

THE TRANSVERSE DUFOUR EFFECT

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Experiments have been performed to study the influence of a magnetic field on the Dufour effect (or diffusion-thermo effect) in an equimolar N_2 -Ar mixture at room temperature. By comparing these experimental results with those obtained previously for the field effect on the thermal diffusion, an Onsager relation between these field effects is confirmed.

1. Introduction

In the region of linear response the relation between thermodynamic forces, X_i , and fluxes, J_i , is given by

$$J_i = \sum_j L_{ij} X_j, \quad (1)$$

The transport coefficients, L_{ij} , defined in this way have two important properties that reflect the symmetry of the equilibrium state of the system. For the spatial symmetry they were formulated by Curie, whereas the time reversal symmetry gives rise to the Onsager-Casimir relations

$$L_{ij} = \pm L_{ji}, \quad (2)$$

where the sign corresponds to the product of the time reversal behavior of X_i and X_j . A test of such an Onsager relation is done in the 1946 study by Waldmann^{1,2)} of the thermal diffusion effect and its counterpart, the diffusion thermo effect, in a dilute gas. This situation is illustrated by the two phenomenological equations for the heat flux, q , and the particle flux, j_i , in a binary gas mixture

$$q = -\lambda \nabla T - \frac{p}{x_A x_B} \mathcal{D}_{T_1} \nabla x_1, \quad (3)$$

$$j_l = -\frac{n}{T} D_{T_l} \nabla T - n D \nabla x_l, \quad l = A \text{ or } B. \quad (4)$$

While in a gas mixture a temperature gradient, ∇T , gives rise to a particle flux (thermal diffusion), a concentration gradient, ∇x_l , will give rise to a heat flux (diffusion thermo or Dufour effect). In eqs. (3) and (4) p is the pressure, $x_l = n_l/n$ are the mole fractions of species l and $n = \sum_l n_l$ is the density. The Onsager relation gives here

$$D_{T_l} = \mathcal{D}_{T_l}. \quad (5)$$

The Senftleben–Beenakker effect offers the possibility to study the more general case of the reciprocity relations in the presence of an external field, more specifically in a magnetic field, \mathbf{B} . In this case the transport coefficients in eqs. (3) and (4) have to be replaced by tensors:

$$\mathbf{q} = -\lambda \cdot \nabla T - \frac{p}{x_A x_B} \mathcal{D}_{T_l} \cdot \nabla x_l, \quad (6)$$

$$j_l = -\frac{n}{T} \mathbf{D}_{T_l} \cdot \nabla T - n \mathbf{D} \cdot \nabla x_l, \quad l = A \text{ or } B. \quad (7)$$

Here the convention of labeling the species of a binary mixture customary in Senftleben–Beenakker effects is used: In a mixture of a polyatomic gas with a noble gas the polyatomic molecules have label A. This label specifying the molecule will henceforth be dropped on D_{T_l} and \mathcal{D}_{T_l} . The 3×3 matrix for \mathcal{D}_T in the cartesian representation reduces by the Curie principle, to the form

$$\begin{pmatrix} \mathcal{D}_T^\dagger & -\mathcal{D}_T^{\text{tr}} & 0 \\ \mathcal{D}_T^{\text{tr}} & \mathcal{D}_T^\dagger & 0 \\ 0 & 0 & \mathcal{D}_T^{\parallel} \end{pmatrix}, \quad (8)$$

where the field is taken in the z -direction and the choice of the sign of $\mathcal{D}_T^{\text{tr}}$ is by convention (spatial symmetry only requires $(\mathcal{D}_T)_{xy} = -(\mathcal{D}_T)_{yx}$). Schemes analogous to (8) hold for λ , \mathbf{D}_T and \mathbf{D} . The diagonal components are even and the off-diagonal ones are odd in the magnetic field. Onsager relations yield a connection between the coefficient of ∇x_l in eq. (6) and that of ∇T in eq. (7). With the expression for the entropy production of ref. 3, written down for the case of an ideal gas,

