Laboratori Nazionali di Frascati

G. Careri, J. Reuss and J. M. Beenakker: THE DIFFUSION COEFFI-
CIENT IN DILUTE H_2-D_2 AND ^{3}He - ^{4}He LIQUID MIXTURES.

The Diffusion Coefficient
in Dilute H_2-D_2 and ^{3}He-^{4}He Liquid Mixtures.

G. CARERI (*), J. REUSS and J. M. BEENAKKER

Laboratori Nazionali dell'I.N.F.N. - Frascati
Kamerling Onnes Laboratorium - Leiden

Summary. — An apparatus has been built to measure the diffusion coefficient in liquids at very low temperatures. This technique has been applied to the hydrogen-deuterium dilute mixtures, and the results can be expressed by an Arrhenius type equation as function of the absolute temperature $D = 64 \exp [48/T] \cdot 10^{-5}$ cm²/s. The same technique was more difficult to use for the helium isotope mixtures. The results are affected by large errors and roughly $D = (4 \pm 2) \cdot 10^{-5}$ cm²/s in the temperature range above the λ point.

1. – Introduction.

So far, only the viscosity and heat conductivity have been measured at very low temperature, but no direct measurements of the diffusion coefficient have been reported.

For the above reasons an apparatus has been designed, which seems well adapted to this kind of experiments. It is the purpose of this paper to describe the technique and the results obtained for the hydrogen-deuterium mixtures and some attempts concerning the ^{3}He-^{4}He mixtures (**).

(*) Now at the Istituto di Fisica dell'Università di Padova.

(**) This technique has been very briefly outlined by us a few years ago [1], and in the meantime following our procedure, this apparatus has been used at liquid air temperature by other workers [2].

[1] G. CARERI, J. M. BEENAKKER and K. W. TACONIS: *Communication on Congrès de la Physique des Basses Températures* (Paris, 1955), p. 393.

[2] G. CINI-CASTAGNOLI, G. PIZZELLA and F. P. RICCI: *Nuovo Cimento*, **10**, 309 (1958).

2. – Experimental technique.

The method used in these experiments is substantially the « capillary method » already used in high temperature work [3]. In principle, one must allow diffusion to take place between a capillary of length L and an infinite large reservoir. If c_0 is the initial uniform concentration and $\bar{c}$ the average final one in the capillary after a time τ, one has

$$(1) \qquad \frac{\bar{c}}{c_0} = \frac{8}{\pi^2} \sum \left\{ (1/(2\pi+1)^2) \cdot \right.$$
$$\left. \cdot \exp\left[-(2n+1)^2\pi^2 D\tau/4L^2\right] \right\},$$

which gives the diffusion coefficient in terms of known quantities, if the capillary concentrations are measured as it is the case.

With reference to Fig. 1, the above conditions have been fulfilled in practice by a brass capillary of 0.5 mm diameter and 40 mm length, closed at both ends by the valves V_1 and V_2. Opening the V_1 valve, the capillary can be brought in contact with the reservoir below the capillary, and opening the upper valve V_2, the capillary can be filled and evacuated. The reservoir volume is about 10^3 times the capillary volume, and can be filled and evacuated independently. With the exception of the capillary and the reservoir which are made of brass and copper respectively, all other elements are of neusilber.

Fig. 1. – The diffusion apparatus. V_1 and V_2 are stainless steel needle valves.

The apparatus is placed in a cryostat, and the valve system is operated from the outside by means of « O rings » sealing. The capillary is connected to a Toeppler pump to take away the mixture from it after the diffusion took place
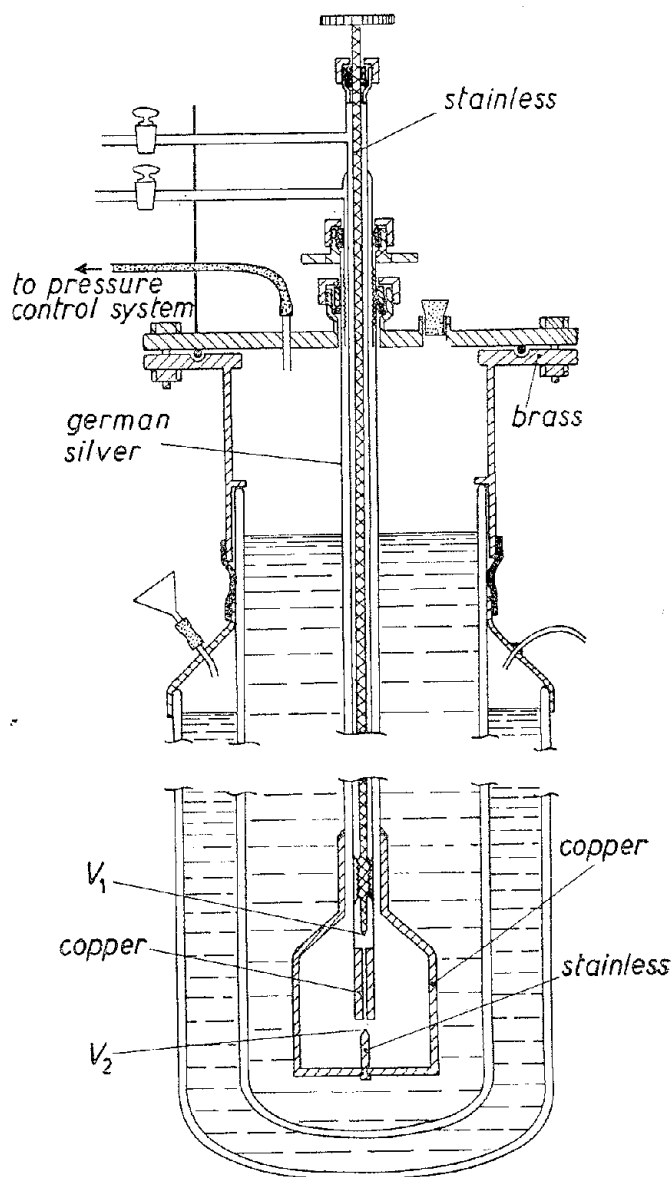
[3] J. S. ANDERSON and K. SADDINGTON: *Journ. Chem. Soc.*, 8, 381 (1949).

