CONCENTRATION DEPENDENCE OF THE ISOTOPIC THERMAL DIFFUSION FACTOR FOR MIXTURES ^{3}He — ^{4}He AND H_2 — D_2

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SUMMARY — Experimental data for mixtures of ^3He — ^4He and H_2 — D_2 have been interpreted by means of the isotopic approach for the thermal diffusion factor, including a concentration-dependent term.

It is shown that for ^3He — ^4He mixtures the approach is quite satisfactory, regarding the mass effect and the concentration dependence. For H_2 — D_2 mixtures the mass coefficient $(m_1 - m_2)/(m_1 + m_2)$ is already too large and general expressions for α_T might be preferred.

1 — INTRODUCTION

In a previous paper (1), we have theoretically studied, in terms of the Lennard-Jones and the exponential-six models, the convergence and the concentration dependence of the isotopic approach to the thermal diffusion factor, α_T, as given by the expression

$$\alpha_T = \alpha_0 M_{12} [1 + \gamma (x_1 - x_2) M_{12}]$$
$$M_{12} = \frac{m_1 - m_2}{m_1 + m_2} \, ; \, x_1 + x_2 = 1 \qquad [1]$$

where

α_0 is the reduced isotopic thermal diffusion factor;

γ is a small, slowly varying function of the temperature;

m_1, m_2 and x_1, x_2 are, respectively, the molecular masses and the mole fractions of isotopes of kind 1 and 2.

According to Kihara-Mason and Chapman-Cowling schemes of approximations, γ is respectively given by

$$[\gamma]^K = \frac{5 - 3A^*}{2(5 + 2A^*)} \qquad [2]$$

$$[\gamma]^C = [\gamma]^K + (5 - 4B^*)\,\frac{3/5 + 15/8\,(5 + 2A^*)}{5 + 2A^* + 3(5 - 4B^*)/8} \qquad [3]$$

where the upper-scripts K and C refer to the scheme of approximation and A^* and B^* are the usual ratios of reduced collision integrals.

The Chapman-Cowling first approximation to the reduced isotopic thermal diffusion factor, which we denote by $[\alpha_0]_1^C$, is given by the expression

$$[\alpha_0]_1^C = \frac{15(6C^* - 5)}{16A^*} \cdot \frac{2A^* + 5}{2A^* + 5 + 3(5 - 4B^*)/8} \qquad [4]$$

Kihara expression for the first approximation, $[\alpha_0]_1^K$, can be obtained from equation [4] by dropping the factor $(5 - 4B^*)$.

Second approximations for both schemes are too complicated and can be found in ref. (2).

In the majority of practical cases, $(5 - 4B^*) > 0$. Hence, $[\gamma]^C > [\gamma]^K$ and, therefore, the Chapman-Cowling scheme predicts somewhat higher concentration dependence for the isotopic thermal diffusion factor.

For the same reason, usually we have

$$[\alpha_0]_1^K > [\alpha_0]_1^C$$

At least for higher temperatures, say for $T^* > 3$, the convergence α_0 is faster for Kihara-Mason scheme of approximation (1).

The information on the validity of equation [1] for light isotopes is rather scarce, both theoretically and experimentally.

As far as we know, the concentration-dependent term involving the quantity γ has always been neglected in experiments, even in the case of ^3He — ^4He mixtures (3, 4, 5, 6), which, nevertheless, provides a good example for comparison with theory.

Indeed, the mass coefficient, $M_{12} = 1/7$, might *a priori* be regarded as sufficiently small and, on the other hand, the concentration dependence as predicted by equation [1] is experimentally significant.

In this paper, we also use the mixtures $H_2 - D_2$ for comparison with the theory, in order to have an idea about the experimental limits of application of equation [1], regarding the mass influence and the concentration dependence, which is also an approach to the more general linear dependence of $1/\alpha_T$ with concentration (7, 8, 9, 10, 11).