$$\sigma = -\mathbf{q} \cdot \frac{\nabla T}{T^2} - \mathbf{j}_A \cdot \frac{k \nabla x_A}{x_A x_B} \quad (9)$$

the thermodynamic forces $(\nabla T/T^2)$ and $(k \nabla x_A/x_A x_B)$ conjugate to the fluxes \mathbf{q} and \mathbf{j}_A are found. In terms of these forces and fluxes eqs. (6) and (7) can be rewritten as

$$\begin{pmatrix} q_x \\ q_y \\ q_z \\ j_{Ax} \\ j_{Ay} \\ j_{Az} \end{pmatrix} = - \begin{pmatrix} \check{\lambda}^\perp & -\check{\lambda}^{\text{tr}} & 0 & \check{\mathcal{D}}_\dagger^\perp & -\check{\mathcal{D}}_\dagger^{\text{tr}} & 0 \\ \check{\lambda}^{\text{tr}} & \check{\lambda}^\perp & 0 & \check{\mathcal{D}}_\dagger^{\text{tr}} & \check{\mathcal{D}}_\dagger^\perp & 0 \\ 0 & 0 & \check{\lambda}^\parallel & 0 & 0 & \check{\mathcal{D}}_\dagger^\parallel \\ \check{D}_\dagger^\perp & -\check{D}_\dagger^{\text{tr}} & 0 & \check{D}^\perp & -\check{D}^{\text{tr}} & 0 \\ \check{D}_\dagger^{\text{tr}} & \check{D}_\dagger^\perp & 0 & \check{D}^{\text{tr}} & \check{D}^\perp & 0 \\ 0 & 0 & \check{D}_\dagger^\parallel & 0 & 0 & \check{D}^\parallel \end{pmatrix} \begin{pmatrix} \nabla_x T/T^2 \\ \nabla_y T/T^2 \\ \nabla_z T/T^2 \\ k \nabla_x x_A/x_A x_B \\ k \nabla_y x_A/x_A x_B \\ k \nabla_z x_A/x_A x_B \end{pmatrix}, \quad (10)$$

where $\check{\lambda} = \lambda T^2$, $\check{\mathcal{D}}_\dagger = \mathcal{D}_\dagger n T$, $\check{D}_\dagger = D_\dagger n T$ and $\check{D} = D(n x_A x_B/k)$. The Onsager relation

$$L_{ij}(\mathbf{B}) = L_{ji}(-\mathbf{B}) \quad (11)$$

implies, for the scheme of eq. (10) that

$$\left. \begin{aligned} D_\dagger^\perp(\mathbf{B}) &= \mathcal{D}_\dagger^\perp(-\mathbf{B}) = \mathcal{D}_\dagger^\perp(\mathbf{B}) \\ D_\dagger^\parallel(\mathbf{B}) &= \mathcal{D}_\dagger^\parallel(-\mathbf{B}) = \mathcal{D}_\dagger^\parallel(\mathbf{B}) \\ D_\dagger^{\text{tr}}(\mathbf{B}) &= -\mathcal{D}_\dagger^{\text{tr}}(-\mathbf{B}) = \mathcal{D}_\dagger^{\text{tr}}(\mathbf{B}) \end{aligned} \right\} \mathbf{D}_\dagger(\mathbf{B}) = \mathcal{D}_\dagger(\mathbf{B}). \quad (12)$$

In ref. 4 we described measurements on $D_\dagger^{\text{tr}}(\mathbf{B})$, i.e., the transverse component of the thermal diffusion. Here we will present measurements of the inverse effect, i.e., the transverse heat flow that results from a concentration gradient in a magnetic field.

