

EXPERIMENTS ON THE INFLUENCE OF A MAGNETIC FIELD ON DIFFUSION IN N₂-NOBLE GAS MIXTURES

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Experimental results are presented for the magnetic field effect on diffusion in N₂-noble gas mixtures at 300 K. The data show that the polarization produced by a concentration gradient is different from the one produced in a temperature gradient and that this difference is due to a different scalar part of the polarizations.

1. Introduction

The influence of external magnetic and electric fields on the transport properties of dilute polyatomic gases has been studied extensively during the last two decades¹⁻³). So far the magnetic field effects on shear viscosity⁴⁻⁹) and thermal conductivity¹⁰⁻¹⁵) have been measured for various kinds of molecules. It was found that a velocity gradient predominantly creates a polarization with tensorial character $\mathcal{Y}^{(2)}(\mathbf{J})$ (where $\mathcal{Y}^{(q)}(\mathbf{J})$ is a normalized irreducible tensor¹⁶⁻¹⁸) of rank q formed from the angular momentum \mathbf{J} , whereas a temperature gradient predominantly produces a polarization of the type $[\mathbf{W}]^1 \mathcal{Y}^{(2)}([\mathbf{W}]^p)$ ($[\mathbf{W}]^p$ is an irreducible tensor of rank p in the reduced molecular velocity \mathbf{W}). Similar experiments have been carried out in electric fields¹⁹⁻²⁴). For mixtures of polyatomic gases and noble gases the magnetic field effect on the cross phenomena, thermal diffusion and its reciprocal effect, the Dufour effect, were investigated. These measurements successfully confirmed for the first time an Onsager relation in the presence of a magnetic field²⁵⁻²⁷). Attempts to complete the set of measurements with data on the field effect on diffusion have failed so far²⁸). In this paper the existence of such an effect will be verified and results for N₂-noble gas mixtures will be presented.

Measurements of the magnetic field effect on diffusion are interesting in two ways. In the first place these measurements yield information on non-equilibrium polarizations produced by a concentration gradient. Furthermore, data on the field effect on diffusion would give the possibility to perform a check of the

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theoretical description, using a relation between the field effects on diffusion, thermal diffusion and thermal conduction. In this way additional information will be obtained concerning the scalar structure of polarizations. Some details of the theoretical description can be found in the following section. In sections 3 and 4 the experimental set-up is described and in sections 5 and 6 the results are presented and discussed.

2. Theory

In this section theoretical expressions relevant for the magnetic field effect on diffusion will be given. For a survey and detailed explanation the reader is referred to refs. 29 and 30.

In a binary gas mixture a gradient in the concentration generates a particle flux. In the absence of external forces and pressure and temperature gradients the flux of species 1 in the field-free case is given by

$$j_1 = -nD\nabla x_1, \quad (1)$$

where n is the total number density, x_1 is the mole fraction of species 1 and D is the diffusion coefficient. In a magnetic field B this transport coefficient has to be replaced by a tensor,

$$j_1 = -n\mathbf{D} \cdot \nabla x_1. \quad (2)$$

Spatial symmetry considerations require that the diffusion tensor takes the form

$$\mathbf{D} = \begin{pmatrix} D_{\perp} & -D^{\text{tr}} & 0 \\ D^{\text{tr}} & D_{\perp} & 0 \\ 0 & 0 & D_{\parallel} \end{pmatrix}, \quad (3)$$

if the field is in the z -direction. The diagonal elements are even in the field whereas the off-diagonal element D^{tr} is odd.

The polarizations depending on the angular momentum J , observed in experiments on the influence of a magnetic field on thermal conductivity and thermal diffusion, are of the type $[W]^1 \mathcal{Y}^{(2)}(J)$ and $[W]^1 \mathcal{Y}^{(1)}(J)$. If one takes into account these two polarizations, the elements of the diffusion tensor for a polyatomic gas-noble gas mixture change according to

$$\frac{D^{\text{tr}}}{D} = -\psi_{12}[g(\xi_{12}) + 2g(2\xi_{12})] + \psi_{11}g(\xi_{11}), \quad (4)$$

$$\frac{\Delta D^{\perp}}{D} = \frac{D^{\perp}(B) - D(0)}{D} = -\psi_{12}[f(\xi_{12}) + 2f(2\xi_{12})] + \psi_{11}f(\xi_{11}), \quad (5)$$

$$\frac{\Delta D^{\parallel}}{D} = \frac{D^{\parallel}(B) - D(0)}{D} = -2\psi_{12}f(\xi_{12}) + 2\psi_{11}f(\xi_{11}), \quad (6)$$

with the field functions

$$f(x) = \frac{x^2}{1+x^2}, \quad g(x) = \frac{x}{1+x^2}, \quad (7)$$

and the field parameter

$$\xi_{pq} = \frac{g\mu_N kT}{\hbar \{x_1 \langle v_{11} \rangle_0 \mathfrak{S}_{(pqj|i)11} + x_2 \langle v_{12} \rangle_0 \mathfrak{S}_{(pqj|i)12}\}} \frac{B}{p}. \quad (8)$$

