I. Introduction. Constitutive Laws

The influence of a homogeneous magnetic field on the transport properties in pure polyatomic gases — the Senftleben-Beenakker effect — has been studied extensively experimentally as well as theoretically during the last decade. In the last years also the magnetic field effects on viscosity and thermal conductivity in mixtures of linear molecules with noble gas atoms have been investigated. All attempts during this time, however, to find a magnetic field influence on diffusion and thermal diffusion failed. Now, recently Eggermont et al. 7 in Leiden succeeded in detecting the transverse effect (concentration gradient perpendicular to \( \mathbf{H} \) and to the temperature gradient) observed by Eggermont et al. 7:

\[
(\nabla \gamma_1)_{\text{trans}} = -(1/T) k_{\text{trans}}^T (\mathbf{H} \times \nabla T) .
\]

For the rectangular box used by Eggermont with length \( L \) in \( x \)-direction, temperature gradient \( \Delta T/L \) in \( y \)-direction and magnetic field in \( z \)-direction the transverse concentration difference \( \delta \gamma_1 = \gamma_1(x = L) - \gamma_1(x = 0) \) is obtained from Eq. (6) as

\[
\delta \gamma_1 = k_{\text{trans}}^T \frac{\Delta T}{L} .
\]

Since the tensors \( D_{\mu \nu}(\mathbf{H}) \) and \( D_{\text{trans}}(\mathbf{H}) \) have the same \( \mathbf{h} \)-dependence as \( k_{\text{trans}}^T(\mathbf{H}) \) [Eq. (5)], one

If at least one of the components is a polyatomic molecule with a magnetic moment and a constant magnetic field \( \mathbf{H} = H \mathbf{h} \) (\( \mathbf{h} \) is a unit vector in the field direction) is present, the coefficients of diffusion, thermal diffusion and also the thermal diffusion ratio become field dependent second rank tensors connected by

\[
\gamma_1 D_{\text{trans}} = D_{\mu \kappa} k_{\text{trans}}^T .
\]

Then Eq. (2) for the steady state has the form

\[
\frac{\partial \gamma_1}{\partial x_{\mu}} + k_{\text{trans}}^T (\mathbf{H}) \frac{1}{T} \frac{\partial T}{\partial x_{\nu}} = 0 .
\]

The dependence of \( k_{\text{trans}}^T \) on the direction \( \mathbf{h} \) of the magnetic field \( \mathbf{H} \) can easily be specified:

\[
k_{\text{trans}}^T (\mathbf{H}) = k_{\|}^T h_\| h_\| + k_{\perp}^T (\delta_{\mu \nu} - h_\| h_\nu) + k_{\text{trans}}^{\varepsilon_{\mu \nu \rho}} h_\rho ,
\]

\( (\varepsilon_{\mu \nu \rho})_{\text{trans}} \) is the total antisymmetric isotropic third rank tensor. The coefficients \( k_{\|}^T, k_{\perp}^T \) and \( k_{\text{trans}}^{\varepsilon_{\mu \nu \rho}} \) still depend on the magnitude \( H \) of the magnetic field. The last term of the r.h.s. of Eq. (5) gives rise to the transverse effect (concentration gradient perpendicular to \( \mathbf{H} \) and to the temperature gradient) observed by Eggermont et al. 7:
infers from Eq. (3) the following connection between their respective components:

\[
\begin{align*}
\gamma_1 D_{T1}^\parallel &= D_{T1}^\parallel k_T^\parallel, \\
\gamma_1 D_{T1}^\perp &= D_{T1}^\perp k_T^\perp - D_{T1}^\perp k_T^{\text{trans}}, \\
\gamma_1 D_{T1}^{\text{trans}} &= D_{T1}^{\text{trans}} k_T^{\text{trans}} + D_{T1}^{\text{trans}} k_T^\parallel.
\end{align*}
\]

(8 a) (8 b) (8 c)

Up to terms linear in the deviation from isotropy one finds thus from Eqs. (8 b, c)

\[
D_{T1}^{\text{trans}} = \gamma_1 \left( \frac{D_{T1}^{\text{trans}}}{D} - \frac{D_{T1}^{\text{trans}}}{D} \right),
\]

(9)

In practice, one has \( |D_{T1}/D| \ll 1 \) and the second term of the r.h.s. in Eq. (9) may be neglected.

