{pmatrix} -.2721 & .003702 \\ -.3630 & -.2740 \end{pmatrix}, \quad (\tilde{\boldsymbol{\zeta}}) = \begin{pmatrix} .44884 \\ .83333 \end{pmatrix},$$
$$(\tilde{\boldsymbol{\xi}}) = \begin{pmatrix} .070785 \\ .13095 \end{pmatrix}.$$

The eigenvalues of $[\tilde{\varphi}]$ (obtained by using the LAPACK [16] library) are:

$$(\mathbf{b}) = \begin{pmatrix} -.2731 + .03665i \\ -.2731 - .03665i \end{pmatrix},$$

the corresponding eigenvectors are

$$[\mathbf{a}] = \begin{pmatrix} -.002537 - .10045i & .99494 \\ -.002537 + .10045i & .99494 \end{pmatrix},$$

and

$$[\mathbf{a}]^{-1} = \begin{pmatrix} 4.9778i & -4.9778i \\ .50254 + .01269i & .50254 + .01269i \end{pmatrix}.$$

Table 1
Binary and Knudsen diffusion coefficients corresponding to a temperature of 800 °C, atmospheric pressure, and a mean pore radius of half micrometer

$D_{H_2,CO}$	$7.3\varepsilon/\tau$ cm^2 s^{-1}
D_{H_2,CH_4}	$7.4\varepsilon/\tau$ cm^2 s^{-1}
$D_{CH_4,CO}$	$2.0\varepsilon/\tau$ cm^2 s^{-1}
$D^{K}_{H_2}$	$11.2\varepsilon/\tau$ cm^2 s^{-1}
D^{K}_{CO}	$3.0\varepsilon/\tau$ cm^2 s^{-1}
$D^{K}_{CH_4}$	$4.0\varepsilon/\tau$ cm^2 s^{-1}

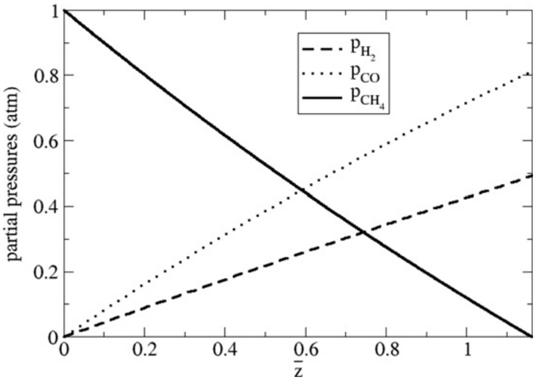

Fig. 4. Partial pressures profiles inside a SOFC anode.

By substituting the obtained values in Eq. (28) and by using, as fuel, pure methane at atmospheric pressure ($\tilde{p}^{\mathrm{in}}_{CH_4} = 1$, $\tilde{p}^{\mathrm{in}}_{H_2} = 0$, $\tilde{p}^{\mathrm{in}}_{CO} = 0$) we get:

$$\tilde{p}_{H_2}(z) = .709[1 - \exp(-.2731\tilde{z})\cos(.03665\tilde{z})] - .182\exp(-.2731\tilde{z})\sin(.03665\tilde{z}) + .262\tilde{z}$$

$$\tilde{p}_{CO}(z) = 1.624[1 - \exp(-.2731\tilde{z})\cos(.03665\tilde{z})] + 7.064\exp(-.2731\tilde{z})\sin(.03665\tilde{z}) + .13\tilde{z}.$$

By using Eq. (24), we get:

$$\tilde{p}_{CH_4}(z) = 1 - 2.333[1 - \exp(-.2731\tilde{z})\cos(.03665\tilde{z})] - 6.882\exp(-.2731\tilde{z})\sin(.03665\tilde{z}) - .132\tilde{z}.$$

In Fig. 4, the solutions are plotted as a function of the dimensionless coordinate $\tilde{z}$. For $\tilde{z} = 1.162$, the methane molar fraction goes to zero and the hydrogen molar fraction reaches its maximum.