Here g is the rotational g -factor of the polyatomic molecule, μ_N the nuclear magneton, $\langle v \rangle$ a relative thermal speed and the $\mathfrak{S}_{(pqj|i)kl}$ effective cross sections governing the decay due to the collisions of species k and l ($1 =$ polyatomic gas, $2 =$ noble gas) of the pqj -polarization (rank p in W , rank q in J and scalar factor characterized by j). For the magnitude of the contributions from the polarizations we can write down

$$\psi_{pq} = \frac{(1 - \frac{1}{2}\delta_{p1}\delta_{q2})x_2 \langle v_{12} \rangle_0 \mathfrak{S}_{(pqj|i)12}^2}{\mathfrak{S}_{(i0|1)12} [x_1 \langle v_{11} \rangle_0 \mathfrak{S}_{(pqj|i)11} + x_2 \langle v_{12} \rangle_0 \mathfrak{S}_{(pqj|i)12}]}, \quad (9)$$

where $\mathfrak{S}_{(i0|1)12}$ describes the production of the pqj -polarization in a concentration gradient due to collisions between species 1 and 2 and $\mathfrak{S}_{(i0|1)12}$ the field free diffusion.

In the derivation of eqs. (4) through (6) the approximation has been made that the irreducible tensor parts of $[W]^l \mathcal{Q}^{(2)}$ and $[W]^l \mathcal{Q}^{(1)}$ all have the same decay time. This approximation is strictly valid for a spherical potential³¹⁾ and is therefore generally referred to as the "spherical approximation". Measurements of the field effects on thermal diffusion and thermal conductivity showed that the spherical approximation yields a satisfactory description of the experimental results²⁵⁾.

It has been shown that for the field induced change in the generalized phenomenological coefficients L ,

$$\Delta L_{\mu\mu}^{jj}(\infty) \Delta L_{\mu\mu}^{qq}(\infty) = [\Delta L_{\mu\mu}^{jq}(\infty)]^2, \quad (10)$$

if one assumes that in the three experiments the same polarization is present^{29,30)}. In our case L^{jj} is the diffusion coefficient, L^{qq} the thermal conductivity coefficient and L^{jq} the coefficient of the cross effect, thermal diffusion. Using the relation between these generalized phenomenological coefficients and the usual transport coefficients D , λ and D_T (cf. ref. 29) and the relations

$$\lim_{B \rightarrow \infty} \frac{\Delta D^T}{D} = c\psi_{pq}^T, \quad \lim_{B \rightarrow \infty} \frac{\Delta \lambda}{\lambda} = c\psi_{pq}^\lambda, \quad \lim_{B \rightarrow \infty} \frac{\Delta D}{D} = c\psi_{pq}^D, \quad (11)$$

with c a numerical constant (cf. e.g., eqs. (4) through (6)), we can rewrite eq. (10) as

$$(\psi_{pq}^T)^2 = \frac{x_1 x_2 \lambda}{nkD} \psi_{pq}^D \psi_{pq}^\lambda \tag{12}$$

This is the relation which was established by Eggermont et al.³⁰⁾ on the basis of the above stated assumption, using explicit expressions for the ψ 's. According to ref. 29 the equality has in general to be replaced by an inequality. If more than one single type of polarization is produced and there is no coupling between these polarizations, the relation between the field effects on thermal conduction, thermal diffusion and diffusion (12) remains still valid for the contributions from each type separately. Substitution of data on the magnetic field effect on thermal conduction and thermal diffusion into this relation show that a (small) magnetic field effect on diffusion should exist (see, e.g., ref. 25). The measurement of such an effect would therefore be an interesting direct test of the description.

3. Description of the experimental set-up

For the accurate determination of small effects, such as the magnetic field effect on diffusion, measurements of transverse effects (which occur only in the presence of a magnetic field) are indicated. The central part of the apparatus is formed by

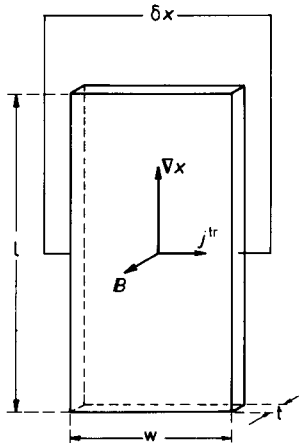


Fig. 1. Schematic diagram of the apparatus for the measurement of the magnetic field effect on diffusion. The dimensions are: $l = 60$ mm, $w = 20$ mm and $t = 0.7$ mm. The field orientation is the one for the measurement of D^D . The indicated directions for ∇x and j^{tr} are those for N_2 in a N_2 -noble gas mixture. The cells for measuring the transverse concentration difference δx are located at 0.75 m from the field centre. In the absence of a magnetic field $j^{tr} = 0$.

