PHYSICAL REVIEW A VOLUME 15, NUMBER 5 MAY 1977

Search for isotope effects in the diffusion of methane in krypton at various densities*

P. Codastefano, M. A. Ricci, and D. Rocca
Istituto di Fisica dell'Università di Roma, Roma, Italy
(Received 4 January 1977)

Experimental measurements of the diffusion coefficient of CH_4 in Kr at $T = 220°K$ in the density range $0 < \rho \leq 2\rho_c$ are reported. The experimental data are compared with self-diffusion for Kr and CH_4 and with the data for diffusion of Kr in CH_4 at about the same reduced temperature. The behavior of the mass effect on the diffusion process is shown clearly for the first time. At $\rho \leq \rho_c$ the deviation from Enskog's predictions is already marked, whereas at $\rho \geq 1.5\rho_c$ the mass effect is of the same kind as for hard spheres.

INTRODUCTION

In the last few years many authors have studied the influence of tracer mass M_T on the diffusion process (isotope effect), both from the theoretical[1,2] and from the experimental standpoint.[3-8]

In the low-density limit ($\rho \ll \rho_c$) the Chapman-Enskog[9] solution of Boltzmann's equation says that in a binary mixture the diffusion coefficient D is inversely proportional to the square root of the reduced mass μ of the two species. Such behavior has been checked experimentally many times.[9]

For increasing density in hard-sphere fluids, the extrapolation of Boltzmann's equation was performed by Enskog[9] with the assumption that the fluid's dynamics follow from uncorrelated binary collisions, so that a behavior of D of the kind $D \propto 1/\sqrt{\mu}$ is deduced. However, Enskog's theory fails already at densities greater than the critical density both insofar as the value of the self-diffusion coefficient is concerned[10] and in the picture of the dependence of D on the mass,[11,12] in the case of binary diffusion.

No complete theory, like Enskog's theory for hard spheres, is available for real fluids. Some attempts with perturbation theories[1,2] show that, at densities around the triple point, D is nearly independent of the tracer mass M_T. Such behavior seems to be confirmed by the existing experimental data both on Lennard-Jones[2] fluids and on a real fluids,[3,6-8] with the exception only of isotopic diffusion in C_6H_6, where it is claimed that $D \propto 1/\sqrt{M_T}$.[5]

At intermediate densities, $\rho_c \leq \rho < \rho_{tr}$, little information is available about the dependence of D on M_T. Indeed, we have no theoretical estimate in this range and, from the experimental standpoint, only one datum is available by molecular dynamics in hard spheres,[11] while in the case of real fluids, we only have some diffusion measurements of Kr in CH_4 (at infinite dilution of Kr).[13] Unfortunately these measurements supply only an indication of the mass effect on the diffusion process since the observed effect nearly falls within the experimental errors, for the considered mixture and density range.

Since the intermediate density range is important in order to study the evolution of many-body effects in the diffusion process, we have studied the behavior of D vs ρ in the diffusion of CH_4 in the mixture CH_4-Kr (CH_4 at tracer concentration) at $T = 220°K$ and in the density range $0 < \rho \leq 2\rho_c$. Since Kr and CH_4 have nearly the same molecular parameters, we expect a comparison between the density evolutions of the self-diffusion coefficients in Kr-Kr and in Kr-CH_4 to exhibit the mass effect only. Moreover, in our measurements the difference between a D dependence on $\sqrt{\mu}$ and a dependence on $\sqrt{M_S}$ is more evident than in Ref. 13.

EXPERIMENTAL RESULTS

Measurements have been performed by means of Anderson and Saddington's[14] capillary method. The experimental setup and the procedure used have been described already in Ref. 15. The only modification of apparatus was the replacement of the Geiger-Muller counter by a scintillation counting system which allows the counting of ^{14}C. The Kr-CH_4 mixture (where CH_4 was at tracer concentration) was prepared with Kr pure to within 0.003%, CH_4 was labeled by ^{14}C.[16] The radius of our capillary was $R = 0.4$ mm and its length was $L = 4.81$ cm.

The error in D mainly follows from errors in the CH_4 concentration measurements. Values of the density have been computed using the PVT data given in Ref. 17.

The experimental data are reported in Table I. In the last column, all the $D\rho$ values have been normalized at $T_0 = 220°K$, using the scale factor $(T_0/T)^{0.9}$ (see Refs. 15 and 18). We plot in Fig. 1 the normalized $D\rho$ values vs ρ. The continuous line is an interpolation curve drawn by hand.

