# Communications

## Validating the Darken Relation for Diffusivities in Fluid Mixtures of Varying Densities by Use of MD Simulations

By *R. Krishna** and *J. M. van Baten*

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Molecular Dynamics (MD) simulations have been carried out to determine the self-diffusivities, $D_{i,self}$, of the pure hydrocarbons methane (C1), ethane (C2), propane (C3), and n-hexane (nC6) at various fluid densities. The MD simulations are in reasonable agreement with published experimental data. The influence of fluid density on both $D_{i,self}$ and the Maxwell-Stefan (M-S) diffusivities, $Đ_{ij}$, in binary C1-C2, C1-C3, C2-C3, and C1-nC6 mixtures was also investigated. The MD simulations show that the M-S diffusivities in binary fluid mixtures can be estimated with good accuracy using the Darken relation.

## 1 Introduction

De-methanizers, de-ethanizers, de-propanizers, C2-C3 splitters, are important distillation operations that are carried out at high pressures. A common characteristic of such operations is that the vapor and liquid densities are closer to each other than in conventional atmospheric operations. For accurate column design the non-equilibrium (NEQ) stage approach [1–3] is recommended; these NEQ models require information on the Maxwell-Stefan (M-S) diffusivities. For binary mixtures the M-S diffusivity, $Đ_{12}$, is defined by1):

$$-\frac{1}{RT}\nabla\mu_1 = \frac{x_2(u_1 - u_2)}{Đ_{12}} \tag{1}$$

The M-S diffusivities are strongly influenced by both the fluid mixture density [4] and composition. For ideal gas mixtures $Đ_{12}$ is independent of the mixture composition. For liquid mixtures, in general, $Đ_{12}$ is dependent on the mixture composition and the Darken relation [5] postulates:

$$Đ_{12} = x_2 D_{1,self} + x_1 D_{2,self} \tag{2}$$

where $D_{1,self}$ and $D_{2,self}$ are the self-diffusivities of components 1 and 2, respectively, in the mixture. The $D_{1,self}$ and $D_{2,self}$ are more easily accessible, both experimentally [6–8] and from Molecular Dynamics (MD) simulations [9–12], than the $Đ_{12}$. A recent work [13–15] has confirmed the applicability of Eq. (2) for liquid mixtures. In the present study MD simulations are used to study the diffusion in light hydrocarbons (methane (C1), ethane (C2), propane (C3), and n-hexane (nC6)) and in their binary mixtures (C1-C2, C1-C3, C2-C3, and C1-nC6). The major objective is to examine whether the Darken relation (Eq. (2)) holds for fluid mixtures with widely varying densities.

## 2 MD Simulations

The details of the MD simulation technique to determine diffusivities in pure components and mixtures are well documented in the literature [9–13]; the simulation details are essentially the same as reported in an earlier publication [13]. For alkanes the united atom model is employed and the $CH_x$ groups are considered as single, chargeless interaction centers with their own effective potentials. The beads in the chain are connected by harmonic bonding potentials. A harmonic cosine bending potential models the bond bending between three neighboring beads, a Ryckaert-Bellemans potential controls the torsion angle. The beads in a chain separated by more than three bonds interact with each other through a Lennard-Jones potential. The Lennard-Jones potentials are shifted and cut at 12 Å. The force fields for n-alkanes have been given in detail in Dubbeldam et al. [16]. A minimum of $N$ = 60 molecules was used and the size of the simulation box was adjusted on the basis of the mixture densities estimated from the Peng-Robinson equation of state.

This yields to simulation box sizes varying from 24 Å to 44 Å, depending on the mixture composition. For example, for the C1-C3 mixture at a total pressure of $p$ = 5 MPa and a temperature of $T$ = 333 K the molecular loadings and box sizes were:

(a) $x_1$ = 0.05, $N$ = 100, box size = 25.5235 Å,
(b) $x_1$ = 0.50, $N$ = 100, box size = 40.0017 Å, and
(c) $x_1$ = 0.95, $N$ = 100, box size = 43.8720 Å.