a capillary of rectangular cross section (see fig. 1; dimensions: length $l = 60$ mm, width $w = 20$ mm, thickness $t = 0.7$ mm; material: brass). Across the length of this capillary a concentration gradient is set up by connecting each end to a 50 l bulb containing one of the components of the mixture to be measured. Under the influence of a magnetic field B a transverse particle flow is produced (cf. eq. (2), let $B = (0, 0, B)$ and $\nabla x = (\nabla x, 0, 0)$):

$$j_1^{tr} = j_{1,y} = -nD^{tr}\nabla x_1. \tag{13}$$

This flow gives rise to a small concentration differences δx across the width of the capillary. For the set-up of fig. 1 one has in the stationary state

$$\delta x = \frac{w}{l} \frac{D^{tr}}{D} \Delta x, \tag{14}$$

where $\Delta x = l\nabla x$ is the applied concentration difference.

In order to be able to disentangle the contributions of the various polarizations, data on at least two independent elements (or combinations of elements) of the diffusion tensor are required. For this purpose the apparatus was designed in such a way that the orientation of the magnetic field with respect to the gradient can be changed. In the case of the orientation shown in fig. 2 (let $B = (0, 0, B)$ and $\nabla x = (0, -\frac{1}{2}\sqrt{2}\nabla x, \frac{1}{2}\sqrt{2}\nabla x)$) also a transverse particle flow

$$j_1^{tr} = \frac{1}{2}\sqrt{2}(j_{1,y} + j_{1,z}) = -\frac{1}{2}n(D^{\parallel} - D^{\perp})\nabla x_1 \tag{15}$$

will occur due to the fact that D^{\parallel} is not equal to D^{\perp} (and thus j^{\parallel} differs from j^{\perp}). The concentration difference across the width of the capillary is then given by

$$\delta x = \frac{1}{2} \frac{w}{l} \frac{D^{\parallel} - D^{\perp}}{D} \Delta x. \tag{16}$$

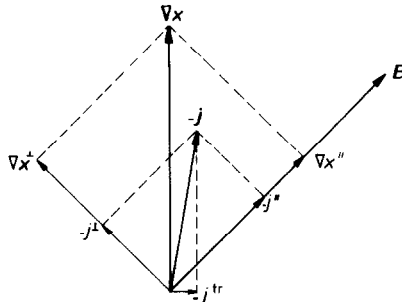


Fig. 2. The field orientation for measuring the difference between the two longitudinal diffusion coefficients D^{\parallel} and D^{\perp} . Note that the magnetic field B now lies in the plane of drawing and makes an angle of 45° with the concentration gradient ∇x . In the absence of a magnetic field $D^{\parallel} = D^{\perp}$, consequently $j^{\parallel} = j^{\perp}$ and thus $j^{tr} = 0$.

The transverse concentration differences, which occur under both orientations (typical value 1×10^{-5}), are detected by measuring the difference in heat conductivity between the gas mixtures at both sides of the capillary, using a matched pair of katharometer type thermistors (bead size: 1 mm; bead temperature: 8 K above ambient temperature) arranged in a Wheatstone bridge. For optimum stability the measuring cells containing these thermistors are located in one single thermally isolated copper block, which is kept at constant temperature by means of a thermoelectric heat pump. To avoid effects of magnetic stray fields on the thermistors this block is placed at 0.75 m from the field centre inside a double magnetic shield of Netic S3 alloy. A high sensitivity is attained: in a N_2 -He mixture concentration differences as small as 2×10^{-7} can still be detected. In a similar way also the applied concentration gradient, which slowly decays (relaxation time approximately 2 hours for N_2 -Ar at $p = 250$ Pa), is monitored. The capillary and the detection section are placed inside a vacuum jacket, while the bulbs and the leads are stabilized with water from a thermostat.

The differences in thermal conductivity are related to concentration differences by calibrating them with mixtures of known composition. To ensure reproducibility, the pressures of the mixtures introduced in the apparatus are compared to a reference pressure using a high accuracy differential capacitance manometer.

4. Experimental checks and corrections

Several corrections have to be applied to the expressions in eqs. (14) and (16) in order to take into account the non-ideal experimental conditions. First of all, as in Hall experiments, the ends of the capillary have a short-circuiting effect on the transverse flow. To account for this effect, which vanishes when $l \gg w$, a correction³²⁾ $\epsilon = 2 \times 10^{-2}$ has been incorporated. Eqs. (14) and (16) then read

$$\left(\frac{\Delta D}{D}\right)_m = (1 + \epsilon) \frac{l}{w} \frac{\delta x}{\Delta x}, \quad (17)$$

where m stands for "measured at pressure p ".