2 — MIXTURES OF $^3He - ^4He$

Recently, PAUL, HOWARD & WATSON (12) carried out accurate determinations of the variation with concentration of the thermal diffusion factor for $^3He - ^4He$ mixtures.

Instead of using the isotopic approach of equation [1], those authors interpret the experimental data in terms of the general expressions for the thermal diffusion factor, considering the Chapman-Cowling first approximation, $[\alpha_T]_1^C$, and Kihara-Mason first and second approximations, $[\alpha_T]_1^K$ and $[\alpha_T]_2^K$, respectively.

It was also assumed that $1/\alpha_T$ was linear with concentrations, as proposed by one of us (7, 8, 9).

The exponential-six model was used, with intermolecular potential parameter $\alpha = 12.8$ and $\varepsilon/k = 9.34° K$ previously determined (6) by thermal diffusion for mixtures of $50\,\% \; ^3He - 50\,\% \; ^4He$.

Experimental errors of α_T were of the order of $1.5\,\%$ and the mean temperature was approximately $160° K$, which corresponds to a mean reduced temperature $T^* = 17.34$.

Following the authors' interpretation, our least square fit of experimental data gives

$$1/\alpha_T\,(\exp) = 14.7_6\, x_4 + 14.0_1\, x_3 \qquad [5]$$

where x_3 and x_4 denote the mole fractions of ^3He and ^4He, respectively.

Therefore, the limiting values of $\alpha_T\,(\exp)$ as $x_4 = 1$ and $x_3 = 1$ are, respectively,

$$[\alpha_T\,(\exp)]_{x_4 = 1} = 0.071_4 \quad ; \quad [\alpha_T\,(\exp)]_{x_3 = 1} = 0.068_2 \qquad [6]$$

If we interpret now the experimental data in terms of the isotopic approach of equation [1], we have, instead, a linear dependence:

$$\alpha_T\,(\exp) = 0.071_2\, x_4 + 0.067_6\, x_3 \qquad [7]$$

which also provides a good fit, as shown in fig. 1. Also, the corresponding values of $[\alpha_T(\mathrm{exp})]_{x_4=1}$ and $[\alpha_T(\mathrm{exp})]_{x_3=1}$ are practically the same as those mentioned above, eq. [6].

Therefore, both linear dependences may be accepted and are not in practical contradiction, since the concentration dependence is small.

For comparison of the experiments with theory we use:

a) The general expressions for the thermal diffusion factor, as done by PAUL, HOWARD & WATSON (12):

$$\alpha_T = (6\,C^* - 5)\,.\,\frac{x_1 S_1 - x_2 S_2}{x_1^2 Q_1 + x_2^2 Q_2 + x_1 x_2 Q_{12}}\,.\,(1 + x_{12}) \qquad [8]$$

where the letters have their usual meaning, and x_{12} refers to higher approximations, i.e., $x_{12} = 0$ for first approximations.

b) The expressions for the isotopic approach, i.e., by applying equation [1]. In this equation we use the first and the second approximations to the reduced isotopic thermal diffusion factor, α_0, according to Chapman-Cowling and Kihara-Mason schemes.

The concentration dependence is brought in evidence, in both procedures, by means of the ratio

$$R_{43} = [\alpha_T]_{x_4=1} / [\alpha_T]_{x_3=1} \qquad [9]$$

which for the isotopic approach is simply

$$R_{43} = \frac{1 + \gamma M_{43}}{1 - \gamma M_{43}} \qquad [10]$$

For ^3He — ^4He mixtures, $M_{43} = 1/7$ and the Kihara and Chapman values of γ, given by eq. [2] and [3], are, respectively

$$[\gamma]^K = 0.1054 \quad ; \quad [\gamma]^C = 0.1607$$

The comparison of the theory with experiments is summarized in table I and is illustrated in fig. 1 in terms of the isotopic approach. Theoretical curves have been normalized in the figure to cut the experimental one at $x_4 = 0.50$.