Periodic boundary conditions were employed. The self-diffusivities were determined from the formula:

$$D_{i,self} = \frac{1}{6N_i}\lim_{\Delta t\to\infty}\frac{1}{\Delta t}\left\langle\left(\sum_{l=1}^{N_i}\left(r_{l,i}(t+\Delta t) - r_{l,i}(t)\right)^2\right)\right\rangle \tag{3}$$

where $r_{l,j}(t)$ denotes the position vector of molecule l of species i, $N_i$ is the number of molecules of species i, and the no-

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[*] R. Krishna (author to whom correspondence should be addressed, r.krishna@uva.nl), J. M. van Baten, Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

1) List of symbols at the end of the paper.

tation ⟨...⟩ denotes ensemble averaging. It was also calculated a set of Onsager coefficients $\Lambda_{ij}$:

$$\Lambda_{ij} = \frac{1}{6} \lim_{\Delta t \to \infty} \frac{1}{N} \frac{1}{\Delta t} \left\langle \left( \sum_{l=1}^{N_i} \left( r_{l,i}(t+\Delta t) - r_{l,i}(t) \right) \right) \left( \sum_{k=1}^{N_j} \left( r_{k,j}(t+\Delta t) - r_{k,j}(t) \right) \right) \right\rangle \quad (4)$$

where $N_i$ and $N_j$ are the number of molecules of species i and j, respectively, in the simulations box and $N$ represents the total number of molecules. The M-S diffusivity, $Đ_{12}$, is then calculated from the following relation derived earlier [13]:

$$\begin{aligned} Đ_{12} \equiv \Delta_{11} &= x_2\left(\frac{\Lambda_{11}}{x_1} - \frac{\Lambda_{12}}{x_2}\right) - x_1\left(\frac{\Lambda_{21}}{x_1} - \frac{\Lambda_{22}}{x_2}\right) \\ &= \frac{x_2}{x_1}\Lambda_{11} + \frac{x_1}{x_2}\Lambda_{22} - \Lambda_{12} - \Lambda_{21} \end{aligned} \quad (5)$$

The simulations were carried out on clusters of PCs equipped with Intel Xeon processors running at 3.4 GHz on the Linux operating system. Each simulation campaign was run for a period of 48 h; this was sufficient to obtain reliable statistics to determine the diffusivities.

## 3 Simulation Results and Discussion

Fig. 1 shows the simulation data of the self-diffusivities $D_{i,self}$ of methane (C1), ethane (C2), propane (C3), and n-hexane (nC6) as functions of the fluid mass density. The MD simulations are in reasonably good agreement with the experimental data of Greiner-Schmid et al. [17] and Helbaek et al. [8] and testify to the reliability of the MD simulations, along with the force fields.

Then, the simulations of $D_{i,self}$ and $Đ_{12}$ for binary C1-C2 mixtures at total system pressures of 5, 10, 20, 30, 40, and