It is the task of the kinetic theory of mixtures of polyatomic molecules in a magnetic field\(^{10}\), based on the Waldmann-Snider kinetic equation, to derive the constitutive law, Eq. (4), and to obtain expressions for the coefficients \( k_1^\parallel, k^\perp \) and \( k^{\text{trans}} \) which contain properties of the single molecules (e.g. the magnetic moment) and their nonspherical interaction (e.g. the binary scattering amplitude and resulting molecular cross sections\(^{12}\)). It should be mentioned that recently also classical model calculations for the field effects on diffusion and thermal diffusion have been performed by Cooper et al.\(^{13}\) for several mixtures.

The present paper proceeds as follows: In Section II the transport relaxation equations (moment equations) needed for the treatment of thermal diffusion in an applied magnetic field are reviewed. It is assumed that the Kagan polarization is the decisive nonequilibrium velocity-rotational angular momentum correlation. This assumption is well established for linear molecules\(^1\). A general expression for the tensorial thermal diffusion ratio \( k_{T\nu\nu} \) in terms of Waldmann-Snider collision integrals is derived. In Section III the important special case of a mixture of linear molecules with noble gas atoms is considered. In particular, the concentration dependence of the transverse effect is discussed. If the coupling between Kagan polarization and translational heat flux is neglected compared with the corresponding coupling with the rotational heat flux all collision integrals occurring are available except from the coupling between Kagan vector and velocity. This new Waldmann-Snider collision integral can be extracted from Eggermont's measurements and the mole fraction dependence of the transverse concentration difference can be graphically displayed for \( \text{N}_2 - \text{Ar} \) and \( \text{N}_2 - \text{Ne} \) mixtures. Finally, the order of magnitude of the transverse Senftleben-Beenakker effect of diffusion is estimated.

### II. Transport-Relaxation Equations. General Expression for \( k_{T\nu\nu}(H) \)

#### 1) Moment Equations

Starting point for the treatment of transport phenomena in mixtures of polyatomic gases is the linearized Waldmann-Snider equation for the deviation \( \phi_i \) of the distribution operator \( f_i \) for the molecules of species \( i \) form the equilibrium distribution \( f^\text{eq}_i \):

\[
\frac{\partial \phi_i}{\partial t} + c \cdot \frac{\partial \phi_i}{\partial x} - i \omega_{H1} [H \cdot J, \phi_i] - \sum_i \omega_{ij} (\phi_j) = 0,
\]

(10)

This equation is

\[
\frac{\partial \phi_i}{\partial t} + c \cdot \frac{\partial \phi_i}{\partial x} - i \omega_{H1} [H \cdot J, \phi_i] - \sum_i \omega_{ij} (\phi_j) = 0
\]

(10)

where \( c \) is the molecular velocity, \( J \) is the operator for the dimensionless (units \( \hbar \)) molecular rotational angular momentum, \( \omega_{H1} = \mu_1 H/\hbar J \) is the precession frequency of the magnetic moment \( \mu_1 \) about the field direction \( H \) and \( \omega_{ij} (...) \) is the linearized Waldmann-Snider collision operator\(^{10,11}\) which contains the binary scattering amplitude matrix and its adjoint. By help of the moment method\(^9\), Eq. (10) can be transformed into an infinite set of coupled differential equations for the moments of the distribution function (transport relaxation equations). For a brief review let us recover that in the moment method \( \phi_i \) is expanded into a complete set of orthonormalized irreducible tensors built up from \( c \) and \( J \):

\[
\phi_i = \sum_{\ell = 1}^{\infty} \sum_{i = 1}^{\infty} \sum_{k_1 = 1} a_{i\mu\ldots\mu_1}^{(P\ldots\ldots\mu_1 t)} (x, t) \phi_i^{(P\ldots\ldots\mu)}(c, J)
\]

(11)

\( (P = \text{parity}, \ell = \text{tensor rank}, k_1 \) counts the various tensors for fixed \( \ell \) \). The \( \phi_i^{(P\ldots\ldots\mu)}(c, J) \) are orthonormalized with respect to the equilibrium distribution (an equilibrium average is denoted by \( \langle \ldots \rangle^\text{eq} \)) according to\(^{10}\)

\[
\langle \phi_i^{(P\ldots\ldots\mu)} \phi_i^{(P'\ldots\ldots\mu')} \rangle^\text{eq} = \delta^{PP'} \delta_{\ell' \ell} \delta_{k_1 k_1'} A_{\mu_1 \ldots \mu_1', \ldots, \eta_1 \ldots \eta_n}.
\]