By means of the ratio R_{43}, equations [9] and [10], table I shows that the same kind of approximations to the thermal diffusion factor, either given by the general expression or by the isotopic approach, practically predict the same concentration dependence.

In this aspect, the Chapman-Cowling approximations are in better accordance with experiments.

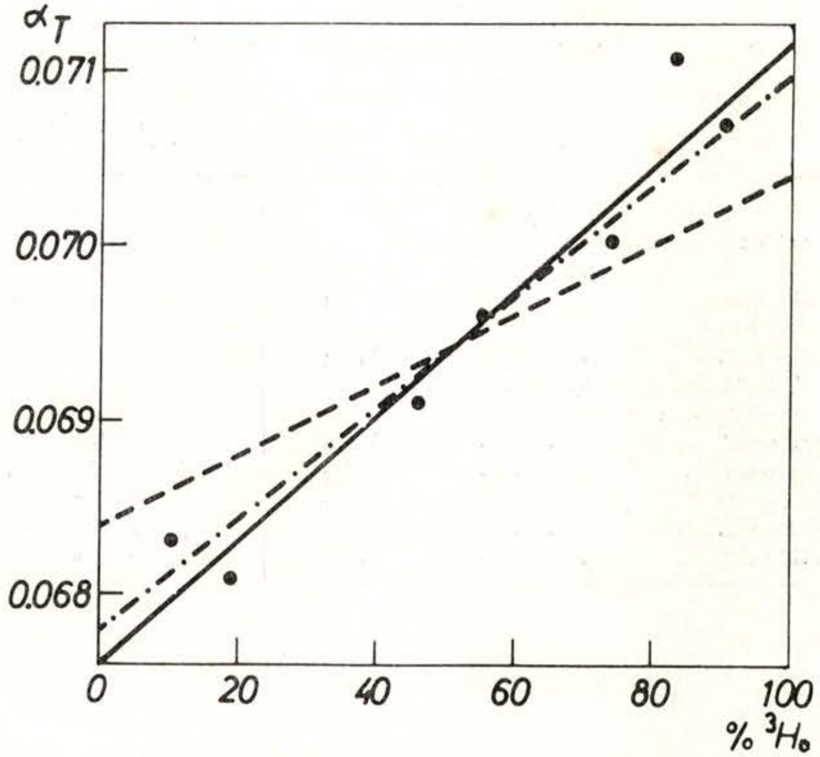

Fig. 1 — Thermal diffusion factor for ^3He — ^4He mixtures.

.	Experimental data, ref. (12).
———	Least square fit for α_T linear with concentration.
—·—	Theoretical curve for Chapman-Cowling scheme.
— —	Theoretical curve for Kihara-Mason scheme.

Theoretical curves correspond to the isotopic approach, eq. [1], have been normalized to cut the experimental one at $x_3 = 50\,\%$.

On the other hand, the values of $[\alpha_T]_{x_4 = 4.5}$ in the table show that the Kihara-Mason scheme of approximation is more convergent, what is the common behaviour predicted by us in ref. (1), at least for higher reduced temperatures. In this case, $T^\star = 17.34$.

As an over all conclusion, we may say that the isotopic approach of equation [1] for the thermal diffusion factor is valid for ^3He — ^4He mixtures, and is as good as the very complicated general expressions of equation [8], regarding the mass influence as well as the concentration dependence.