The extrapolation to zero density agrees within the experimental errors with the value of Ref. 13

TABLE I. Experimental results for diffusion of CH_4 in a CH_4-Kr mixture.

T (°K)	P (atm)	ρ (g/cm^3)	Diffusion time t (sec)	D (10^{-3} cm^2/sec)	$D\rho(220/T)^{0.9}$ (10^{-3} g/cm sec)
219.33	18.98	0.099	1800	3.50 ± 0.33	0.35 ± 0.04
219.69	43.59	0.283	1800	1.27 ± 0.06	0.36 ± 0.02
219.47	53.73	0.407	1800	0.97 ± 0.05	0.395 ± 0.025
219.55	59.87	0.52	1800	0.70 ± 0.02	0.365 ± 0.015
219.37	63.69	0.63	1800	0.61 ± 0.02	0.39 ± 0.02
219.36	68.24	0.84	1800	0.51 ± 0.01	0.43 ± 0.02
219.62	70.74	0.94	1800	0.42 ± 0.02	0.39 ± 0.02
219.44	72.16	1.02	1860	0.47 ± 0.01	0.48 ± 0.02
219.80	73.04	1.03	1800	0.47 ± 0.01	0.485 ± 0.015
219.31	73.43	1.08	1800	0.37 ± 0.01	0.400 ± 0.015
219.49	76.74	1.16	1800	0.33 ± 0.01	0.385 ± 0.010
219.74	81.77	1.24	2700	0.30 ± 0.01	0.370 ± 0.015
219.62	97.82	1.40	2700	0.197 ± 0.007	0.28 ± 0.01
219.09	100.03	1.43	2700	0.190 ± 0.007	0.27 ± 0.01
215.05	97.62	1.50	2700	0.18 ± 0.02	0.28 ± 0.03
201.86	96.92	1.71	2700	0.107 ± 0.009	0.20 ± 0.02
180.39	94.75	1.96	3600	0.062 ± 0.003	0.146 ± 0.008
174.66	95.19	2.01	3600	0.056 ± 0.005	0.14 ± 0.01

while it disagrees with the value predicted by Chapman-Enskog theory using, for Kr and CH_4, a Lennard-Jones intermolecular potential with the following parameters[19]:

$$\sigma_{Kr} = 3.68\ \text{Å},\quad \epsilon_{Kr}/K_B = 174.7\ ^\circ\text{K},$$

$$\sigma_{CH_4} = 3.68\ \text{Å},\quad \epsilon_{CH_4}/K_B = 166.8\ ^\circ\text{K},$$

and using the following combination rules for σ_{12} and ϵ_{12}:

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j),\quad \epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}\ .$$

DISCUSSION

Self-diffusion data of Kr at 220 °K,[15,20] of CH_4 at 194.8 °K,[18] and data on the diffusion of Kr in CH_4 at 203 °K[13] are available in the literature. The whole of these data cover about the same reduced density range ($0 \leqslant \rho/\rho_c \leqslant 2$) as ours, and are recorded at about the same reduced temperature.

Our first aim is to compare the behavior of $D\rho$ vs ρ for our data with that obtained in the other three cases. In order to perform such a comparison, we have plotted in Fig. 2 the ratio $D\rho/(D\rho)_{\rho\to 0}$ vs ρ/ρ_c for the four series of measurements. We have used reduced quantities in order to eliminate the trivial differences due to different molecular parameters. It turns out from the analysis of Fig. 2, that in the case of diffusion of impurities, the analytic behavior of $D\rho$ vs ρ depends on the solvent and not on the tracer, as already pointed out in Ref. 13. Moreover, while the data for diffusion in CH_4 can be fitted very well by a second-order polynomial in ρ,[13] the data for diffusion in Kr can only be fitted by a polynomial of much higher order (at least sixth order).

Our second aim is to study the variation of the mass effect with density in the diffusion process. With this aim, we compute as in Ref. 13 the quantity

$$y = \frac{(D\rho_{CH_4\text{-}Kr})/(D\rho_{CH_4\text{-}Kr})_{\rho\to 0}}{(D\rho_{Kr\text{-}Kr})/(D\rho_{Kr\text{-}Kr})_{\rho\to 0}}\ . \tag{1}$$

Since we consider the ratio $D/D_{\rho\to 0}$ both in the case of diffusion of impurities and in the case of self-diffusion, we eliminate in this way the small differences of temperature and of intermolecular parameters between CH_4 and Kr.