Secondly, Knudsen effects have to be taken into account. These effects occur because at low pressures the mean free path of the molecules becomes comparable to the thickness of the capillary. The corrections for these effects on the magnitude and the position of the field effect are applied to the individual pressure runs according to¹²⁾

$$\left(\frac{\Delta D}{D}\right) = \left(\frac{\Delta D}{D}\right)_m \left[1 + \frac{K_A}{p}\right] \quad (18)$$

and

$$\left(\frac{B}{p}\right) = \left(\frac{B}{p}\right)_m \left[1 + \frac{K_p}{p}\right]^{-1}, \quad (19)$$

where the K 's are the Knudsen correction coefficients. The values of K_A and K_p , resulting from a linear fit of the experimental values of $(D^{\text{tr}}/D)_{\text{max}}^{-1}$ and $(B/p)_{\text{max}}$ as a function of $1/p$ respectively, are listed in table I.

As we are dealing with rather small effects, a number of consistency tests were performed in order to be sure that no systematic errors are present. It was verified that

- 1) no field effect occurs in noble gases;
- 2) no field effect occurs at zero gradient;
- 3) the field effect is proportional to the magnitude of the applied gradient;
- 4) the field effect is proportional to the geometrical factor l/w (see section 5);
- 5) D^{tr} is odd in the field, and
- 6) $D^{\parallel} - D^{\perp}$ is even; and that
- 7) the sign of the effect is in accordance with theory (positive ψ , cf. eqs. (2) through (6) and figs. 1 and 2).

5. Experimental results

Experiments have been carried out for N_2 -He, N_2 -Ne and N_2 -Ar mixtures at room temperature. The effect has been studied as a function of the noble gas concentration.

The experimental data and the results of the data analysis are listed in table I. Some of the systems investigated are illustrated in figs. 3 through 5. The theoretical curves of eqs. (4) through (6) have been fitted to the experimental points using the ψ 's and the ξ 's as adjustable parameters. As one can see, the field dependence of the data points is in perfect agreement with the theoretical behaviour. Analogous to the results of the magnetic field effect on thermal diffusion²⁵), the measurements can very well be described using one single $[W]^{1\mathcal{Q}(2)}$ type of polarization in the case of N_2 -He, but for N_2 -Ne and N_2 -Ar also a second polarization of the type $[W]^{1\mathcal{Q}(1)}$ has to be taken into account.

In fig. 6 the quantity $B/p\xi_{12}$, which is related to the position of the effect, is plotted as a function of the noble gas concentration. It is clear from these graphs that this quantity depends linearly on the concentration in agreement with eq. (8). The lines are fitted to the data points in such a way that they extrapolate to the same value for pure N_2 . Extrapolations to $x_2 = 0$ and 1 yield values for the two decay cross sections occurring in eq. (8), see table II.

TABLE I
Experimental results for N₂-noble gas mixtures (T = 300 K)

Gas	x ₂	10 ³ × (D ¹¹ /D) _{max}	(B/P) _{max} (mT/Pa)	K ₄ (Pa)	K _p (Pa)	10 ³ × ψ ₁₂	B/pξ ₁₂	10 ³ × ψ ₁₁ (mT/Pa)	B/pξ ₁₁ (mT/Pa)
N ₂ -He	0.30	0.12	3.0	11	22	0.084	4.9	<0.002	-
	0.50	0.23	2.4	40	37	0.16	3.9	<0.002	-
	0.75	0.39	1.7	19	84	0.27	2.8	<0.002	-
N ₂ -Ne	0.30	0.15	3.1	<5	<5	0.11	5.1	0.028	4.4
	0.50	0.24	3.1	<5	<5	0.19	4.9	0.053	3.0
	0.75	0.41	2.5	16	15	0.35	4.4	0.19	3.8
N ₂ -Ar	0.30	0.23	3.5	64	<5	0.20	6.0	0.11	4.5
	0.50	0.43	3.6	77	<5	0.37	6.5	0.21	6.1
	0.75	0.59	3.5	39	<5	0.50	6.3	0.27	6.0
N ₂ -Ar ^a	0.50	0.39	3.4	44	<5				

^a Measured in a different apparatus: l = 60 mm, w = 10 mm and t = 1.4 mm.