Because the hydrogen electrochemical reduction is generally much faster than the methane one, the larger is the hydrogen molar fraction, the more efficient becomes the global electrochemical energy transformation. Therefore, the optimal depth of the anode diffusion layer should be around the value of $z = \frac{D_{\mathrm{ref}}}{N_{\mathrm{ref}}}\frac{p_{\mathrm{ref}}}{RT}1.162 = \frac{\varepsilon 2F}{\tau I}\frac{1}{RT}1.162 = 2.544\frac{\varepsilon}{\tau I}$ cm, where the current density is expressed in units of ampere per square centimeter.

5. Discussion and conclusions

In this paper we provide a matrix procedure for the solution of Eq. (11) and a quantitative estimate of the maximum error made while using it. Here we discuss the limits of the error estimate, the numerical advantages of using the matrix procedure and the possible extensions to multi-dimensional problems.

5.1. Physical considerations

The relatively small contribution of the convective term to the molar fraction variations derives from two main reasons.

First, the Darcy mechanism is an indirect mechanism: a certain number of gas–gas collisions are required in order to transfer the momentum of a single molecule to the porous media. Therefore, it is, in general, less effective than the Stefan–Maxwell mechanism where, *unless the components of the mixture have very similar velocities*, a single collision is sufficient to transfer large part of the molecule momentum.

Second, when the molecular species composing the mixture have the same mass, the Darcy mechanism has no effect on the mixture composition: the total pressure may change but the molar fractions do not.

The first point is verified only when the species composing the gas mixture have different velocities. When the molar fluxes are driven by chemical reactions, as for the transport problems considered in this paper, the molar fluxes are known *a priori* and this condition can be easily checked. On the other hand, when the molar fluxes are driven by pressure gradients, the velocities depend on the problem solution and, in general, the convective term can not be neglected.

The second point, which helps in keeping the convective contribution small unless the molecular species have very different masses (see Figs. 2 and 3), holds only for the molar fractions profiles. The convective contribution to the partial pressure variations remains small due to the first point considerations, but does not depend very much on the molecular mass ratios. Therefore, the error estimates given in Figs. 2 and 3 and in Eqs. (20) and (21) for the molar fraction profiles, are not directly applicable to the partial pressures. However, once the molar fractions are known, by using Eq. (15) it is possible to estimate the error on the pressures and, in case, to calculate the exact pressure profile.

5.2. Numerical considerations

The matrix procedure, on one hand, contains an eigenvalue problem, which often requires numerical solution algorithms, but, on the other hand, it is *zero-dimensional*, as no spatial discretization is required. As a consequence, this procedure has a number of advantages with respect to the numerical ones:

- the solution is computationally faster;
- the numerical errors are generally smaller;
- explicit solutions exist in simple cases (see the examples in the previous section).

5.3. The Stefan–Maxwell limit

In the limit of large pores, the Knudsen diffusion coefficients become very large. As a consequence, the vector $(\boldsymbol{\xi})$ becomes negligible, the elements of the vector $(\boldsymbol{\zeta})$ become:

$$\zeta_i = -\frac{N_i p^{\mathrm{in}}}{p D_{i,n}},$$

while the matrix $[\boldsymbol{\varphi}]$ remains unchanged. In this limit, aside from a slight difference in notation, Eq. (26) and its matrix solution Eq. (27) become equal to Eqs. (11) and (19) of the classic Krishna and Standart paper [17].

5.4. Extension to higher dimensionality

The 1D problem given by Eq. (13) with known fluxes and boundary inlet values for the molar fraction, can be generalized in 2 or 3D as follows: when the gas molar fractions are known on the inlet side of the diffusive region, and the molar fluxes at the boundary with the reactive region (see Fig. 1), the flux Eq. (13) can be solved together with the mass conservation Eq. (3) to obtain the molar fraction profiles.