Following Enskog's theory, y should be constant and equal to 1 in the entire range of density considered, since for Kr and CH_4 we have $g(\sigma_{12}) \simeq g(\sigma_{11})$ in the entire range of density.

However, if, as pointed out in Refs. 3, 6, and 8, at $\rho \simeq \rho_{tr}$ D is independent of M_T, y must decrease with density, in our case approaching the value 0.57 at $\rho \simeq \rho_{tr}$. Indeed, $y \simeq [2M_T/(M_T + M_S)]^{1/2}$.

In Fig. 3 experimental values of y from our measurements and from Ref. 15, are plotted versus ρ. The shaded region shows the uncertainty in y due to the errors in the diffusion coefficients.

It is evident from Fig. 3 that, even at very low densities, y disagrees with the value it should have following Enskog's theory, which, at densities around ρ_c, falls well outside the experimental error. With increasing density, y decreases rapidly, showing the increasing importance of many-particle correlations.

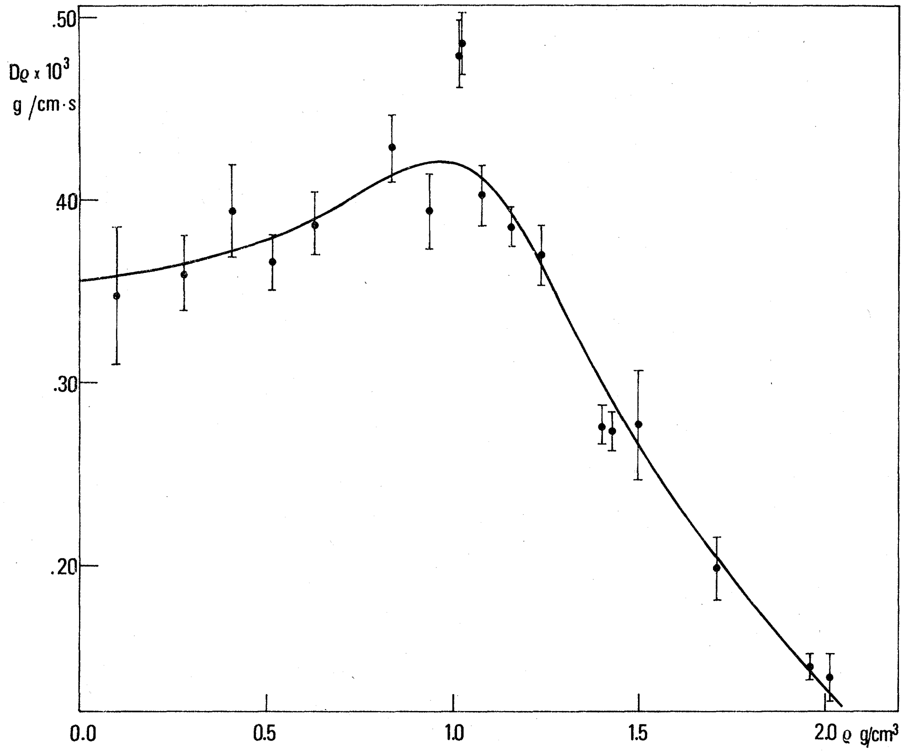

FIG. 1. Experimental data for $D\rho$ vs ρ normalized at $T = 220\,°\mathrm{K}$. The curve has been drawn by hand through the experimental data.

It is interesting now to compare the behavior of y vs ρ for real fluids with the one we have for a system of hard spheres, for which there are computer experiments[11] at two densities only, $V/V_0 = 1.6$ and 3. At both densities the computer-experiment results indicate that

$$y = \left(\frac{2M_S}{M_T + M_S}\right)^{1/2} \left(\frac{M_T}{M_S}\right)^{\alpha},$$

where $\alpha = 0.44$ at $V/V_0 = 1.6$ and $\alpha = 0.36$ at $V/V_0 = 3$ (see Ref. 12).