(12)

For the isotropic tensor \( A_{\ldots} \) which is irreducible in both sets of indices see Ref.\(^{14}\). In the linearized
theory, the \( a^{(P_k)}_{\mu_1 \ldots \mu_k}(x,t) \) are then given as the nonequilibrium averages

\[
a^{(P_k)}_{\mu_1 \ldots \mu_k} = \langle q^{(P_k)}_{\mu_1 \ldots \mu_k} \rangle_i
\]

with the exception of the average of \( q_1 = 1 \), which is \((n_i - n_{i0})/n_{i0}\), i.e. the relative deviation of the number density of species \( i \) from its equilibrium one.

The choice of a finite subset of moments depends on the problem considered. For the treatment of thermal diffusion of linear molecules the set of expansion tensors shown in Table 1 is used for each species \( i \):

<table>
<thead>
<tr>
<th>Expansion tensor</th>
<th>Average (moment)</th>
<th>Physical meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_i^\ell = (n_i - n_{i0})/n_{i0} )</td>
<td>Relative deviation of the particle number density from the equilibrium one</td>
<td></td>
</tr>
<tr>
<td>( a_i^\tau = \sqrt{\frac{2}{3}} \frac{T_i^\tau - T_0}{T_0} )</td>
<td>Relative deviation of the translational temperature from the equilibrium temperature</td>
<td></td>
</tr>
<tr>
<td>( a_i^{\tau_{rot}} = \sqrt{\frac{1}{2}} \frac{T_i^{\tau_{rot}} - T_0}{T_0} )</td>
<td>Relative deviation of the rotational temperature from the equilibrium temperature</td>
<td></td>
</tr>
<tr>
<td>( a_{\mu}^\nu = \frac{m_1}{k_B T_0} \nu_{\mu} )</td>
<td>Dimensionless local particle velocity</td>
<td></td>
</tr>
<tr>
<td>( a_{\mu}^{\tau_{tr}} = \frac{2 m_1}{5 k_B T_0} \left( \frac{m_1}{2 k_B T_0} \frac{T_i^\tau - T_0}{T_0} \right) c_{\mu} )</td>
<td>Dimensionless translational heat flux, ( p_{i0} = n_{i0} k_B T_0 )</td>
<td></td>
</tr>
<tr>
<td>( a_{\mu}^{\tau_{rot}} = \frac{1}{p_{i0}} \sqrt{\frac{2 m_1}{5 k_B T_0}} q_{\mu}^{\tau_{rot}} )</td>
<td>Dimensionless translational heat flux</td>
<td></td>
</tr>
<tr>
<td>( b_{\mu \nu \lambda} = \frac{15 m_1}{2 k_B T_0 (J_\mu J_\nu - J_\lambda)} c_{\mu} J_\nu J_\lambda )</td>
<td>Dimensionless flux of tensor polarization</td>
<td></td>
</tr>
</tbody>
</table>

In Table 1, \( \epsilon_i(J^2) = \hbar^2 J^2/2 k_B T_0 \Theta_i \) is the dimensionless rotational energy and \( c_{\mu \nu \lambda} \) is the rotational specific heat per molecule of species \( i \). Notice, that the flux of tensor polarization is not irreducible with respect to all indices and correctly its three irreducible components should be taken. In the following, however, it will be assumed that these irreducible components have the same relaxation times. This is confirmed by the experiments\(^1\) and can be shown to be rigorously valid in the case of small nonsphericity of the interaction\(^4\). Under this assumption it is sufficient to use the reducible tensor \( b_{\mu \nu \lambda} \) (cf. Ref.\(^{15}\)). The Kagan vector \( a^{K}_{\mu} \) which is known from the experiments with linear molecules to be the decisive nonequilibrium alignment is obtained by contraction:

\[
a^{K}_{\mu} = \sqrt{\frac{2}{3}} b_{\mu \nu \lambda} \ast .
\]

Next, the corresponding transport relaxation equations are stated for the stationary case. Translational and rotational temperatures can then be replaced by the local temperature \( T(x) \). Although it would, in principle, not be necessary to make any restriction with respect to the number of components, we restrict here ourselves to the case of a binary mixture. In the following, the matrix notation (with respect to species labels) of Refs.\(^4,16,17\) will be used: \( 2 \times 2 \) matrices in the species labels will be denoted by boldface Greek letters (e.g. \( \omega^\nu \)), columns by boldface Latin letters (e.g. \( a^\nu_{\mu} \)). The dot \( \circ \) denotes the matrix multiplication. The inverse matrix of \( \omega \) is called \( \tau \). The ensuing moment equations in matrix form then are (cf. Ref.\(^{10}\)):