2. Experimental arrangement for the transverse Dufour effect

In this section we will treat the solution of the phenomenological vector eqs. (6) and (7) under certain experimental (boundary) conditions. All components of \mathbf{q} , \mathbf{j} , ∇x and ∇T (12 in total) are known when 6 of them are fixed by spatial boundary conditions. In the experiments on the transverse Dufour coefficient a concentration gradient is applied in the y -direction, the magnetic field is in the z -direction and a temperature difference is detected in the x -direction (see fig. 1a). Thus: $(\nabla x)_y = \text{constant}$, $(\nabla T)_y = 0$, if steady state is reached: $j_x = j_z = 0$ and when the heat conductance through the walls is neglected $q_x = q_z = 0$. The two equations for the heat flux and the particle flux in the x -direction read in the steady state case

$$0 = -\lambda^\perp (\nabla T)_x - \frac{p}{x_A x_B} \mathcal{D}_\dagger^\perp (\nabla x)_x + \frac{p}{x_A x_B} \mathcal{D}_\dagger^{\text{tr}} (\nabla x)_y, \quad (13)$$

$$0 = -\frac{n}{T} D_\dagger^\perp (\nabla T)_x - n D^\perp (\nabla x)_x + n D^{\text{tr}} (\nabla x)_y. \quad (14)$$

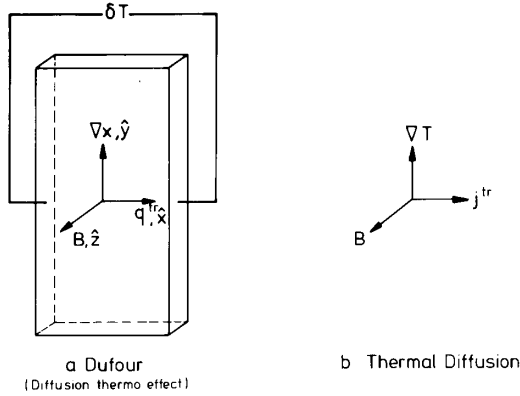


Fig. 1. a) Schematic diagram of the apparatus. The direction of the applied N_2 concentration gradient and of the observed heat flux are indicated, b) Direction of the observed N_2 flux in the thermal diffusion experiment.

Solving $(\nabla x)_x$ from eq. (14) and substituting the result in eq. (13) yields an expression for the transverse temperature difference in terms of the applied concentration gradient

$$\lambda^\perp (\nabla T)_x = \frac{p}{x_A x_B} \mathcal{D}_T^{\text{tr}} (\nabla x)_y \left(1 - \frac{D^{\text{tr}} \mathcal{D}_T^\perp}{D^\perp \mathcal{D}_T^{\text{tr}}} \right) \left(1 - \frac{p}{x_A x_B \lambda^\perp T} \frac{\mathcal{D}_T^\perp D_T^\perp}{D^\perp} \right)^{-1}. \quad (15)$$

$pD/(x_A x_B \lambda T)$ is of the order of unity for most gas mixtures and $\mathcal{D}_T^\perp/D^\perp = D_T^\perp/D^\perp \approx k_T$, the field free thermal diffusion ratio, being only of the order of 10^{-2} for most gas mixtures. Consequently the correction term $p\mathcal{D}_T^\perp D_T^\perp/(x_A x_B \lambda^\perp T D^\perp)$ is 10^{-3} at the most and can be disregarded. In an experimental situation the walls of the apparatus will also conduct heat so that λ^\perp in eq. (15) has to be replaced by an effective thermal conductivity of walls and gas. For this reason one will in practice calibrate the temperature difference $(\nabla T)_x$ to a heat flux (see section 4). The appropriate equation then reads

$$q^{\text{tr}} = \frac{p}{x_A x_B} \mathcal{D}_T^{\text{tr}} \left(1 - \frac{D^{\text{tr}} \mathcal{D}_T^\perp}{\mathcal{D}_T^{\text{tr}} D^\perp} \right) \nabla x. \quad (16)$$

The last term, $(D^{\text{tr}} \mathcal{D}_T^\perp)/(\mathcal{D}_T^{\text{tr}} D^\perp)$, can be neglected since $D^{\text{tr}} \ll \mathcal{D}_T^{\text{tr}}$ and again $\mathcal{D}_T^\perp/D^\perp \approx k_T$ is of the order of 10^{-2} . It is noted that a similar correction term is present when transverse thermal diffusion is investigated (see ref. 4). Thus the term will only influence the value of $\mathcal{D}_T^{\text{tr}}$ calculated from the experiment, but not the ratio between \mathcal{D}_T and D_T as determined from the experiments.