Clearly, the matrix procedure cannot be used in this case, as the molar fluxes are not constant in 2 or 3D. On the other hand, it is easy to see that the equations derived in Appendix C are still valid. Therefore, for such class of problems, Eq. (21) is still valid when we consider δ is the ratio between the maximum *modulus* of the diffusive and convective terms. As a consequence, Eq. (21) provides a general (not limited to 1D) criteria to check if the convective term of the flux equations is negligible.

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Appendix A. Comparison between convective and diffusive terms for a binary mixture

In the case of a two-component gas, Eq. (13) becomes:

$$\frac{p}{RT}\nabla x_1 = \underbrace{\frac{x_1 N_2}{D_2^{\mathrm{K}}} - \frac{x_2 N_1}{D_1^{\mathrm{K}}} - \frac{x_2 N_1 - x_1 N_2}{D_{1,2}}}_{\text{diffusive terms}} \underbrace{+ \frac{B_0 p}{\mu} \frac{x_1 x_2 \left(\frac{N_1}{D_1^{\mathrm{K}}} + \frac{N_2}{D_2^{\mathrm{K}}}\right)\left(\frac{1}{D_1^{\mathrm{K}}} - \frac{1}{D_2^{\mathrm{K}}}\right)}{1 + \frac{B_0 p}{\mu}\left(\frac{x_1}{D_1^{\mathrm{K}}} + \frac{x_2}{D_2^{\mathrm{K}}}\right)}}_{\text{convective term}}. \tag{A1}$$

To compare the last term of Eq. (A1) (the convective term) to the first three terms (the diffusive terms) we evaluate the ratio δ between the diffusive and the convective terms of Eq. (A1):

$$\delta = \frac{x_1 \frac{N_2}{D_2^{\mathrm{K}}} - x_2 \frac{N_1}{D_1^{\mathrm{K}}} - \frac{x_2 N_1 - x_1 N_2}{D_{1,2}}}{\frac{B_0 p}{\mu} x_1 x_2 \left(\frac{N_1}{D_1^{\mathrm{K}}} + \frac{N_2}{D_2^{\mathrm{K}}}\right)\left(\frac{1}{D_1^{\mathrm{K}}} - \frac{1}{D_2^{\mathrm{K}}}\right)} \left(1 + \frac{B_0 p}{\mu}\left(\frac{x_1}{D_1^{\mathrm{K}}} + \frac{x_2}{D_2^{\mathrm{K}}}\right)\right). \tag{A2}$$

By introducing the dimensionless variables:

$$\gamma = \frac{B_0 p D_{1,2}}{\mu D_1^{\mathrm{K}} D_2^{\mathrm{K}}}, \quad \vartheta = \frac{D_1^{\mathrm{K}} + D_2^{\mathrm{K}}}{2D_{1,2}}, \quad X = x_1 - x_2,$$
$$N = \frac{N_1 + N_2}{N_1 - N_2}, \quad D = \frac{D_2^{\mathrm{K}} - D_1^{\mathrm{K}}}{D_2^{\mathrm{K}} + D_1^{\mathrm{K}}},$$

and after a few algebraic manipulations, Eq. (A2) becomes:

$$\delta = \frac{\left(X(N+D) - 1 - ND + (1-D^2)(NX-1)\vartheta\right)\left(1 + (1+DX)\gamma\vartheta\right)}{(1-X^2)D(N+D)\gamma\vartheta}, \tag{A3}$$

ϑ varies from zero to infinity following the predominance of the Knudsen or Stefan–Maxwell diffusion mechanism. As can be verified immediately, in both limits $\vartheta = 0$ and $\vartheta = \infty$, δ goes to infinity, meaning that the convective term is negligible. To find if it is negligible also in the intermediate range, we look for the minimum of δ with respect to the parameter ϑ:

$$\vartheta_{\min} = \sqrt{\frac{X(N+D) - 1 - ND}{(1+DX)(1-D^2)(NX-1)\gamma}}$$
$$\delta(\vartheta_{\min}) = -\frac{\left(\sqrt{(1-D^2)(1-NX)} + \sqrt{(1+DX)\gamma(1+ND-X(N+D))}\right)^2}{(1-X^2)D(N+D)\gamma}. \tag{A4}$$