**Equation for the velocities:**

\[
\frac{1}{2} \nabla_\mu (\sqrt{2} \hat{a}^\mu + \sqrt{2} \hat{a}^{\tau_{tr}}) + \omega^{\nu \ast} \circ a^\mu_{\nu} + \omega^{\tau_{tr}} \circ a^{\tau_{tr}}_{\mu} + \omega^{\tau_{rot}} \circ a^{\tau_{rot}}_{\mu} + \omega^{\nu} \circ a^{K}_{\mu} = 0 .
\]

**Equation for the translational heat fluxes:**

\[
\sqrt{\frac{2}{3}} \circ \nabla_\mu (T/T_0) + \omega^{\tau_{tr}} \ast \circ a^\mu_{\nu} + \omega^{\tau_{tr}} \ast \circ a^{\tau_{tr}}_{\mu} + \omega^{\tau_{rot}} \ast \circ a^{\tau_{rot}}_{\mu} + \omega^{\nu} \ast \circ a^{K}_{\mu} = 0 .
\]
Equation for the rotational heat fluxes:
\[
\frac{1}{\sqrt{3}} \mathbf{e}_{\mu} \nabla_{\mu} (T/T_0) + \omega^{\text{rot},v} \circ \mathbf{a}^{v} + \omega^{\text{rot},\text{qtr}} \circ \mathbf{a}^{\text{qtr}} + \omega^{\text{rot},K} \circ \mathbf{a}^{K} = 0. \tag{17}
\]

Equation for the flux of tensor polarization:
\[
\mathbf{q} \cdot H_{\mu'\nu',\nu''} b_{\lambda'\mu'\nu''} + \sqrt{\frac{2}{3}} \mathbf{A}_{\mu'\nu',\lambda'} \mathbf{T}^{K} \circ [\omega^{K,v} \circ \mathbf{a}^{v} + \omega^{K,\text{qtr}} \circ \mathbf{a}^{\text{qtr}} + \omega^{K,\text{rot}} \circ \mathbf{a}^{\text{rot}}] + \mathbf{b}_{\lambda'\mu'} = 0. \tag{18}
\]

In Eqs. (15) – (18), \(\omega^{\text{rot}}\) denotes the matrix of reduced Waldmann-Snider collision brackets \(\omega_{ij}\) introduced in Ref. 10. Matrices with one superscript are matrices of relaxation coefficients, those with two superscripts are matrices of coupling coefficients. Furthermore, the following abbreviations have been used:
\[
\hat{a}_i = c_0 a_i \quad \text{with} \quad c_0 = \sqrt{3} k_B T_0 / m_1. \tag{19}
\]

In Eq. (16) the column \(\mathbf{c} \equiv \{c_0\}\) and in Eq. (17) the column \(\mathbf{c} \equiv \{c_0 \nabla_{\text{rot},i} / k_B\}\) appears. In Eq. (18) the fourth rank tensor
\[
H_{\mu'\nu',\nu''} = \varepsilon_{\mu'\nu'\nu''} h_{13} \delta_{\nu'',\nu} + \varepsilon_{\nu''\nu'\nu'} h_{13} \delta_{\mu',\mu''}
\]
describes the infinitesimal rotation of a second rank tensor about \(\mathbf{h}\) (cf. Ref. 18). The matrix \(\mathbf{q}\) is defined by
\[
\mathbf{q}_{ij} = \omega_{ij} \mathbf{T}^{K}, \tag{20}
\]
where \(\mathbf{T}^{K} = (\omega^{K})^{-1}\).

Equation (23) is now inserted into Eqs. (16), (17) and \(\mathbf{a}_{\mu}^{\text{qtr}}\) and \(\mathbf{a}_{\mu}^{\text{rot}}\) are expressed in terms of \(\nabla_{\mu} (T/T_0)\). Re-insertion of the result into Eq. (22) then also yields the Kagan vector in terms of the temperature gradient. Here, the usual approximation is made that only terms at most bilinear in the “coupling matrices” \(\omega^{\text{qtr},K}, \omega^{K,\text{qtr}}, \omega^{\text{rot},K}, \omega^{K,\text{rot}}, \omega^{\text{rot},\text{qtr}}, \text{ and } \omega^{\text{rot},\text{rot}}\) are retained. Since these matrices vanish for a purely spherical molecular interaction\(^{18}\) this approximation works very well for molecules with small nonsphericity but it is reasonable also in the more general case.