3. Formal expressions for the Dufour effect

The theoretical treatment of the magnetic field influence on the Dufour effect in terms of effective molecular cross sections and precession angles is analogous to the theory for thermal diffusion. In fact one finds the same expressions for \mathbf{D}_T and \mathcal{D}_T in accordance with the Onsager relations. For a detailed outline of the theory the reader is referred to ref. 5. Here it suffices to give expressions for the field dependence of the components of the Dufour tensor. For a binary mixture of a diatomic gas with a noble gas one has

$$\frac{\Delta \mathcal{D}_T^{\dagger}(\mathbf{B})}{D} = \frac{\mathcal{D}_T^{\dagger}(\mathbf{B}) - \mathcal{D}_T(0)}{D} = \Psi_{11}^T \frac{\xi_{11}^2}{1 + \xi_{11}^2} - \Psi_{12}^T \left(\frac{\xi_{12}^2}{1 + \xi_{12}^2} + 2 \frac{4\xi_{12}^2}{1 + 4\xi_{12}^2} \right), \quad (17a)$$

$$\frac{\Delta \mathcal{D}_T^{\parallel}(\mathbf{B})}{D} = \frac{\mathcal{D}_T^{\parallel}(\mathbf{B}) - \mathcal{D}_T(0)}{D} = \Psi_{11}^T 2 \frac{\xi_{11}^2}{1 + \xi_{11}^2} - \Psi_{12}^T 2 \frac{\xi_{12}^2}{1 + \xi_{12}^2}, \quad (17b)$$

$$\frac{\mathcal{D}_T^{\parallel}(\mathbf{B})}{D} = \Psi_{11}^T \frac{\xi_{11}}{1 + \xi_{11}^2} - \Psi_{12}^T \left(\frac{\xi_{12}}{1 + \xi_{12}^2} + 2 \frac{2\xi_{12}}{1 + 4\xi_{12}^2} \right), \quad (17c)$$

where

$$\xi_{pq} = \frac{g\mu_N kT}{\hbar} \{x_A v_{AA} \mathfrak{S}_{(pq00|A)AA} + x_B v_{AB} \mathfrak{S}_{(pq00|A)AB}\}^{-1} \frac{B}{p}, \quad pq = 11 \text{ or } 12 \quad (18)$$

is a field parameter and $v_{kl} = \sqrt{8kT(m_k + m_l)/\pi m_k m_l}$ is a thermal velocity. Ψ_{11}^T and Ψ_{12}^T determine the contributions of the \mathbf{WJ} and \mathbf{WJJ} polarization, respectively. The Ψ_{pq}^T 's can be expressed in terms of effective molecular cross sections, \mathfrak{S} , thermal velocities, and mole fractions of the components of the gas mixture and are proportional to $x_A x_B$. The Ψ^T 's can have either sign. Furthermore it is noted that according to eq. (18) the effects will be a unique function of B/p .

4. Description of the apparatus

The apparatus is essentially the same as the apparatus used by Eggermont et al. for measuring the viscomagnetic heat flux^{6,7}). It consists of a rectangular channel, as shown in fig. 2. The length, l , of the channel is 80 mm, the width, w , is 10 mm and the thickness, t , is 1.0 mm. The channel walls are made of low thermal conductance polyester "mylar", of thickness 75 μm . A concentration gradient across the length of the channel is set up by connecting each end of the channel to a 20l bulb filled with a pure component. This concentration gradient decays with a relaxation time of approximately five hours at 1 mm