In order to plot the hard-sphere data of y on Fig. 3, which describes the situation in real fluids, it is necessary to define the value of V_0, i.e., the close packing volume of Kr. We chose $V_0 = N\sigma_{\mathrm{HS}}^3/\sqrt{2}$, consistent with the self-diffusion measurements in Kr at the same temperature. In Ref. 20

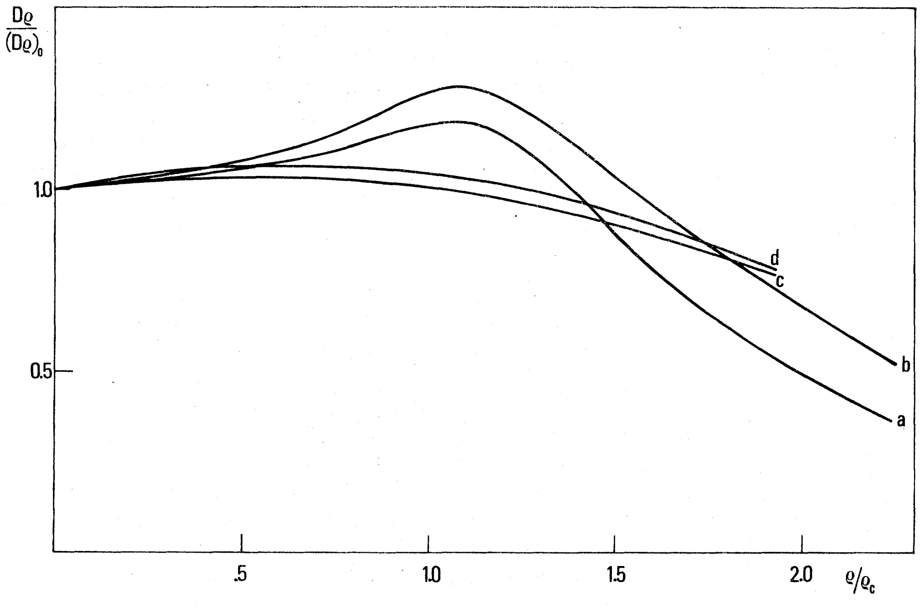

FIG. 2. $(D\rho)/(D\rho)_{\rho\to 0}$ vs ρ/ρ_c for (a) our measurements of the diffusion coefficient of CH_4 in Kr, (b) self-diffusion of Kr (Ref. 15), (c) self-diffusion of CH_4 (Ref. 18), (d) diffusion of Kr in CH_4 (Ref. 13). The curves (a) and (b) have been drawn by hand through the experimental data; the curves (c) and (d) represent the best fit of experimental data (Ref. 13).

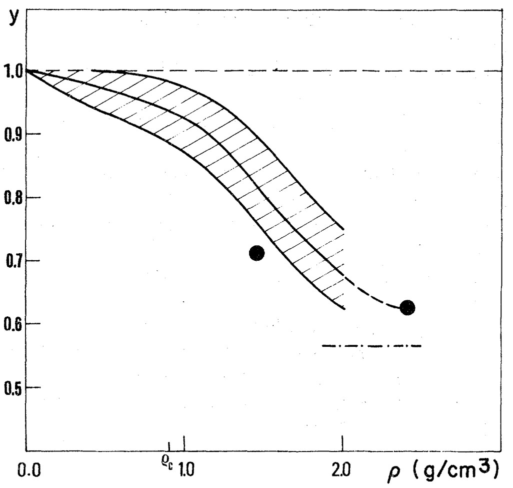

FIG. 3. y vs ρ from Eq. (1) of the text. The level $y=1$ indicates the reduced mass behavior. Dash-dotted line indicate the value $y=0.57$, corresponding to the M_T independence of D. The filled circles are the results of molecular dynamics at $V/V_0=1.6$ and $V/V_0=3$ in a hard-sphere mixture. The solid line represents our experimental data; the shaded region gives a measure of experimental errors.

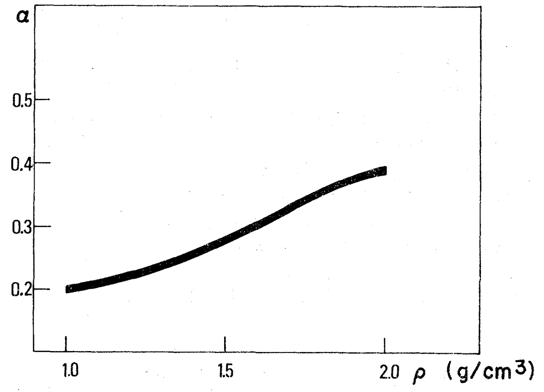

FIG. 4. α vs ρ from our data and Eq. (2) in the text.

the effective hard-sphere diameter, σ_{HS}, is worked out for Kr at 220 °K as a function of density (see Fig. 5 of Ref. 20).

With this choice of V_0, the computer-experiment data at $V/V_0=1.6$ and 3 are plotted in Fig. 3, and correspond to $\rho=2.45$ and 1.45 g/cm^3, respectively.