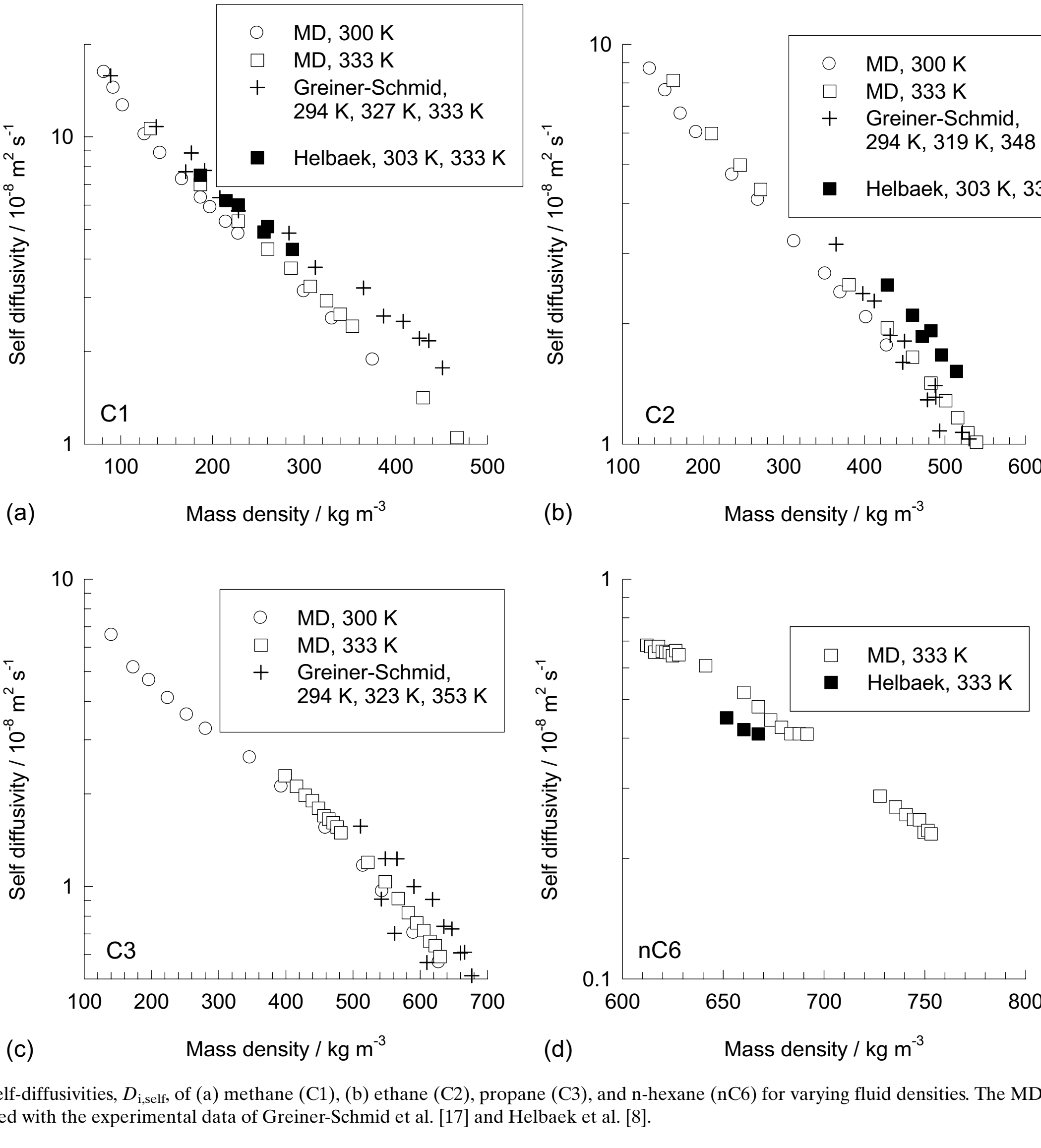

**Figure 1.** Self-diffusivities, $D_{i,self}$, of (a) methane (C1), (b) ethane (C2), propane (C3), and n-hexane (nC6) for varying fluid densities. The MD simulation results are compared with the experimental data of Greiner-Schmid et al. [17] and Helbaek et al. [8].

50 MPa were carried out. The results are shown in Fig. 2. The continuous solid lines represent the calculations of $Đ_{12}$ using the Darken relation (Eq. (2)). The Darken relation is of reasonably good accuracy for all pressures and over the entire composition range.

Similar good agreements between the Darken relation (Eq. (2)) and the MD simulated $Đ_{12}$ were obtained for C1-C3 and C2-C3 mixtures; see Figs. 3 and 4. The tests of the Darken relation – as presented in Figs. 2–4 – are particularly stringent because with varying composition $x_i$ at a specified total pressure $p$, the fluid mixture density is also varied. For illustration, the C1-C3 mixtures are considered at $p$ = 5 MPa. At this pressure, the pure component mass densities are 31 and 449 kg/m$^3$, respectively, for C1 and C3, and the mixture density varies rather sharply in the region of $0.2 \le x_1 \le 0.4$ (see Fig. 3c)). This is reflected also in a sharp

