



## Review

## The Maxwell–Stefan description of mixture diffusion in nanoporous crystalline materials



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## ABSTRACT

The efficacy of nanoporous crystalline materials in separation applications is often influenced to a significant extent by diffusion of guest molecules within the pores of the structural frameworks. The Maxwell–Stefan (M–S) equations provide a fundamental and convenient description of mixture diffusion. The M–S formulation highlights two separate factors that cause mixture diffusion to be intrinsically coupled: correlation effects, and thermodynamic coupling.

By careful and detailed analyses of a variety of published experimental data on (a) mixture permeation across nanoporous membranes, (b) transient uptake of mixtures within crystals, and (c) transient breakthrough characteristics of fixed bed adsorbers, we identify conditions that require the use of M–S equations including both correlation effects and thermodynamic coupling. Situations are also identified in which either of the coupling effects can be ignored.

Correlation effects cause slowing-down of more-mobile-less-strongly-adsorbed molecules by tardier-more-strongly-adsorbed-partner species; such slowing-down effects are often essential for modeling mixture permeation across nanoporous membranes. Overshoots in the transient uptake of the more mobile partners in single crystals are essentially the consequence of thermodynamic coupling, originating from sizable off-diagonal elements of thermodynamic correction factors  $F_{ij}$ .

In the case of transient breakthrough of hexane isomers in a fixed bed of MFI zeolite, we show that thermodynamic coupling effects lead to a significant improvement in the separation performance.

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## 1. Introduction

Ordered crystalline nanoporous materials such as zeolites (crystalline aluminosilicates), metal–organic frameworks (MOFs),

zeolitic imidazolate frameworks (ZIFs), covalent organic frameworks (COFs), and porous aromatic frameworks (PAFs) offer considerable potential for a wide variety of separations. The technologies used in such separations are either fixed bed adsorption units (examples listed in Table 1), or membrane permeation devices (examples are listed in Table 2). The separation performance is dictated by a combination of adsorption and diffusion

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**Notation**

$c_i$	molar concentration of species $i$ in gas mixture, mol m <sup>-3</sup>	$y_i$	mole fraction of component $i$ in bulk vapor phase, dimensionless
$c_{i0}$	molar concentration of species $i$ in gas mixture at inlet to adsorber, mol m <sup>-3</sup>	$V_p$	pore volume, m <sup>3</sup> kg <sup>-1</sup>
$c_t$	total pore concentration in adsorbed mixture, mol m <sup>-3</sup>	$z$	distance along the adsorber, and along membrane layer, m
$\mathcal{D}_i$	Maxwell–Stefan diffusivity, m <sup>2</sup> s <sup>-1</sup>		
$\mathcal{D}_{12}$	M–S exchange coefficient for binary mixture, m <sup>2</sup> s <sup>-1</sup>		
$D_i$	Fick diffusivity of species $i$ , m <sup>2</sup> s <sup>-1</sup>		
$f_i$	partial fugacity of species $i$ , Pa		
$L$	length of packed bed adsorber, m		
$n$	number of species in the mixture, dimensionless		
$N_i$	molar flux of species $i$ , mol m <sup>-2</sup> s <sup>-1</sup>		
$p_i$	partial pressure of species $i$ in mixture, Pa		
$p_t$	total system pressure, Pa		
$q_i$	component molar loading of species $i$ , mol kg <sup>-1</sup>		
$\bar{q}_i$	spatially averaged component molar loading of species $i$ , mol kg <sup>-1</sup>		
$r$	radial direction coordinate, m		
$r_c$	radius of crystallite, m		
$R$	gas constant, 8.314 J mol <sup>-1</sup> K <sup>-1</sup>		
$S_{perm}$	permeation selectivity, dimensionless		
$t$	time, s		
$T$	absolute temperature, K		
$u$	superficial gas velocity in packed bed, m s <sup>-1</sup>		
$v$	interstitial gas velocity in packed bed, m s <sup>-1</sup>		
$x_i$	mole fraction of species $i$ in adsorbed phase, dimensionless		
		<b>Greek letters</b>	
		$\delta$	membrane thickness, m
		$\delta_{ij}$	Kronecker delta, dimensionless
		$\varepsilon$	voidage of packed bed, dimensionless
		$\Gamma_{ij}$	thermodynamic correction factors, dimensionless
		$[\Gamma]$	matrix of thermodynamic correction factors, dimensionless
		$\mu_i$	molar chemical potential, J mol <sup>-1</sup>
		$\Pi_i$	permeance of species $i$ in mixture, mol m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup>
		$\Theta_i$	loading of species $i$ , molecules per unit cell
		$\Theta_{i,sat}$	saturation loading of species $i$ , molecules per unit cell
		$\Theta_t$	total molar loading of mixture, molecules per unit cell
		$\rho$	framework density, kg m <sup>-3</sup>
		$\tau$	dimensionless time, dimensionless
		<b>Subscripts</b>	
		$i$	referring to component $i$
		$t$	referring to total mixture

characteristics, that can be manipulated by proper choice of pore size, pore topology, connectivity, and interactions (both van der Waals and electrostatic) of the guest molecules with the framework atoms. While membrane permeation units are commonly operated under steady-state conditions, the operations of fixed bed adsorption units are intrinsically transient in nature, i.e., the gas (or fluid) phase concentrations vary both with distance along the adsorber,  $z$ , and time,  $t$  [1–3]. The uptake within any crystallite in the fixed-bed adsorber has also a transient character. The description of transient mixture diffusion places a greater burden on process modeling than the corresponding description of steady-state characteristics.