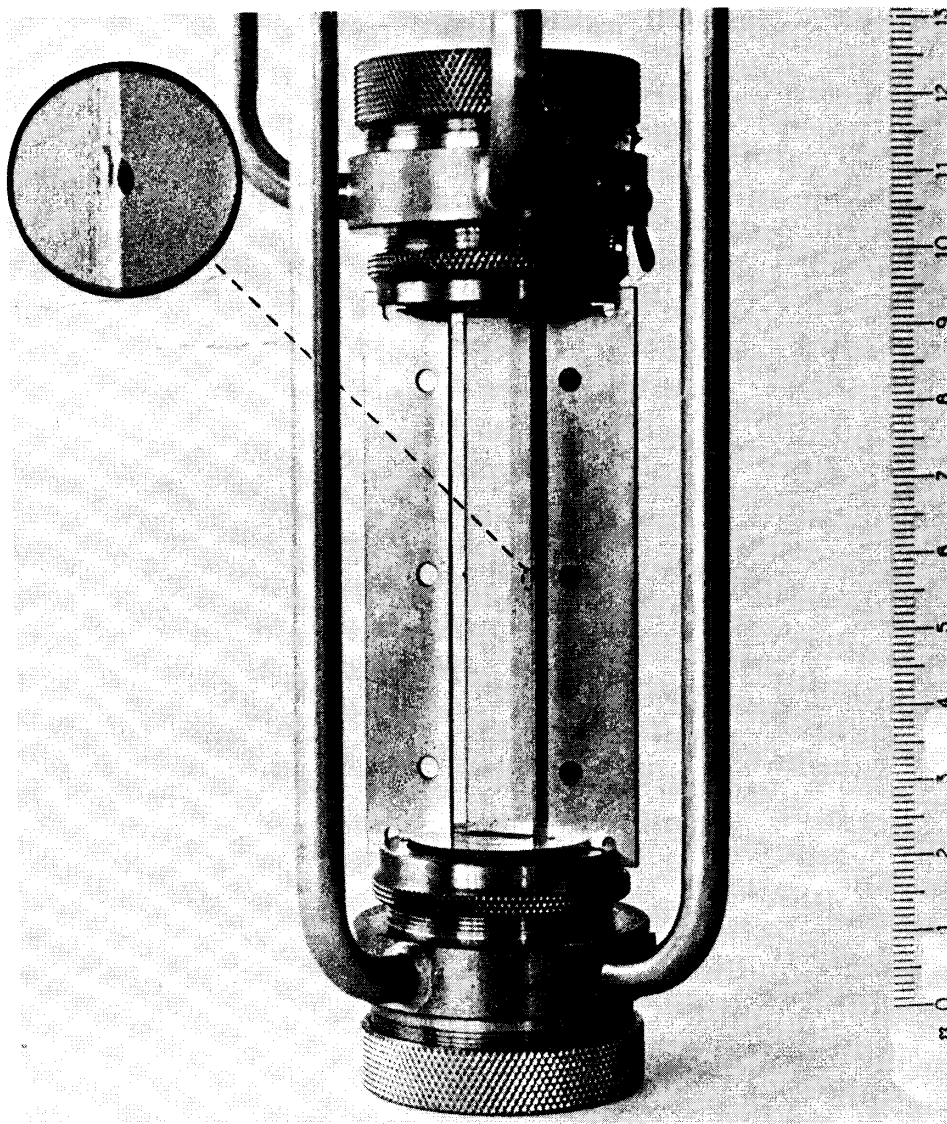


Fig. 2. Picture of the apparatus, without a heat sink (see text). Radiation shield and vacuum jacket have been removed.

Hg (10^2 Pa) for N_2 -Ar mixtures. It is monitored by measuring the difference in thermal conductivity between the gas mixtures directly at the ends of the channel. For this purpose use is made of katharometer type thermistors, electrically heated in a Wheatstone bridge arrangement. The differences in thermal conductivity are calibrated to concentration differences by monitoring

the signal of the Wheatstone bridge when several mixtures of known composition are introduced into the apparatus. To ensure the reproducibility of the pressure for the various mixtures a high accuracy manometer is used (Datametrics Barocel, type 570D).