X depends on the problem solution and varies between -1 and 1. In both limits $X = -1$ and $X = 1$, δ goes to infinity. We look for the minimum of δ with respect to the parameter X as well:

$$X_{\min} = \frac{1 - \sqrt{1-N^2}}{N}$$
$$\delta(\vartheta_{\min}, X_{\min}) = -\frac{\left(\frac{N}{\sqrt{\gamma}}\sqrt{1-D^2} - D\sqrt{1-N^2} + N + D\right)^2}{2D\left(1 - \sqrt{1-N^2}\right)(N+D)}, \tag{A5}$$

which is Eq. (18) of the text.

By introducing the value of $X_{\min}$ in $\vartheta_{\min}$ we obtain a very simple expression:

$$\vartheta_{\min}(X_{\min}) = [\gamma(1-D^2)]^{-\frac{1}{2}}. \tag{A6}$$

Appendix B. Evaluation of γ

In Ref. [9] the dimensionless variable $\gamma_1 = \frac{B_0 p D_{1,2}}{\mu (D_1^{\mathrm{K}})^2}$ is estimate to be of the order of 0.11. The estimate given there is quite rough as it uses the approximations $D_{1,2} \approx D_{1,1}$ and $\mu \approx \mu_1$ that can be quite wrong when the masses of species 1 and 2 differ significantly. It can be easily seen by exchanging the 1 and 2 indices that $\frac{\gamma_1}{\gamma_2} = \frac{M_1}{M_2}$ and therefore γ is not constant as it depends on the molecular mass.

The symmetric form

$$\gamma = \frac{B_0 p D_{1,2}}{\mu D_1^{\mathrm{K}} D_2^{\mathrm{K}}}, \tag{B1}$$

seems more promising.

For pores with circular sections we can write [9]:

$$B_0 = \frac{\varepsilon a^2}{8\tau},$$
$$D_i^{\mathrm{K}} = \frac{2\varepsilon a}{3\tau}\sqrt{\frac{8RT}{\pi M_i}}.$$

An expression for the pair diffusion coefficients can be found in [12]:

$$pD_{1,2} = \frac{\varepsilon}{\tau} 2.628 \times 10^{-3} \sqrt{T \frac{M_1 + M_2}{2M_1 M_2}} \frac{T}{\sigma_{12}^2 \Omega_D} (\mathrm{atm\ cm^2\ s^{-1}}).$$

An expression for the gas viscosity of a pure gas is given in Ref. [18]:

$$\mu = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2 \Omega_\mu} (\mathrm{g\ cm^{-1}\ s^{-1}}).$$

The gas viscosity of a multi-component mixture can be obtained by combining with quite complex formulas [12] the gas viscosities of the pure components. For the sake of the present estimate, it is sufficient to use the above formula by considering the quantities on it as having values comprised between the 1 and 2 species values.

By substituting the above expressions in Eq. (B1), we get:

$$\gamma = \frac{9\pi}{256} \frac{262.80}{2.6693R} \left(\sqrt{\frac{M_1 + M_2}{2M}} \frac{\sigma^2 \Omega_\mu}{\sigma_{12}^2 \Omega_D} \right)$$
$$= .1325 \sqrt{\frac{M_1 + M_2}{2M}} \left(\frac{2\sigma}{\sigma_1 + \sigma_2} \right)^2 \frac{\Omega_\mu}{\Omega_D}.$$

The quantity in parenthesis oscillates around the value of one. The collision integrals Ω_μ and Ω_D are quite similar, and when the 1 and 2 species have similar masses and diameters, the factor in parenthesis becomes very close to one. To estimate what happens when, in the opposite limit, the 1 and 2 species are significantly different, let's suppose $M_1 = xM_2$ and $\sigma_1 = x^{1/3}\sigma_2$. With M and σ varying from the 1 and 2 species values, and x larger than one, we get:

$$2\sqrt{2}\frac{(1+x)^{1/2}}{(1+x^{1/3})^2} < \sqrt{\frac{M_1 + M_2}{2M}} \left(\frac{2\sigma}{\sigma_1 + \sigma_2} \right)^2$$
$$< 2\sqrt{2}\frac{(1+x)^{1/2}}{(1+x^{1/3})^2} x^{1/6}.$$