TABLE I

Comparison of the theory with experiments for $^3He - ^4He$ mixtures

Approximations for α_T	R_{34}	$[\alpha_T]_{x_4} = 0.5$
a) General expressions, $1/\alpha_T$ linear with concentration:		
Experimental	1.05_4	0.069_5
1st Chapman	1.05_1	7 $^0/_0$ lower than exp.
1st Kihara	1.03_1	4.4 $^0/_0$ » » »
2nd Kihara	1.03_4	3.8 $^0/_0$ » » »
b) Isotopic approach, α_T linear with concentration:		
Experimental	1.05_3	0.069_4
1st Chapman	1.04_7	6.2 $^0/_0$ lower than exp.
2nd Chapman	1.04_7	1.3 $^0/_0$ » » »
1st Kihara	1.03_2	3.6 $^0/_0$ » » »
2nd Kihara	1.03_2	2.1 $^0/_0$ » » »

3 — MIXTURE OF $H_2 - D_2$

For this mixture we might expect that the isotopic approach might not be valid. Indeed, the mass coefficient, $M_{12} = 1/3$, is rather large and certainly higher powers of M_{12} would be considered in equation [1].

Also, there is some experimental evidence that the potential parameters for H_2 and D_2 are slightly different.

Nevertheless, the comparison of experimental data with theory is of interest, since it may provide some information about the limits of application of equation [1], regarding the mass influence and the concentration dependence.

We adopted the same procedure of the preceeding paragraph, using the experimental data for $H_2 - D_2$ mixtures recently obtained by PAUL, HOWARD & WATSON (12), over the range from 0.080 to 0.900 in H_2 mole fraction.

The exponential-six model was applied, with $\alpha = 14.0$ and $\varepsilon'_x = 37{,}3^\circ K$, from ref. (13).

Experimental errors of α_T were estimated as about 1 %, and the mean temperature was 160° K, i.e., $T^* = 4.29$.

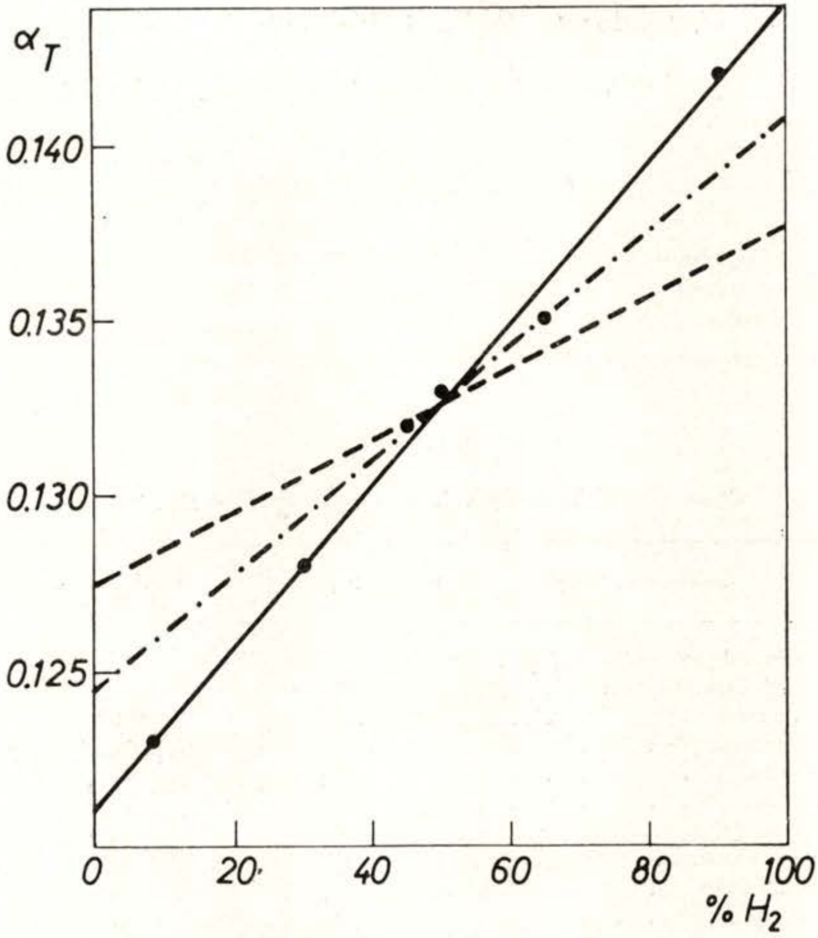

Fig. 2 — Thermal diffusion factor for $H_2 - D_2$ mixtures.