Under the influence of a magnetic field a heat flux q'' is produced giving rise to a transverse temperature difference, δT , across the width of the channel. In stationary state the back heat flow caused by δT balances q'' . The temperature difference ($\delta T_{\max} \approx 10^{-4}$ K) is detected by means of two thermistors glued unto the narrow walls of the channel and electrically circuited in a second Wheatstone bridge. In order to account for heat losses, the observed temperature difference is calibrated to a heat flux as follows. The field induced heat flux q'' is simulated by electrically heating one of the two narrow walls. To this end both narrow walls are covered by mylar strips (1 mm wide, 80 mm long and 15 μm thick) coated with a thin layer (thickness 5 nm) of aluminum having a resistance of about 500 Ω . Calibration is obtained by electrically producing a well defined heat input Q in one of the channel walls and observing the resulting temperature difference, $(\delta T)_{\text{cal}}$, across the channel in the stationary state. The field induced heat flux must then be derived from the corresponding temperature difference, δT , with the formula

$$q = \frac{1}{2} \frac{Q}{lt} \frac{\delta T}{(\delta T)_{\text{cal}}}. \quad (19)$$

This expression can be easily derived, e.g., from an electric analogue under the assumption of equal heat losses for both halves of the apparatus. To check how well the apparatus performs according to these assumptions the following experiment has been undertaken. For several different mixtures calibrations were performed and thermal conductivity coefficients were calculated with

$$\lambda_{\text{eff}} = f \frac{Q}{lt} \frac{w}{(\delta T)_{\text{cal}}}, \quad (20)$$

where f should take the value $\frac{1}{2}$ for an ideal symmetric apparatus. In fig. 3 the results of λ_{eff}/f are plotted against literature values for the thermal conductivity of these gases, λ_{lit} . The vacuum losses are subtracted. As is seen from fig. 3 the slope of the curve corresponds indeed to $f = \frac{1}{2}$. Deviations from $\frac{1}{2}$ are partially due to the asymmetry of the apparatus and to the fact that the thermal conductance of the apparatus from top to bottom is not negligible in comparison to the thermal conductance of the apparatus from left to right. By a further check the same measurements were also performed while one side wall of the apparatus was attached to a heat sink. In this case $f = 1$ should be expected. This is indeed found as is shown in fig. 3. Finally, with the heat sink

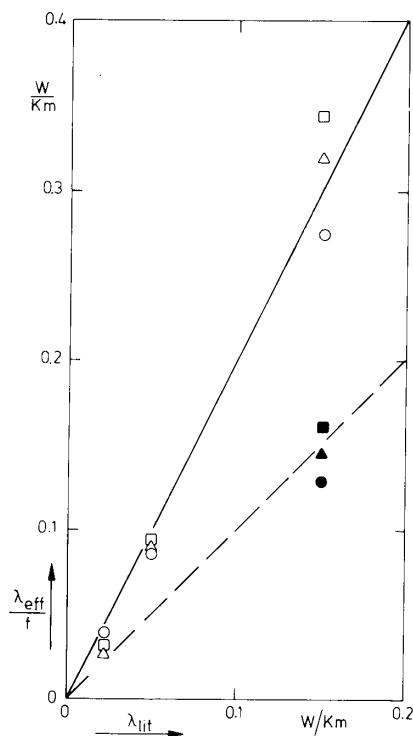


Fig. 3. Plot of the experimentally observed $\lambda_{\text{eff}}/f = Qw/(lt\delta T)$ versus λ_{lit} (see text). Without heat sink: \circ 130 Pa; \triangle 260 Pa; \square 390 Pa. With heat sink: \bullet 130 Pa; \blacktriangle 260 Pa; \blacksquare 390 Pa.

attached to one side of the channel, measurements of the transverse Dufour effect were performed with the factor $\frac{1}{2}$ in eq. (19) dropped. The results show no systematic differences with those performed without the heat sink. For temperature stabilization the channel is placed inside a vacuum jacket, which in turn is placed in a dewar with a noncirculating waterbath.