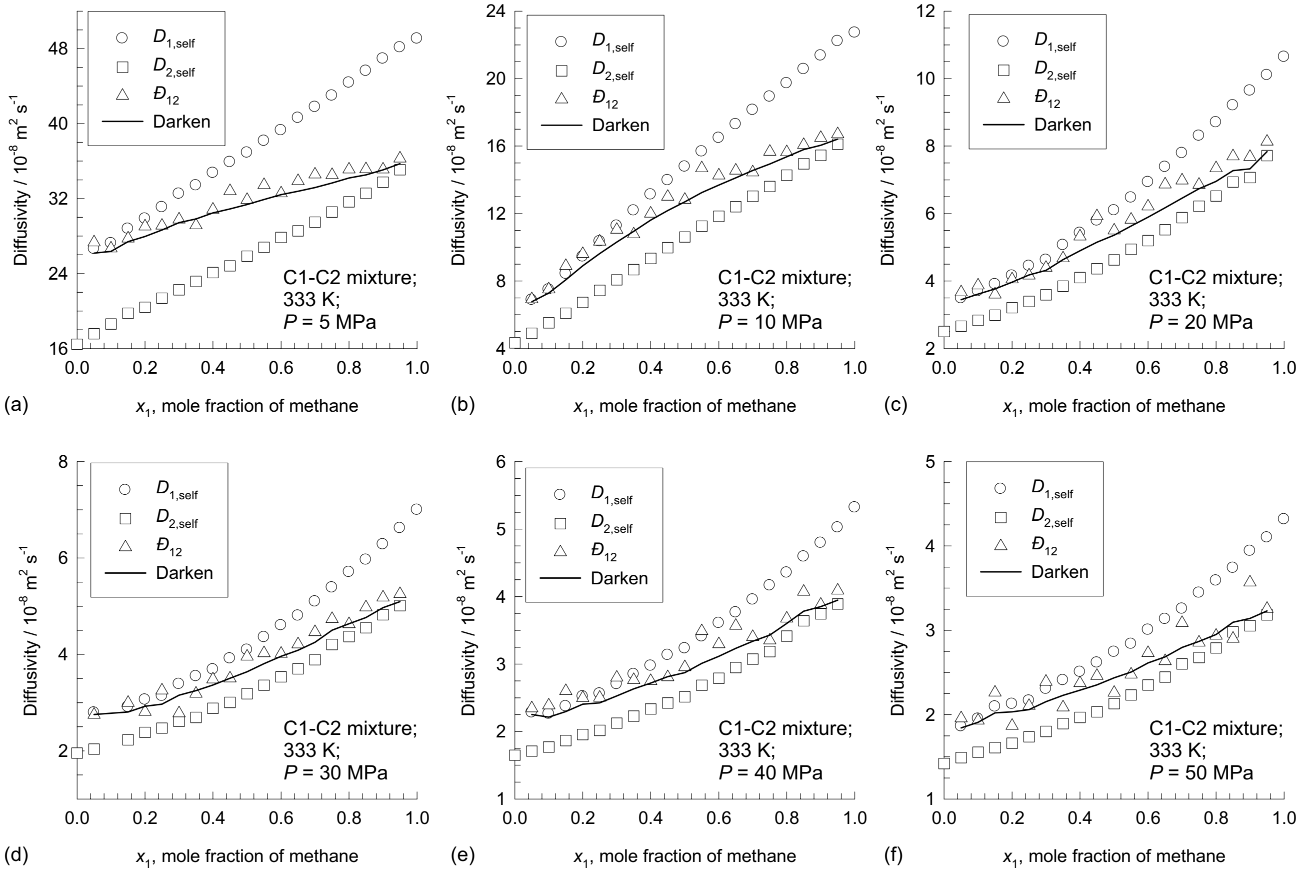

**Figure 2.** Self-diffusivities, $D_{i,\mathrm{self}}$, and M-S diffusivites, $Đ_{12}$, of C1-C2 mixtures at $T$ = 333 K and (a) $p$ = 5 MPa, (b) 10 MPa, (c) 20 MPa, (d) 30 MPa, (e) 40 MPa, and (f) 50 MPa. The continuous solid lines represent the calculations of the M-S diffusivity from the Darken relation (Eq. (2)).