· Experimental data, ref. (12).
——— Least square fit for α_T linear with concentration.
—·— Theoretical curve for Chapman-Cowling scheme.
— — Theoretical curve for Kihara-Mason scheme.

Theoretical curves correspond to the isotopic approach, eq. [1], have been normalized to cut the experimental one at $x_2 = 50$ %.

Assuming that $1/\alpha_T$ (exp) was linear with concentration, our least square fit gave

$$1/\alpha_T\,(\text{exp}) = 6.90_6\, x_2 + 8.20_5\, x_4 \qquad [11]$$

where x_2 and x_4 represent, respectively, the mole fractions of H_2 and D_2. Hence,

$$[\alpha_T\,(\mathrm{exp})]_{x_2=1} = 0.144_8 \quad ; \quad [\alpha_T\,(\mathrm{exp})]_{x_4=1} = 0.121_9$$

On the other hand, assuming α_T linear in accordance with the isotopic approach, we have

$$\alpha_T\,(\mathrm{exp}) = 0.144_0\,x_2 + 0.121_3\,x_3 \qquad [12]$$

This equation fits as well the experimental data within the magnitude of the errors, as shown in fig. 2. In this figure we also present the theoretical curves corresponding to the isotopic approach, which have been normalized to cut the experimental one at $x_2 = 0.5$.

TABLE II

Comparison of the theory with experiments for H_2 — D_2 mixtures

Approximations for α_T	R_{42}	$[\alpha_T]_{x_2=0.5}$
a) General expressions, $1/\alpha_T$ linear with concentration:		
Experimental	1.18_8	0.132_4
1st Chapman	1.15_5	4.8 % higher than exp.
1st Kihara	1.12_4	4.6 % » » »
2nd Kihara	1.12_5	2.2 % » » »
b) Isotopic approach, α_T linear with concentration:		
Experimental	1.18_7	0.132_6
1st Chapman	1.13_0	7.8 % higher than exp.
2nd Chapman	1.13_0	11 % » » »
1st Kihara	1.08_1	11 % » » »
2nd Kihara	1.08_1	10 % » » »

The values of γ for Chapman and Kihara approximations are, respectively,

$$[\gamma]^C = 0.1831 \quad ; \quad [\gamma]^K = 0.1165$$

In table II we summarize the comparison between theory and experiments, following a procedure similar to the preceeding paragraph.

It can be seen that the theoretical isotopic approach of equation [1] to the thermal diffusion factor gives rise to smaller concentration dependence and higher values of α_T than those predicted by the general expression [8], the last ones being as well more in accordance with experiments.

Numerical differences are already significant, therefore we may conclude that a mass coefficient equal to 1/3, as that of $H_2 - D_2$ mixtures, is too large for application of equation [1] to the isotopic thermal diffusion factor.

4 — CONCLUSIONS

The isotopic approach of equation [1] to the thermal diffusion factor represents the first terms of a series development of the general equation [8], when the mass coefficient, M_{12}, is assumed to be small and the potential parameters are equal for both isotopes.

The mixtures $^3He - {}^4He$ and $H_2 - D_2$ provide significant examples for theoretical comparisons in the case of light isotopic mixtures and give practical information about the upper limits of M_{12} which may be accepted experimentally, in order that equation [1] be a valid approach regarding the mass influence and concentration dependence.

Of course, the major advantage of this equation over the general expression [8] is its formal simplicity, which reduces appreciably numerical computations, but it is also remarkable that it splits out in a simple way the major dependences of the thermal diffusion factor with potential models, molecular masses and concentrations of the isotopes, namely through α_0, M_{12} and γ, which therefore may be considered separately.

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