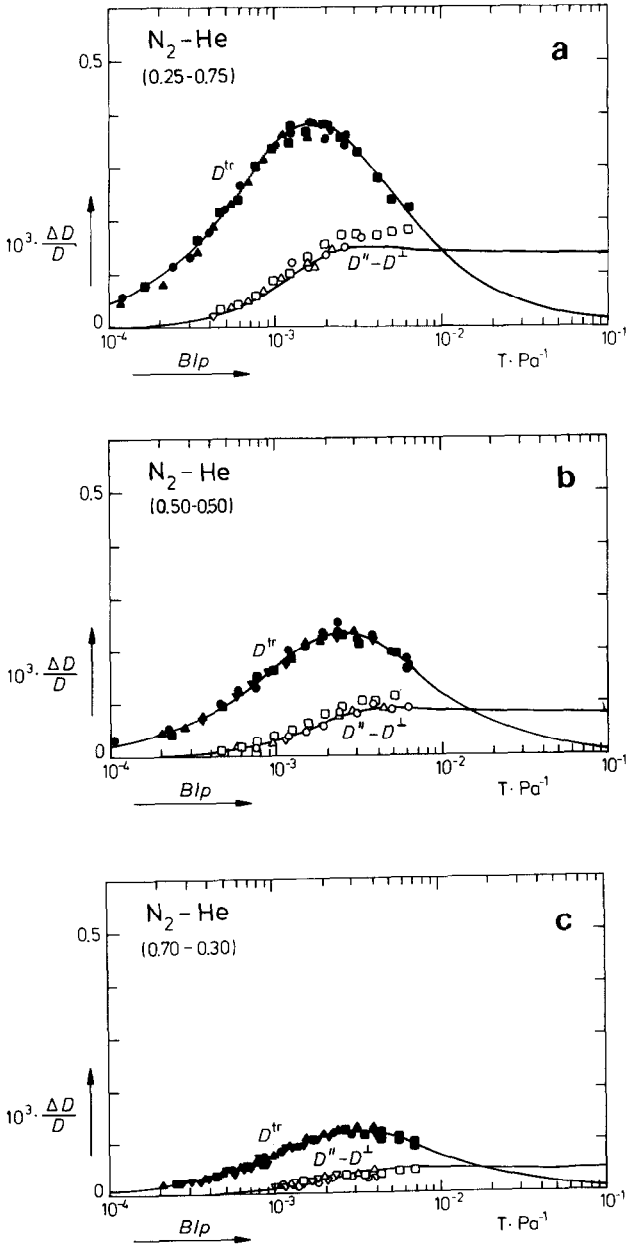


Fig. 3. Experimental results for N_2 -He at 300 K for three noble gas concentrations: $x_2 = 0.75$: \square \blacksquare 269 Pa, \circ \bullet 534 Pa, \triangle \blacktriangle 934 Pa, ∇ \blacktriangledown 934 Pa, $x_2 = 0.50$: \square \blacksquare 284 Pa, \circ \bullet 291 Pa, \triangle \blacktriangle 560 Pa, ∇ \blacktriangledown 941 Pa, $x_2 = 0.30$: \square \blacksquare 271 Pa, \circ \bullet 548 Pa, \triangle \blacktriangle 552 Pa, ∇ \blacktriangledown 967 Pa. The drawn lines are the theoretical curves of eqs. (4) through (6) scaled to fit the experimental points. The fit parameters are $\psi_{12} = 2.7, 1.6, 0.83 \times 10^{-4}$ and $B/p\xi_{12} = 2.8, 3.9, 4.9$ mT/Pa, respectively, with $\psi_{11} = 0$.

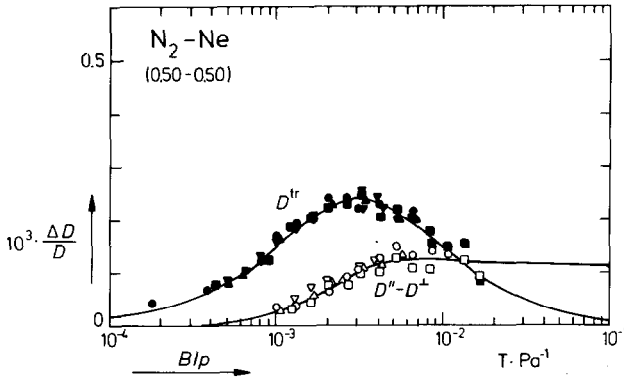


Fig. 4. Experimental results for N_2 -Ne (0.50-0.50) at 300 K. \square \blacksquare 134 Pa, \circ \bullet 189 Pa, \triangle \blacktriangle 293 Pa, ∇ \blacktriangledown 547 Pa. The drawn lines are the theoretical curves of eqs. (4) through (6) scaled to fit the experimental points. The fit parameters are $\psi_{12} = 1.9 \times 10^{-4}$, $B/p\xi_{12} = 4.9$ mT/Pa, $\psi_{11} = 0.53 \times 10^{-4}$, $B/p\xi_{11} = 3.0$ mT/Pa.