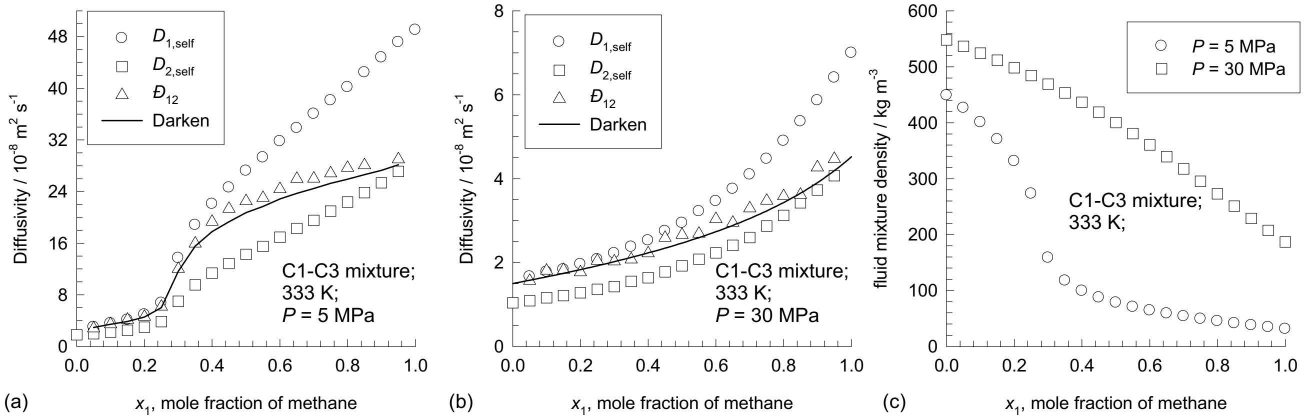

**Figure 3.** Self-diffusivities, $D_{i,\mathrm{self}}$, and M-S diffusivites, $Đ_{12}$, of C1-C3 mixtures at $T$ = 333 K and (a) $p$ = 5 MPa, and (b) $p$ = 30 MPa. The continuous solid lines represent the calculations of the M-S diffusivity from the Darken relation (Eq. (2)). The fluid mixture densities are shown in (c).

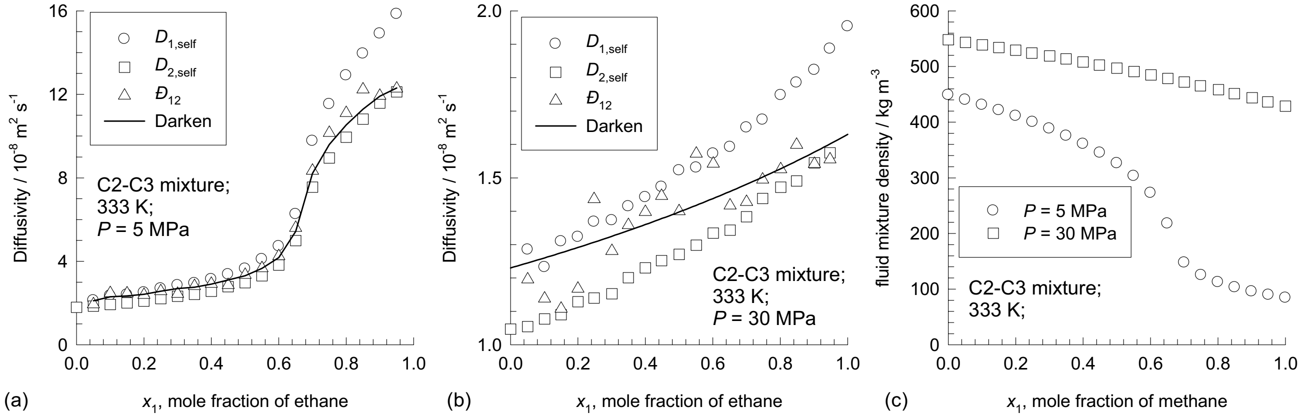

**Figure 4.** Self-diffusivities, $D_{i,self}$, and M-S diffusivites, $Đ_{12}$, of C2-C3 mixtures at $T$ = 333 K and (a) $p$ = 5 MPa, and (b) $p$ = 30 MPa. The continuous solid lines represent the calculations of the M-S diffusivity from the Darken relation (Eq. (2)). The fluid mixture densities are shown in (c).