5. Experimental results and discussion

It has been verified that the observed transverse temperature difference is linear in ∇x and odd in the field. The quantity $p\mathcal{D}_T^{\text{tr}}$ is calculated from the measurements with the use of

$$(p\mathcal{D}_T^{\text{tr}})_{\text{meas}} = x_A x_B q^{\text{tr}}/\nabla x, \quad (21)$$

neglecting the term $D^{\text{tr}}\mathcal{D}_T^{\text{tr}}/(\mathcal{D}_T^{\text{tr}}D^{\perp})$ in eq. (16). When the mean free path of the molecules becomes comparable with the dimensions of the apparatus a small

pressure dependence of $p\mathcal{D}_T^{\text{tr}}$ is found. The experimental values of $p\mathcal{D}_T^{\text{tr}}$ are corrected to infinite pressure with the Knudsen correction relation

$$p\mathcal{D}_T^{\text{tr}} = (p\mathcal{D}_T^{\text{tr}})_{\text{meas}}(1 + K/p). \tag{22}$$

The value of K is found in the usual way by plotting $(p\mathcal{D}_T^{\text{tr}})_{\text{meas}}^{-1}$ versus p^{-1} . In fig. 4 the final results for an equimolar $\text{N}_2\text{-Ar}$ mixture are plotted versus B/p , where Knudsen corrections are applied with $K = 24$ Pa. It is seen that the effect is a unique function of B/p . The solid curve is a theoretical line according to eq. (17c) fitted to the experiment with $\Psi_{11}^T = 0$. It describes the measurements well. This, however, has no implications for the strength of the \mathbf{WJ} term, since the shape of the curves for the different components of a transport tensor is not very sensitive to Ψ_{11}^T , but only their ratio is.

The dashed curve in fig. 4 is a smoothed line of experimental results for pD_T^{tr} from transverse thermal diffusion measurements. In order to arrive at those values from the experimentally determined quantity D_T^{tr}/D , a value⁸⁾ of $0.197 \text{ cm}^2/\text{s}$ is used for the field free diffusion coefficient at atmospheric pressure. The positions of $p\mathcal{D}_T^{\text{tr}}$ and pD_T^{tr} along the B/p axis agree remarkably well (within 1%) and their magnitudes are equal to within 7%. This is well within the joint experimental errors. These errors are mainly systematic.

The signs of the two effects are the same as can be seen in fig. 1. When, for the two experiments, the thermodynamic forces ∇x and ∇T are pointing in the same direction, and the directions of the magnetic field also correspond, then the transverse fluxes, q^{tr} and j^{tr} have the same direction. It is noted that

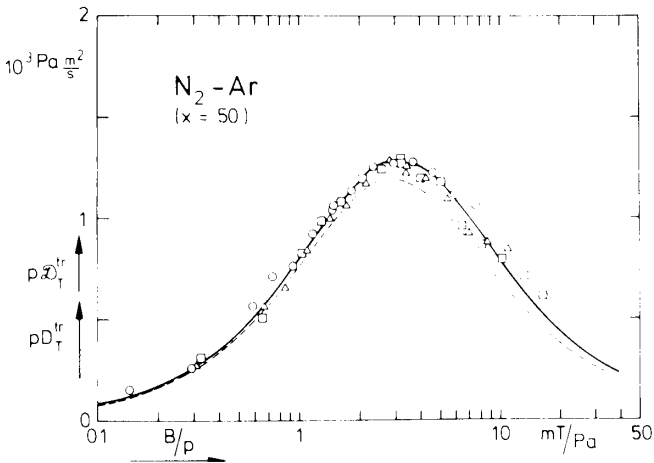


Fig. 4. Measured values of $p\mathcal{D}_T^{\text{tr}}$ as a function of field to pressure ratio. \square 112 Pa; \triangle 196 Pa; \circ 258 Pa. The dashed curve represents pD_T^{tr} obtained from thermal diffusion measurements. Note that 1 mT/Pa corresponds to 1333 G/Torr.

in fig. 1 ∇x is the concentration gradient for N_2 and j^{tr} the particle flux of N_2 . Thus it is concluded that the Onsager reciprocity relation of eq. (12) is confirmed by these experiments over the whole range of magnetic field strengths studied. One can also draw another conclusion: the agreement of the two sets of widely different measurements makes the presence of large systematic errors in any of the two improbable. This last conclusion is of importance for a later verification of the relation between D_T^{tr} , D^{tr} and λ^{tr} .

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