During the last decade, there been a considerable amount of information and insights gained from Molecular Dynamics (MD) simulations to underscore the persuasive advantages in adopting the Maxwell–Stefan (M–S) diffusion equations [4–6], that can be written for a binary mixture as follows

$$-\rho \frac{q_1}{RT} \nabla \mu_1 = \frac{x_2 N_1 - x_1 N_2}{\mathcal{D}_{12}} + \frac{N_1}{D_1} \quad (1)$$

$$-\rho \frac{q_2}{RT} \nabla \mu_2 = \frac{x_1 N_2 - x_2 N_1}{\mathcal{D}_{12}} + \frac{N_2}{D_2}$$

There are three M–S diffusivities that characterize binary mixture diffusion. The M–S diffusivities:  $\mathcal{D}_1$  and  $\mathcal{D}_2$  portray the interaction of species 1 and 2 with the pore walls. The exchange coefficient,  $\mathcal{D}_{12}$  reflects correlation effects in binary mixture diffusion [7].

The chemical potential gradients can be related to the gradients in molar loadings

$$\frac{q_i}{RT} \nabla \mu_i = \sum_{j=1}^n \Gamma_{ij} \nabla q_j; \quad \Gamma_{ij} = \frac{q_i}{f_i} \frac{\partial f_i}{\partial q_j}; \quad i, j = 1, \dots, n \quad (2)$$

The elements  $\Gamma_{ij}$  can be determined from models describing mixture adsorption equilibrium such as the Ideal Adsorbed Solution Theory (IAST) [8].

Eqs. (1) and (2) can be combined to yield explicit expression for the fluxes

$$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = -\frac{\rho}{1 + \frac{x_1 \mathcal{D}_2}{\mathcal{D}_{12}} + \frac{x_2 \mathcal{D}_1}{\mathcal{D}_{12}}} \begin{bmatrix} \mathcal{D}_1 \left(1 + \frac{x_1 \mathcal{D}_2}{\mathcal{D}_{12}}\right) \frac{x_1 \mathcal{D}_1 \mathcal{D}_2}{\mathcal{D}_{12}} \\ \frac{x_2 \mathcal{D}_2 \mathcal{D}_1}{\mathcal{D}_{12}} \\ \mathcal{D}_2 \left(1 + \frac{x_2 \mathcal{D}_1}{\mathcal{D}_{12}}\right) \end{bmatrix} \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \begin{pmatrix} \nabla q_1 \\ \nabla q_2 \end{pmatrix}. \quad (3)$$

Eq. (3) demonstrates that there are two different factors that contribute to strong “coupling” in mixture diffusion. Values of  $\mathcal{D}_i/\mathcal{D}_{12}$  in the range of 1–20 imply strong correlation effects; this results in significant contribution of the off-diagonal elements in the first matrix to the right Eq. (3). Often, but not always, strong correlation effects cause slowing-down of more-mobile-less-strongly-adsorbed molecules by tardier-more-strongly-adsorbed-partner species. Such is the case, for example, for diffusion of H<sub>2</sub>/CO<sub>2</sub>, CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub>, and CH<sub>4</sub>/nC<sub>4</sub>H<sub>10</sub> mixtures structures such as MFI, FAU, and MgMOF-74 [9]. As illustration, Fig. 1a shows MD simulation data on  $\mathcal{D}_1/\mathcal{D}_{12}$  for H<sub>2</sub>/CO<sub>2</sub> mixtures in MgMOF-74, IRMOF-1, MFI, and LTA-Si, expressed as a function of the total concentration,  $c_t = (q_1 + q_2)/V_p$ , of the adsorbed mixture within the pores. The use of pore concentrations  $c_t$  rather than the molar loadings affords a fairer comparison of different host materials as explained in previous works [4,5,10]. For any guest/host combination,  $\mathcal{D}_1/\mathcal{D}_{12}$  is seen to increase as the pore concentration increases; this implies that correlation effects are expected to be stronger for separations operating at higher pressures. Correlations are strongest in one-dimensional (1D) channel structures (e.g., MgMOF-74), intersecting channels (e.g., MFI), and “open” structures (e.g., IRMOF-1, FAU, NaX) consisting of large cages separated by wide windows. For such cases, the more

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