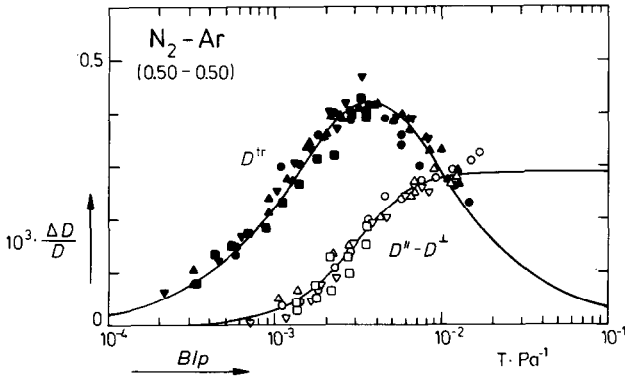


Fig. 5. Experimental results for N_2 -Ar (0.50-0.50) at 300 K. \circ \bullet 137 Pa, \triangle \blacktriangle 190 Pa, ∇ \blacktriangledown 270 Pa, \square \blacksquare 586 Pa. The drawn lines are the theoretical curves of eqs. (4) through (6) scaled to fit the experimental points. The fit parameters are $\psi_{12} = 3.7 \times 10^{-4}$, $B/p\xi_{12} = 6.5$ mT/Pa, $\psi_{11} = 2.2 \times 10^{-4}$, $B/p\xi_{11} = 6.1$ mT/Pa.

Using eq. (9) and the values for $\mathfrak{S}_{(10|1)_2}^{(10|1)_2}$, which follow from data on the field-free diffusion coefficient, one can now determine the absolute value of the production cross sections for the diffusion for each concentration studied. The results are shown in fig. 7. Since cross sections do not depend on the concentration the data points should lie on a straight horizontal line, which is indeed found.

We will now compare the present results with data on the field influence on thermal conduction¹⁴⁾ and thermal diffusion²⁵⁾. As far as the position along the B/p axis is concerned these results showed some discrepancies for N_2 -Ne and N_2 -Ar, see fig. 6. If compared now also to the present results, the discrepancies

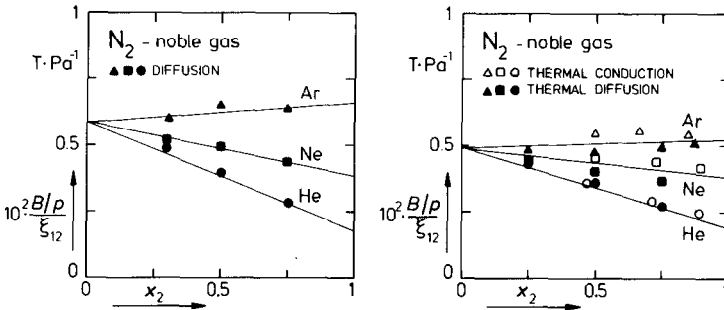


Fig. 6. The position of the magnetic field effect for N_2 -noble gas mixtures as a function of the mole fraction of the noble gas. Left: field effect on diffusion. Right: field effects on thermal conduction¹⁴⁾ (open symbols) and thermal diffusion²⁵⁾ (closed symbols).

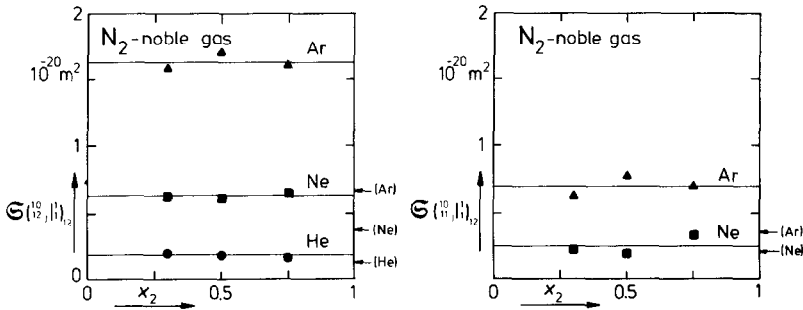


Fig. 7. The production cross section for the $[W]^{1\psi(2)}$ -polarization and the $[W]^{1\psi(1)}$ -polarization for N_2 -noble gas mixtures versus the mole fraction of the noble gas. The arrows indicate the values predicted from the combined results of experiments on thermal conduction and thermal diffusion using eq. (12).

TABLE II

Effective cross sections for the production and decay of the polarizations in diffusing N_2 -noble gas mixtures. The values in parentheses are calculated from the results of thermal conduction¹⁴⁾ and thermal diffusion²⁵⁾ measurements, using relation (12).