for the time τ, and is accomplished by simply closing the valve V_1 and opening V_2 towards the Toeppler bulb. The Toeppler system is also useful to condense the mixture in the capillary at a pressure somewhat larger than the saturation pressure at the corresponding temperature, this overpressure being needed to avoid bubble formation and incomplete filling of the capillary.

The analysis of the isotopic mixtures has been performed by a Nier type mass spectrometer at the University of Rome. No details of this standard technique will be given here.

3. – Results.

3'1. *The hydrogen-deuterium mixtures*. – A first group of runs has been carried out by placing a 2% deuterium mixture in the capillary and pure hydrogen in the reservoir. In this way the amount of deuterium lost in every run was negligible and the analysis, at the mass spectrometer, very easy; but the results were erratic, since the mixture in the capillary was heavier at the top than at the bottom and convection took place in an uncontrolled way.
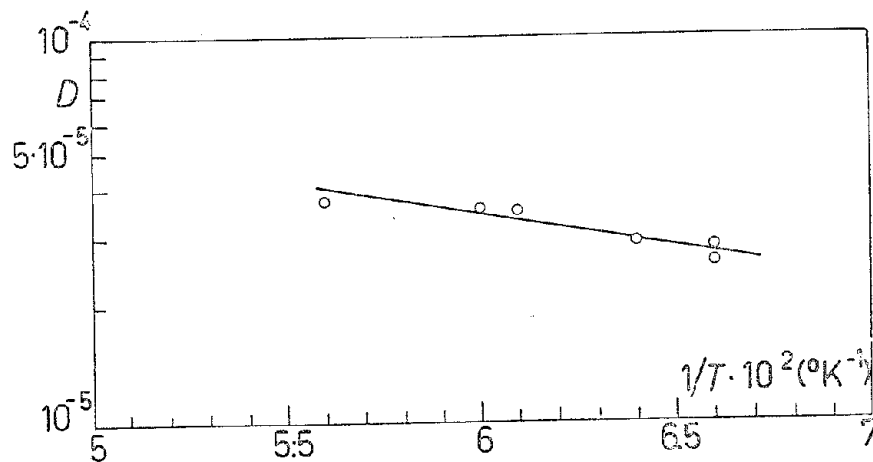

Fig. 2. – The diffusion coefficient of deuterium in liquid hydrogen plotted versus absolute temperature.

In the following runs the heavier mixture was then placed in the reservoir, and pure hydrogen was condensed in the capillary. This being the case, if $c_{H_2}^0$ and $\bar{c}_{H_2}$ are respectively the hydrogen concentration in the reservoir and in the capillary at the end of the run, the deuterium concentration ratio $\bar{c}/c_0$ of eq. (1) will now be given by

$$(\bar{c}_{H_2} - c_{H_2}^2)/(1 - c_{H_2}^0) .$$

The concentration in the reservoir $c_{H_2}^0$ was found to change slightly during the runs, for incomplete mixing in the reservoir and especially for a low rate

distillation above the reservoir which tried to increase the hydrogen content in the capillary. The inaccuracy in $c_{H_2}^0$ is believed to be the major source of error in the experimental results.

Of the many runs which have been carried out, the ones carried out when the bath temperature of the cryostat was not sufficiently steady have not been found reproducible. This is easy to understand, since convection currents may easily take place as an effect of the thermal gradients and a long time is needed to remove these gradients. These runs have been discarded, since they were not reproducible and all gave higher values of D, as an obvious result of the convection currents.