From the constance of the total pressure \(p\) (the thermomagnetic pressure difference\(^{8}\) is negligibly small) which is in the linearized theory given by
\[
p = n_0 k_B T + (n - n_0) k_B T_0,
\]
the relation
\[
\nabla_{\mu} \left( \sqrt{3} a_{\mu}^1 + \sqrt{2} d_{\mu}^1 \right) = \sqrt{3} c_{10} (n_0/n_{10}) \nabla_{\mu} \gamma_1 \tag{24}
\]
is easily derived. Thus taking the \(i = 1\) component of Eq. (15) we arrive at the desired connection between concentration gradient and temperature gradient, Eq. (4), with the following expression for the tensorial thermal diffusion ratio \(k_{T\mu\nu}\):

\[
k_{T\mu\nu} = (n_{10}/n_0) c_{10} \left\{ \left[ \omega^{v,\text{qtr}} \circ \mathbf{T}^{\text{qtr}} \circ (- \sqrt{3} \mathbf{c} + \omega^{\text{rot},\text{qtr}} \circ \mathbf{T}^{\text{rot}} \circ \mathbf{c}) \right] \delta_{\mu\nu} + \omega^{v,\text{rot}} \circ \mathbf{T}^{\text{rot}} \circ (- \mathbf{c} + \sqrt{3} / 2 \omega^{\text{rot},\text{qtr}} \circ \mathbf{T}^{\text{qtr}} \circ \mathbf{c}) \delta_{\mu\nu} - \left[ \omega^{v,K} - (\omega^{v,\text{qtr}} \circ \mathbf{T}^{\text{qtr}} \circ \omega^{\text{rot},K} + \omega^{v,\text{rot}} \circ \mathbf{T}^{\text{rot}} \circ \omega^{\text{rot},K}) \right] \mathbf{K}_{\mu\nu} \right\}^{1/2}. \tag{25}
\]
This complicated expression is valid for binary mixtures of linear diamagnetic molecules. The term with \( \delta_{xy} \) represents the thermal diffusion ratio in the Wang Chang-Uhlenbeck approach (orientation effects are disregarded). With the use of Eq. (23), the components \( k_{11}^\parallel (H) \), \( k_2^\parallel (H) \) and \( k_{11}^{\text{trans}} (H) \) can easily be extracted from Equation (25). In the term with \( K_{\text{rot}} (\varphi) \), bilinear expressions in the coupling matrices may be neglected compared with \( \omega_{V,K} \), but the remaining expression is still too unwieldy. To obtain a better tractable expression, we restrict ourselves in the following section to the case that the "molecules 2" are noble gas atoms.

III. Special Case: Mixtures of Linear Molecules with Noble Gas Atoms

In this section binary mixtures of linear molecules (labelled with "1") and noble gas atoms (labelled with "2") are considered. This causes not only essential simplifications in the theoretical expression for \( k_{\text{rot}} \) but is also the most important case from the experimental point of view: Sentelleben-Beenakker experiments have been performed mainly for such mixtures and a lot of collision integrals have been determined.

1) Explicit Expressions for \( k_{\text{T}}^\parallel \), \( k_1^\parallel \) and \( k_{11}^{\text{trans}} \)

For noble gas atoms, the rotational heat flux, the Kagan vector, the rotational heat capacity and the precession frequency \( \omega_{HI} \) are zero. This implies, that the following matrices and columns in the species label space can be treated as numbers (i.e. only the 1-1-element and the 1-element, respectively, occur): \( \omega_{\text{rot}} \), \( \omega_{V,K} \), and \( \omega_{V,K,\text{rot}} \). Consequently \( \tau_{\text{rot}} \) and \( \tau_{V,K} \) have to be replaced by \( 1/\omega_{HI}^{\text{rot}} \) and \( 1/\omega_{HI}^{\text{K,rot}} \), respectively. Only one precession angle \( \varphi = \omega_{HI}/\omega_{HI}^{\text{K,rot}} \) (which is proportional to \( H/p \)) appears.