Gas	$ \mathcal{G}(\frac{10}{12} 1)_{12} $ (10^{-20} m^2)	$ \mathcal{G}(\frac{10}{11} 1)_{12} $	$\mathcal{G}(\frac{12}{12} 1)_{12}$	$\mathcal{G}(\frac{12}{11} 1)_{11}$	$\mathcal{G}(\frac{11}{11} 1)_{12}$	$\mathcal{G}(\frac{11}{11} 1)_{11}$
N_2 -He	0.18 (0.12)	< 0.01 (< 0.01)	7.4 (8.7)	48 (41)	- -	- -
N_2 -Ne	0.63 (0.37)	0.24 (0.18)	28 (29)	48 (41)	23 (39)	35 (16)
N_2 -Ar	1.4 (0.66)	0.69 (0.34)	58 (47)	48 (41)	60 (26)	35 (16)

become even more significant: differences up to 30% occur whereas the experimental error equals 10% at most (cf. fig. 6 and table IV).

No agreement at all is found when we combine the magnitudes ψ of the magnetic field effects on thermal conduction, thermal diffusion and diffusion in

TABLE III
Comparison of the present results with the predictions from thermal conduction and thermal diffusion, using relation (12), for $x_2 = 0.5$

Gas	$10^3 \times \psi_{12}^i$	$10^3 \times \psi_{12}^T$	$10^3 \times \psi_{12}^D$	$10^3 \times \psi_{12\text{calc}}^D$
N ₂ -He	1.4	0.25	0.16	0.08
N ₂ -Ne	2.5	0.38	0.19	0.08
N ₂ -Ar	1.9	0.37	0.37	0.10

order to test relation (12), see table III. The contributions from the $[W]^1[\mathcal{D}]^2$ -polarization to the observed effects for N₂-Ar and N₂-Ne are larger than the predicted values by approximate factors of 4 and 3 respectively. Even in the case of N₂-He where no other polarization contributes to the effects and one therefore directly can compare the magnitudes of the various field effects, the field effect on diffusion is approximately twice as large as expected.

It was extensively verified that these discrepancies are not due to systematic experimental errors by performing various experimental checks (see section 4). Measurements have also been performed in an apparatus with different dimensions ($l = 60$ mm, $w = 10$ mm and $t = 1.4$ mm) for an equimolar N₂-Ar mixture. Due to the smaller signal ($w/l = 1/6$ instead of $1/3$) the accuracy was lower than for the previous apparatus, but within the accuracy limits, these measurements reproduced the earlier obtained results (cf. table I).

6. Discussion

The experimental results presented in the previous section clearly show, if we exclude systematic experimental errors, that the theoretical description fails in certain aspects. Summarizing we come to the following conclusions:

1) If we look at each set of measurements separately (i.e., thermal conduction or thermal diffusion or diffusion), everything is internally consistent: field and concentration dependence agree perfectly well with theory.

2) If we compare the results of the three sets of measurements using relation (12), small discrepancies occur for the positions of the effect, while inadmissibly large discrepancies occur for the magnitude.

3) Whereas for N₂-Ar and N₂-Ne the results for the ψ 's and ξ 's follow from a complicated 4-parameter fit and may therefore be inaccurate, for N₂-He only one polarization contributes to the effect and the "raw" experimental data can directly be used for a comparison. Even in this simple case no agreement is found.

Apparently, the assumption which underlies the relation between the three effects, namely that the same polarization is produced in the three cases (see

section 2), is not justified. From the dependence of field effects on the orientation of the field with respect to the gradient we do however know, that the polarizations which give rise to the field effects under consideration all have the same tensorial character. Consequently, their scalar factors, which have always been taken equal, must differ.

In order to try to obtain more detailed information we will now restrict ourselves to the case where just one tensorial type of polarization plays a role and consider two vectors $\Phi^{12j|1}$ and $\Phi^{12q|1}$, corresponding to the polarizations produced by concentration and temperature gradients respectively. These vectors, which have the same – known – tensorial factor, obey the normalization condition

$$\langle \Phi^{12j|1} | \Phi^{12i|1} \rangle = x_1 I \quad (i = j, q), \quad (20)$$

where the brackets denote the usual scalar product in the Hilbert space of velocity and angular momentum dependent expansion functions²⁹⁾ and I is the unit tensor. Let us assume that the two functions $\Phi^{12j|1}$ and $\Phi^{12q|1}$ need not be orthogonal. Their scalar product is a diagonal tensor with elements which we will denote by a_{jq} :

$$\langle \Phi^{12j|1} | \Phi^{12q|1} \rangle = x_1 a_{jq} I. \quad (21)$$

If the experimental results can be described with only one polarization, which is the case for the system N_2 -He, we may assume that $\Phi^{12j|1}$ and $\Phi^{12q|1}$ do not couple to any other polarization. The relation between the three field effects then takes the form^{16-18,29)}

$$(\psi_{pq}^T)^2 = a_{jq}^2 \frac{x_1 x_2 \lambda}{nkD} \psi_{pq}^D \psi_{pq}^\lambda. \quad (22)$$