In Table I are given the runs which are considered satisfactory and also plotted in Fig. 1 versus $1/T$. These results can be fitted by an Arrhenius type equation

$$D = 64 \exp[48/T] \cdot 10^{-5} \ \mathrm{cm^2/s} \ .$$

3'2. *The ³He-⁴He mixtures.* – Essentially, the same procedure was adopted for the helium mixtures, but now one had the additional operational difficulty of the light mixture being so precious to need to be completely recovered at the end of every run. For the same reason a very small dead space had to be used above the capillary; this caused a larger flow resistance and a long time was then necessary to evacuate the capillary. To avoid that the large difference

TABLE I. – *Diffusion coefficients in hydrogen-deuterium dilute mixtures.*

Time (h)	T (°K)	$c_{H_2}^0$	$\overline{c}_{H_2}$	$\overline{c}/c_0$	$D \cdot 10^5 \ \mathrm{cm^2/s}$
1,42'	17.91	0.9776 ± 0.0014	0.9976	0.893 ± 0.006	$3.8 \ \pm 0.5$
2	15.8	0.9976 ± 0.0014	0.9977	0.897 ± 0.006	2.97 ± 0.37
1,15'	16.66	0.9976 ± 0.0014	0.9980	0.910 ± 0.006	3.55 ± 0.45
1,30'	16.89	0.9976 ± 0.0014	0.9978	0.901 ± 0.006	3.59 ± 0.48
2	15.2	0.9872 ± 0.0010	0.9987	0.898 ± 0.008	2.88 ± 0.45
2,30'	15.2	0.9872 ± 0.0010	0.9986	0.890 ± 0.009	2.67 ± 0.45

in the vapour pressure of the two isotopes should produce some unwanted fractioning during the condensation, it was found necessary to condense in the capillary the mixtures by a quick turbulent flow, and to use the same level in the Helium dewar, when condensing both the standard and the diffusion sample.

Owing to the difficulties of this conventional method and to the very recent attempts of GARWIN and REICH [4] who detected diffusion in these mixtures

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[4] R. L. GARWIN and H. A. REICH: *Kamerling Onnes Conference on Low Temperature Physics, Physica* (Sept. 1958), p. 133.

by spin-echoes, we give up our search for a better experimental accuracy. Table II gives the experimental data which show D in these mixture to be roughly temperature independent and to be

$$D = (4 \pm 2) \cdot 10^{-5} \text{ cm/s} .$$

Incidentally, we note that this figure agrees with the extrapolated value reported by other authors [5] above the λ temperature.

TABLE II. – *Diffusion coefficients of dilute ^{3}He-^{4}He mixtures.*

Time (h)	T (°K)	c_0 (%)	$\bar{c}$ (%)	$D \cdot 10^5$ cm²/s
2	2.88	1.01	0.83	3.2 ±0.8
2	2.88	0.553	0.46	2.8 ±1.2
2	2.615	0.55	0.457	2.8 ±1.6
2	3.225	0.561	0.428	5.5 ±2.2
2.09	2.674	0.591	0.449	5.1 ±0.6
3	3.225	0.610	0.422	5.9 ±1.4
0.45	3.2	0.750	0.610	4.08±1.0
(1.05)	3.2	0.745	0.610	2.8 ±1.0

4. – Some theoretical remarks.

At present there is not a theory available, which describes irreversible processes in quantum liquids. The work by KIRKWOOD and co-workers has given some justification of the good fit of the Stokes-Einstein equation, but is only limited to classical liquids.

It is perhaps worth noting that the familiar Stokes-Einstein equation

$$D = kT/6\pi\eta r ,$$

r being the radius of the sphere and η the viscosity of the medium, also describes our H_2-D_2 results inside the experimental error, if one uses

$$r = 1.95 \text{ Å} .$$

This figure has to be compared with the radius calculated from the nearest

[5] J. M. BEENAKKER and K. W. TACONIS: *Progress in Low Temperature Physics*, vol. 1 (Amsterdam, 1955), p. 131.

neighbours distance, which is 1.980 and 1.925 Å for f.c.c. and b.c.c. structures, as calculated by familiar expressions from the liquid hydrogen density.

Similar considerations cannot be made for the ^{3}He-^{4}He mixtures due to much larger experimental error. In spite of this large error, this data have proved useful in a comparison ([6]) with the diffusion coefficient of ions in liquid helium, giving evidence of a clustering around the ions which makes them to diffuse more slowly than ^{3}He atoms.

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We are indebted to Prof. K. W. TACONIS of the Leiden University, for many useful technical suggestions in the early stage of this work.

([6]) G. CARERI, J. REUSS, F. SCARAMUZZI and J. O. THOMSON: *Proc. Int. Conference Low Temperature Physics and Chemistry* (Madison, 1957), p. 155.

RIASSUNTO

È stato costruito un apparecchio per misurare il coefficiente di diffusione in liquidi a bassissime temperature. Questa tecnica è stata applicata a miscele diluite idrogeno-deuterio ed i risultati possono essere espressi da una equazione del tipo Arrhenius in funzioni della temperatura $D = 64 \exp [48/T] \cdot 10^{-5}$ cm²/s. Si sono incontrate maggiori difficoltà nell'usare la stessa tecnica con miscele di isotopi d'elio. I risultati sono affetti da grossi errori e approssimativamente $D = (4 \pm 2) \cdot 10^{-5}$ cm²/s per temperature superiori al punto λ.