Furthermore, it seems to be a good approximation to neglect the coupling matrices \( \omega_{V,\text{qtr}} \), \( \omega_{V,\text{qtr}}^{\text{rot}} \) if they occur in products with terms already containing two other coupling matrices. From the point of view of small nonsphericity this is certainly correct for \( \omega_{V,\text{qtr}}^{\text{rot}} \) (this quantity vanishes for a spherical interaction) but seems somewhat questionable for \( \omega_{V,\text{qtr}} \) since this matrix also exists for a purely spherical interaction. Nevertheless the neglect is justified since the elements of \( \omega_{V,\text{qtr}} \) are in practice of the same order of magnitude as the coupling coefficients involving the rotational heat flux or the Kagan vector (i.e. "nondiagonal" elements of the collision operator are of the same order of magnitude and small compared with diagonal elements). The resulting expressions for \( k_{\text{T}}^\parallel \), \( k_1^\parallel \) and \( k_{11}^{\text{trans}} \) obtained from Eq. (25) are:

\[
k_{\text{T}}^\parallel (\varphi) = k_{\text{T}}(0) \left[ 1 + \frac{\Delta k_{\text{T}}^\parallel}{k_{\text{T}}(0)} \cdot \frac{\varphi^2}{1 + \varphi^2} \right],
\]

\[
k_1^\parallel (\varphi) = k_{\text{T}}(0) \left[ 1 + \frac{1}{2} \frac{\Delta k_1^\parallel}{k_{\text{T}}(0)} \left( \frac{\varphi^2}{1 + \varphi^2} + \frac{8 \varphi^4}{1 + 4 \varphi^2} \right) \right],
\]

and

\[
k_{11}^{\text{trans}} (\varphi) = \frac{3}{2} \Delta k_{11}^{\text{trans}} \varphi \left( \frac{1}{1 + \varphi^2} + \frac{4}{1 + 4 \varphi^2} \right).
\]

The value of the field free thermal diffusion ratio \( k_{\text{T}}(0) \) is given by

\[
k_{\text{T}}(0) = - (n_{10}/n_0) \left\{ V_{\text{c}}^2 (c_{10})^{-1} \left[ (\omega_{V,\text{qtr}} - \omega_{V,\text{rot}} \cdot \omega_{\text{rot},\text{qtr}}(\omega_{HI}^{-1})^{-1} \cdot \tau_{\text{qtr}} \cdot \mathbf{c}) \right] \right\} \]

\[
+ \sqrt{\frac{c_{\text{rot}}}{K_{\text{B}}} (\omega_{\text{rot}}^{-1} (\omega_{V,\text{rot}} - \omega_{V,\text{rot}} \cdot \omega_{\text{rot},\text{qtr}}(\omega_{HI}^{-1})^{-1} \cdot \tau_{\text{qtr}} \cdot \mathbf{c})_{11} + \frac{c_{\text{rot}}}{K_{\text{B}}} (\omega_{V,\text{rot}} - \omega_{\text{K,rot}} \cdot \omega_{\text{rot}} \cdot \mathbf{c})_{11} \right\}. \]

The difference \( \Delta k_{\text{T}} = k_1^\parallel (\infty) - k_{\text{T}}(0) \) is given by

\[
\Delta k_{\text{T}} = \frac{3}{2} \frac{n_{10} \omega_{\text{K,rot}}}{n_0 c_{10} \omega_{HI}^{-1}} \left[ V_{\text{c}}^2 \left( \omega_{\text{K,rot}} \cdot \tau_{\text{qtr}} \cdot \mathbf{c} \right)_{11} + c_{10} \right] \left[ \sqrt{\frac{c_{\text{rot}}}{K_{\text{B}}} \omega_{\text{K,rot}} - \omega_{\text{rot}}^{-1} \cdot \tau_{\text{qtr}} \cdot \mathbf{c} \right].
\]

From Eqs. (26), (27) one infers that \( \Delta k_{\text{T}} = \frac{3}{2} \Delta k_{11}^{\text{trans}} \).