The possibilities for the value of a_{jq} are (we will omit for simplicity the upper index 1)

1) $|a_{jq}| = 1$: This means that the vectors Φ^{12j} and Φ^{12q} coincide: $\Phi^{12j} = \Phi^{12q} = \Phi^{12}$, the same polarization is produced and relation (12) should be valid (note that eq. (22) indeed reduces to eq. (12)).

2) $a_{jq} = 0$: The vectors Φ^{12j} and Φ^{12q} are now orthogonal. In such a case no field effect on the cross effects (thermal diffusion and the Dufour effect), would occur (cf. eq. (22)), which is contradicted by the experiments. When $a_{jq} = 0$, such field effects would only exist if the polarizations couple to each other. In order to reconcile the experimental data the cross section for such a coupling would have to be of the same order of magnitude as the decay cross sections of the polarizations. In turn, such a large off-diagonal cross section would give rise to a more complicated field dependence, which makes $a_{jq} = 0$ highly improbable.

3) $0 < |a_{jq}| < 1$: The vectors Φ^{12j} and Φ^{12q} are neither orthogonal nor identical.

TABLE IV
 Comparison between the measurements of the magnetic field effects on thermal conduction, thermal diffusion and diffusion. The values in parentheses are obtained by interpolation. The values for the field free diffusion coefficient (at 1 atm) are taken from ref. 33, the ones for the thermal conductivity coefficient from ref. 14. From these data the listed values for the scalar product a_{ij} are obtained (see eq. (22)).

Gas	x_2	$B/p\xi_{12}$ (mT/Pa)			$10^3 \times \psi_{12}$			D ($10^{-4} \text{ m}^2 \text{ s}^{-1}$)	λ ($\text{W m}^{-1} \text{ K}^{-1}$)	$ a_{ij} $
		D	λ	D_T	D	λ	D_T			
N ₂ -He	0.30	4.9	(4.4)	(4.2)	0.083	(2.3)	(0.17)	0.722	0.043	0.64
	0.50	3.9	3.7	3.5	0.16	1.4	0.25	0.722	0.058	0.69
	0.75	2.8	(2.9)	2.7	0.27	(0.66)	0.24	0.722	0.088	0.70
N ₂ -Ne	0.30	5.1	(5.0)	(4.4)	0.11	(3.2)	(0.26)	0.328	0.030	0.58
	0.50	4.9	4.7	4.0	0.19	2.5	0.38	0.328	0.034	0.63
	0.75	4.4	(4.3)	3.6	0.35	(1.4)	0.33	0.328	0.040	0.58
N ₂ -Ar	0.30	6.0	(5.4)	(4.8)	0.20	(2.7)	(0.32)	0.197	0.023	0.51
	0.50	6.5	5.4	4.7	0.37	1.9	0.37	0.197	0.021	0.50
	0.75	6.3	(5.3)	4.9	0.50	(0.89)	0.23	0.197	0.020	0.46

Due to the fact that the two polarizations now have a certain common component, also field effects on the cross effects will occur.

Eq. (22) enables us to determine $|a_{ij}|$. The resulting values for this coefficient are listed in table IV. If there is no coupling between the polarizations their decay cross sections must be equal²⁹). In order to check this, the half saturation field-to-pressure ratios are also listed. One should keep in mind that for N₂-He the data are provided directly by the experiment, whereas for N₂-Ne and N₂-Ar a 4-parameter fit is needed to disentangle the contributions from polarizations of different tensorial type. All $|a_{ij}|$ should be smaller than unity, which is indeed found. The inequality derived in ref. 29 is thus experimentally confirmed. For N₂-He the positions of the field effects coincide within the experimental error of 10%. For N₂-Ne and N₂-Ar larger differences between the positions of the $[W]^{(2)}$ contribution to the field effects occur. This may be due to inaccuracies in the determination of these positions. On the other hand, this might also be an indication that there is a slight coupling between the polarizations.

In conclusion we can say that the results of this experiment have shown that concentration and temperature gradients produce different polarizations. The tensorial factors of these polarizations are equal, consequently their scalar factors must be different. From a comparison of the results of the field effects on diffusion, thermal conduction and thermal diffusion the scalar product of these scalar factors has been determined. More information on their exact form can, however, not be obtained from the present experimental data. Finally, the measurements yield numerical values for the production and the decay of the polarization produced by a concentration gradient, see table II.

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