For $x = 10$, this factor is comprised between .94 and 1.38 while for $x = 100$, it is still comprised between .893 and 1.924. We can conclude that even if γ is not completely constant, as it can slightly vary both with the shape of the pores and with the molar masses and molar fractions, its variations should be generally limited within a factor of 2.

Appendix C. Comparison between the maximum convective and diffusive terms for a binary mixture

In this appendix, we maximize, separately, the diffusive and convective terms of Eq. (A1) and compare the resulting expressions. In spite of doing such operation for a generic porous media, to simplify the algebra, we operate in the particular media that maximize the relative convective contribution. In the notations of Appendix A, the dimensionless parameter that characterizes the porous media is ϑ, and Eq. (A7) provides a simple expression of the value of ϑ maximizing the relative convective contribution. By using such expression, and the notation of Appendix A, the diffusive term from Eq. (A1), can be written as:

$$\mathrm{dif} = x_1\frac{N_2}{D_2^{\mathrm{K}}} - x_2\frac{N_1}{D_1^{\mathrm{K}}} - \frac{x_2N_1 - x_1N_2}{\sqrt{\gamma D_1^{\mathrm{K}} D_2^{\mathrm{K}}}}. \tag{C1}$$

Without loss of generality we can suppose $D_1^{\mathrm{K}} > D_2^{\mathrm{K}}$ (otherwise is sufficient to exchange the 1 and 2 indices). In such conditions, and when the modulus of the molar fluxes is limited under a given value $N_{\max}$, the maximum of the diffusive term Eq. (C1) is obtained when $x_1 = 1$ ($x_2 = 0$). We get:

$$\mathrm{dif} < N_{\max}\left(\frac{1}{D_2^{\mathrm{K}}} + \frac{1}{\sqrt{\gamma D_1^{\mathrm{K}} D_2^{\mathrm{K}}}}\right). \tag{C2}$$

The convective term from Eq. (A1), can be written as:

$$\mathrm{conv} = \frac{D}{2}\sqrt{\frac{\gamma}{1-D^2}}\,\frac{1-X^2}{1+\sqrt{\frac{\gamma}{1-D^2}}(1+XD)}\left(\frac{N_1}{D_1^{\mathrm{K}}} + \frac{N_2}{D_2^{\mathrm{K}}}\right). \tag{C3}$$

When the modulus of the molar fluxes is limited under a given value $N_{\max}$, the maximum of the convective term Eq. (C3) is obtained for:

$$X = \frac{1}{D\sqrt{\gamma}}\left(\sqrt{(1-D^2)(1+\gamma) + 2\sqrt{(1-D^2)\gamma}} - \sqrt{1-D^2} - \sqrt{\gamma}\right),$$

and $N_1 = N_2 = N_{\max}$. By substituting these values in Eq. (C3), we get:

$$\mathrm{conv} < \frac{1}{D\sqrt{\gamma}}N_{\max}\left(\frac{1}{D_1^{\mathrm{K}}} + \frac{1}{D_2^{\mathrm{K}}}\right)\left(\sqrt{1-D^2} + \sqrt{\gamma} - \sqrt{(1-D^2)(1+\gamma) + 2\sqrt{(1-D^2)\gamma}}\right). \tag{C4}$$

Finally, by dividing Eq. (C2) by Eq. (C4) we get:

$$\delta = \frac{D}{2}\,\frac{(1+D)\sqrt{\gamma} + \sqrt{1-D^2}}{\sqrt{1-D^2} + \sqrt{\gamma} - \sqrt{(1-D^2)(1+\gamma) + 2\sqrt{(1-D^2)\gamma}}},$$

which is Eq. (21) of the text.

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