2) Concentration Dependence of \( k_{11}^{\text{trans}} \)

Following the notation of previous papers \( 4, 16, 17 \) we denote the mole fraction of the noble gas by \( x \):

\[x = n_{20}/n_0, \quad (31)\]
where \( m_{ij} \) is the reduced mass and \( \sigma_{ij}^{-1} \), \( \sigma_{ij}^{-1} \) are concentration independent, temperature dependent effective cross sections which involve molecular scattering, orientation- and reorientation-cross sections. For their general definition it is referred to Ref. \(^4\). The corresponding effective cross sections \( \sigma^i \) for a pure gas of species \( i \) are given by

\[
\sigma^i = \sigma_{ii}^{-1} + \sigma_{ij}^{-1}.
\]  

(33)

From the conservation of momentum in a collision follows \(^10\) that the effective cross sections \( \sigma^i \) vanish. Thus one infers from Eq. (33) the relation

\[
\omega_{11}^K = n_29 (8 k_B T_0/\pi m_{12})^{1/2} \sigma_{12}^{\nu K \nu}.
\]  

(34)

For the concentration dependence of the other collision integrals Eq. (32) has to be observed. With the use of Eqs. (28), (30) – (34), and explicit expressions for the elements of the matrix \( \tau^{tr} \), we obtain the mole fraction dependence of \( k_T \) as:

\[
k^{trans}_{T} (\varphi, x) = \frac{3}{10} \varphi \left( \frac{1}{1 + \varphi^2} + \frac{4}{1 + 4 \varphi^2} \right) x (1 - x) \left[ (1 - x) a_1^K + x a_2^K \right]^{-1} \sigma_{12}^{\nu K \nu} [A(x) + B(x)].
\]  

(35)

In Eq. (35) we used the abbreviations

\[
A(x) = \sqrt{\frac{5}{2}} \left\{ \left[ (1 - x) a_1^K + x a_2^K \right] \left[ x a_2^2 + (1 - x) \sigma_{21}^{tr \nu} + x \sqrt{m_1/m_2} \sigma_{12}^{tr \nu} \right] \\
+ x \sigma_{12}^{tr \nu} \left[ (1 - x) (a_2 \sigma_{12}^{tr \nu} - a_1 \sigma_{12}^{tr \nu}) + x \sqrt{m_1/m_2} \sigma_{12}^{tr \nu} \right] \right\},
\]  

(36)

and

\[
B(x) = \sqrt{\frac{c_{rot}}{k_B}} \frac{(1 - x) a_1^K \sigma_{12}^{rot} + x a_2^K \sigma_{12}^{rot}}{(1 - x) a_1^K \sigma_{12}^{rot} + x a_2^K \sigma_{12}^{rot}},
\]  

(37)

and

\[
a_1 = \sqrt{2} m_2/(m_1 + m_2), \quad a_2 = \sqrt{2} m_1/(m_1 + m_2).
\]  

(38)

Notice, that also \( \varphi = \omega_{11}/(n_0/8 k_B T_0/\pi m_{12}) \left[ (1 - x) a_1^K + x a_2^K \right] \) is concentration dependent. But the value \( \varphi_{max} \), defined by the maximum of \( k^T_{T} (\varphi) \) is a pure number:

\[
\varphi_{max} = 0.6158 \ sgn(g),
\]  

(39)

where \( g \) is the rotational \( g \)-factor of the molecule.

3) Comparison with the Experiment and Conclusions

a) Explicit Concentration Dependence of the Transverse Effect for \( \text{N}_2 - \text{Ar} \) and \( \text{N}_2 - \text{Ne} \) Mixtures

A comparison of the experimental value of \( k^{T}_{T,\text{max}} \) – obtained after Eq. (7) from the measured value of \( \sigma^{\text{trans}}_T \) for equimolar \( \text{N}_2 - \text{Ar}, \text{Ne} \)-mixtures at room temperature – with the full theoretical expression, Eq. (35), is not yet possible. The reason is that the coupling cross sections of the Kagan vector with the velocity, \( \sigma_{ij}^{\nu K \nu} \), and with the translational heat flux, \( \sigma_{12}^{\nu K \nu} \) and \( \sigma_{12}^{tr \nu} \), have neither been determined from the experiment nor calculated quantum mechanically from a nonspherical potential. While, however, the latter two cross sections could, in principle, be extracted from measurements of the concentration dependence of the Senftleben-Beenakker effect of the heat conductivity \(^3\) the first cross section is an absolutely new quantity. On the other hand, just this cross section is also important for the Senftleben-Beenakker effect of diffusion \(^21\) and for diffusio-birefringence \(^17\).