As we can see from Fig. 3, the behaviors of y vs ρ in a real fluid and in a hard-sphere system are in good qualitative agreement even if, at $\rho=1.45$ g/cm^3, the deviation is at the limit of the experimental error. The same conclusion had already been suggested in Ref. 13, even if, in that case, the situation was rather unclear.

Therefore, if we assume that $y(M_S, M_T, \rho)$ can be written as

$$y=\left(\frac{2M_S}{M_S+M_T}\right)^{1/2}\left(\frac{M_T}{M_S}\right)^{\alpha}, \tag{2}$$

where $\alpha=\alpha(\rho)$ for real fluids too, the present data show that α must have the behavior shown in Fig. 4, where we report the range $1 \leq \rho \leq 2$ g/cm^3 since for $\rho > 1$ g/cm^3 the deviation from Enskog's theory predictions is certainly bigger than the uncertainty due to the experimental errors.

CONCLUSIONS

In the present work we show for the first time in a clear way the behavior of the so-called isotope effect in the diffusion process as a function of density. The isotope effect behavior that we find in the mixture CH_4-Kr is in qualitative agreement with the few results obtained from computer experiments on hard spheres. This shows once more that the general characteristics of a fluid can be described by the behavior of a hard-sphere fluid.

Computer experiments on hard-sphere systems at different densities (for instance $V/V_0=5$ and 2) would be interesting in order to check quantitatively the already discovered good qualitative agreement.

We have also noticed that the general behavior of $D\rho$ vs ρ, along an isotherm, is essentially given by the solvent alone.

It is also interesting to notice that the low-density region, both in our work and in Ref. 13, shows clearly now that, for the CH_4-Kr mixture at $T/T_c \simeq 1.05$, the combination rules for the intermolecular parameter, simply based on the additivity, fail definitely.

ACKNOWLEDGMENTS

We are grateful to Professor F. P. Ricci for useful discussions. Thanks are due also to A. Aloe and A. P. Russo for their technical assistance.

---

*Work supported by Gruppo Nazionale di Struttura della Materia del C.N.R.

[1] H. L. Friedman, *Molecular Motions in Liquids*, edited by J. Lascombe (Reidel, Dordrecht, 1974), p. 87.

[2] I. Ebbsjö, P. Schofield, K. Sköld, and I. Waller, J. Phys. C 7, 3891 (1974).

[3] F. P. Ricci, Phys. Rev. 156, 184 (1967).

[4] M. J. Pikal, J. Phys. Chem. 76, 3038 (1972).

[5] L. Eppstein and J. Albright, J. Phys. Chem. 75, 1315 (1971).
[6] A. W. Castleman, Jr. and J. J. Conti, Phys. Rev. A 2, 1975 (1970).
[7] G. G. Allen and P. J. Dunlop, Phys. Rev. Lett. 30, 316 (1973); I. R. Shankland, P. J. Dunlop, and L. W. Barr, Phys. Rev. B 12, 2249 (1975).
[8] R. Mills, J. Phys. Chem. 79, 8 (1975).
[9] J. O. Hirschfelder, C. R. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
[10] B. J. Alder and T. E. Wainwright, Phys. Rev. A 1, 18 (1970).
[11] P. T. Herman and B. J. Alder, J. Chem. Phys. 56, 987 (1972); B. J. Alder, W. E. Alley, and J. H. Dymond, J. Chem. Phys. 61, 1415 (1974).
[12] F. P. Ricci, M. A. Ricci, and D. Rocca, J. Phys. Chem. 81, 171 (1977).
[13] A. De Santis and F. P. Ricci, Physica (to be published).
[14] J. S. Anderson and K. Saddington, J. Chem. Soc. 5, 381 (1949).
[15] P. Carelli, I. Modena, and F. P. Ricci, Phys. Rev. A 7, 298 (1973).
[16] ^{14}C-labeled methane has been supplied by the Radiochemical Centre of Amersham.
[17] J. Jůza and O. Šifner, Acta Tech. (Prague) 17, 380 (1972).
[18] P. H. Oosting and N. J. Trappeniers, Physica 51, 418 (1971).
[19] T. M. Reed and K. E. Gubbins, *Applied Statistical Mechanics. Thermodynamic and Transport Properties of Fluids* (McGraw-Hill, New York, 1973).
[20] P. Carelli, A. De Santis, I. Modena, and F. P. Ricci, Phys. Rev. A 13, 1131 (1976).