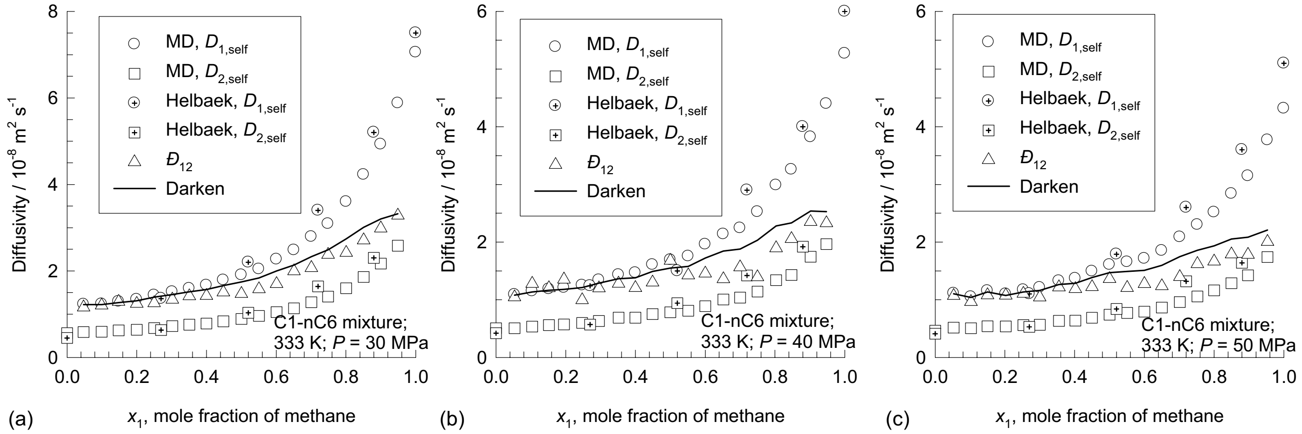

**Figure 5.** Self-diffusivities, $D_{i,self}$, and M-S diffusivites, $Đ_{12}$, of binary C1-nC6 mixtures at total pressures of (a) $p$ = 30 MPa, (b) $p$ = 40 MPa, and (c) $p$ = 50 MPa. The MD simulation results are compared with the experimental data of Helbaek et al. [8]. The continuous solid lines represent the calculations of the M-S diffusivity from the Darken relation (Eq. (2)).

change in the diffusivity values (see Fig. 3a)). For the C2-C3 mixture at $p$ = 5 MPa there is a sharp change in the fluid mixture density in the region of $0.5 \leq x_1 \leq 0.7$ (see Fig. 4c)). This is reflected also in a sharp change in the diffusivity values (see Fig. 4a)).

Fig. 5 presents the MD simulation results of $D_{i,self}$ and $Đ_{12}$ for binary C1-nC6 mixtures at 30, 40, and 50 MPa total pressures. In all three cases the MD simulated $D_{i,self}$ are in good agreement with the experimental data of Helbaek et al. [8]. Furthermore, the calculations using the Darken relation (see Eq. (2)) are in good agreement with the MD simulated $Đ_{12}$.

## 4 Conclusions

Two major conclusions can be drawn from the present study. Firstly, MD simulations are powerful tools to investigate diffusion in fluid mixtures of varying density. Secondly, the Darken relation (Eq. (2)) provides a convenient and simple procedure to estimate the M-S diffusivity $Đ_{12}$ from information on the self-diffusivities $D_{i,self}$. The self-diffusivities in mixtures can be estimated from pure component molecular parameters using theoretical models and mixture rules which are already available in the literature [18].

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## Symbols used

| | | |
|---|---|---|
| $D_{i,self}$ | $[m^2s^{-1}]$ | self-diffusivity |
| $Đ_{12}$ | $[m^2s^{-1}]$ | Maxwell-Stefan diffusivity |
| $N_i$ | [–] | number of molecules of species i in simulation box |

| | | |
|---|---|---|
| $N$ | [–] | total number of molecules in simulation box |
| $p$ | [Pa] | pressure |
| $r$ | [m] | position vector |
| $R$ | [$\mathrm{J\,mol^{-1}K^{-1}}$] | gas constant |
| $t$ | [s] | time |
| $u_\mathrm{i}$ | [$\mathrm{m\,s^{-1}}$] | ensemble-averaged velocity of species i |
| $x_\mathrm{i}$ | [–] | mole fraction of species i |
| $T$ | [K] | absolute temperature |
| $\Lambda_\mathrm{ij}$ | [$\mathrm{m^2\,s^{-1}}$] | Onsager coefficients |
| $\mu_\mathrm{i}$ | [$\mathrm{J\,mol^{-1}}$] | molar chemical potential |

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