To give an estimate of the magnitude of this unknown collision integral we follow Ref. \(^4\) and neglect the coupling of the Kagan vector with the translational heat flux. Using the same approximation, Heemskerk \(^3\) has analyzed his measurements of the magnetic field dependence of the heat conductivity.
in mixtures and has obtained experimental values for the coupling cross section of Kagan vector and rotational heat flux, which are accurate, say, within a factor 1.5. Nevertheless the concentration dependence of the effect could be well reproduced. We now use the same approximation and omit the term $A(x)$ in Equation (35). Then $\sigma_{12}^{K}$ is the only unknown cross section: The effective cross sections $\sigma_1^{K}$, $\sigma_{12}^{K}$, $\sigma_{12}^{K\text{rot}}$ and $\sigma_1^{\text{rot}}$ can be taken from Heemskerk et al., $\sigma_{12}^{K\text{rot}}$ can be calculated in "spherical approximation" (cf. Ref. 18). The values of the effective cross sections used for $N_2$—Ar and $N_2$—Ne mixtures at room temperature are listed in Table 2.

<table>
<thead>
<tr>
<th>Effective cross section</th>
<th>$\sigma_1^{K}$</th>
<th>$\sigma_{12}^{K}$</th>
<th>$\sigma_{12}^{K\text{rot}}$</th>
<th>$\sigma_1^{\text{rot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 300 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N_2$—Ar</td>
<td>48</td>
<td>47</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>$N_2$—Ne</td>
<td>48</td>
<td>30</td>
<td>17.5</td>
<td>5.93</td>
</tr>
</tbody>
</table>

From the value of $\delta \gamma_1^{\text{trans}} (\varphi_{\text{max}}, x = 1/2)$ obtained by Eggermont et al., we can now extract the cross section $\sigma_{12}^{K}$ with the help of Eqs. (7), (35), (37), (39), and Table 2. One finds

$$\sigma_{12}^{K} = \begin{cases} 
-1.56 \text{Å}^2 & \text{for } N_2\text{—Ar,} \\
-0.92 \text{Å}^2 & \text{for } N_2\text{—Ne.}
\end{cases}$$

These are rather small values compared with the values of the other coupling cross sections. They are used in the following to calculate the concentration dependence of $\phi_{\text{trans}}^{\text{max}}$. The results are graphically displayed in Figure 1.

b) Estimate of the Magnitude of the Transverse Senftleben-Beenakker Effect of Diffusion

The transverse Senftleben-Beenakker effect of diffusion is described by the formula

$$D_{\text{trans}}^{\text{max}} (\varphi, z) = -\frac{3}{10} \varphi \left( \frac{1}{1+\varphi^2} + \frac{4}{1+4\varphi^2} \right) \left( \frac{\omega_{11}^{K}}{\omega_{11}} \right)^2 \omega_{11}^{K}.$$  

(40)

The field free value of the diffusion coefficient is

$$D (H = 0) \approx D = x k_B T_0/m_1 \omega_{11}^{K}.$$  

(41)

In passing it should be mentioned that because of momentum conservation similarly to Eq. (34) also

$$\omega_{11} = n_0 x (8 k_B T_0/\pi m_1)^{1/3} \sigma_{12}^{K}$$  

(42)

holds. Together with Eq. (40), Eq. (42) implies that $D_{\text{trans}}^{\text{max}} (x) / D$ is a nearly linear function of $x$. From Eqs. (40), (41), the $\sigma_{12}^{K}$ values obtained above and $D$-values taken from the literature the value of $D_{\text{trans}}^{\text{max}} (x = 1/2)$ can be estimated:

$$D_{\text{trans}}^{\text{max}} (x = 1/2) / D = \begin{cases} 
3.6 \times 10^{-4} & \text{for } N_2\text{—Ar,} \\
2.9 \times 10^{-4} & \text{for } N_2\text{—Ne.}
\end{cases}$$

The absolute value may be correct within a factor 2, the order of magnitude is consistent with the (negative) results of the experiments of Tip et al. who did not find a field effect on diffusion within their accuracy of measurement of $4 \times 10^{-4}$.

It seems to be worthwhile to perform a detailed analysis of the $x$-dependence of the transverse thermal diffusion effect in order to obtain values for the unknown coupling cross sections of the Kagan polarization and the translational heat flux and more precise values for the corresponding couplings with the rotational heat flux and the velocity.

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5 H. F. Vugts, A. Tip, and J. Los, Physica 38, 579 [1968].