

## Diffusion of Neon, HT, and Deuterium in Liquid Hydrogen

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Experimental results about diffusion of Ne, HT, and D<sub>2</sub> in liquid H<sub>2</sub> are reported and analyzed with the corresponding states principle. The features of the quantum deviations are indicated.

### INTRODUCTION

TRANSPORT properties for classical liquids (such as argon, krypton, etc.) have recently been the object of a number of investigations and some promising pictures of the phenomena have been derived.<sup>1</sup> However, in the case of quantum liquids (such as neon, hydrogen, etc.) not so much has been done to understand the nature of quantum deviations. For the time being, probably the first thing to do is to develop some kind of semiphenomenological analysis (such as corresponding states theories which are quite general and simple), and it is therefore necessary to have many experimental data. Since very little experimental work has been done<sup>2-4</sup> in the case of the diffusion coefficient, we have investigated the diffusion of various tracers in liquid hydrogen. We report here the results obtained for the diffusion of neon, HT, and deuterium in liquid hydrogen, as a function of temperature between 15° and 20°K at constant pressure.

These substances are of particular interest, as they have nearly the same parameters for the intermolecular potential (for example, the Lennard-Jones 6-12 poten-

tial) and therefore they behave in first approximation as isotopes with very great mass differences. Furthermore, a comparison between the results of HT and D<sub>2</sub> gives information about the effect, on the diffusion process, of the asymmetry in the center-of-mass system of the diffusing molecule.

### EXPERIMENTAL DETAILS AND RESULTS

The experimental technique has been fully described in previous papers.<sup>5-7</sup> Slight modifications have been made, since at these temperatures thermal inputs are more severe. Our apparatus consists essentially of a capillary (0.04-cm diam and various lengths) in contact with an infinite bath. The capillary is filled with pure hydrogen, and the bath with hydrogen mixed with the substance which has to diffuse. The diffusion of the tracer into the capillary is allowed to proceed for a certain time.

It is possible to calculate the diffusion coefficient from the well-known equation<sup>6</sup> using the tracer concentration of the mixture in the bath, the average tracer concentration in the capillary after diffusion, and the time of diffusion.

The tracer concentration in the bath has been kept very low in all runs, so we are in the case in which it seems that no effect of the concentration upon diffusion

TABLE I. Experimental results for Ne-H<sub>2</sub> diffusion.

Run No.	Length <i>L</i> (cm)	Time <i>t</i> (sec)	Temperature (°K)	<i>D</i> (10 <sup>-5</sup> cm <sup>2</sup> /sec)
1	2.23±0.03	3.600	20.25±0.05	5.85±0.60
2	2.23±0.05	7.200	20.25±0.05	6.34±0.40
3	2.23±0.05	11.340	20.25±0.05	5.91±0.3
4	2.23±0.05	7.200	18.52±0.03	4.82±0.35
5	2.23±0.05	9.000	18.52±0.03	5.20±0.30
6	2.45±0.05	10.800	16.70±0.03	4.45±0.10
7	2.60±0.05	7.380	16.55±0.03	4.40±0.40
8	2.60±0.05	9.120	15.54±0.03	3.42±0.40
9	2.60±0.05	7.200	15.46±0.03	3.43±0.40

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<sup>1</sup> See, for review: F. C. Collins and H. Raffael, *Advances Chem. Phys.* **1**, 135, (1958); S. A. Rice and H. L. Frisch, *Ann. Rev. Phys. Chem.* **11**, 187 (1960).

<sup>2</sup> G. Careri, J. Reuss, and J. M. Beenakker, *Nuovo cimento* **13**, 148 (1959).

<sup>3</sup> R. L. Garwin and H. A. Reich, *Phys. Rev.* **115**, 1478 (1959).

<sup>4</sup> W. P. A. Hass, G. Seidel, and N. J. Poullis, *Physica* **26**, 834 (1960).

TABLE II. Experimental results for HT-H<sub>2</sub> diffusion.

Run No.	Length <i>L</i> (cm)	Time <i>t</i> (sec)	Temperature (°K)	<i>D</i> (10 <sup>-5</sup> cm <sup>2</sup> /sec)
1	2.23±0.05	5.400	20.25±0.05	5.00±0.10
2	2.20±0.05	14.820	20.25±0.05	5.58±0.20
3	2.45±0.05	8.100	18.50±0.03	4.17±0.20
4	2.45±0.05	9.000	15.04±0.03	2.67±0.10
5	2.45±0.05	9.000	16.55±0.03	3.50±0.05

<sup>5</sup> G. Cini-Castagnoli, G. Pizzella, and F. P. Ricci, *Nuovo cimento* **10**, 300 (1958).

<sup>6</sup> G. Cini-Castagnoli and F. P. Ricci, *J. Chem. Phys.* **32**, 19 (1960).

<sup>7</sup> G. Cini-Castagnoli and F. P. Ricci, *Nuovo cimento* **15**, 795 (1960).

is present.<sup>8</sup> (We have 1% for deuterium and neon, and 10<sup>-7</sup>% for HT.)

In each run the diffusion took place under constant pressure of 1.5 atm. The low temperature of the experiment was provided by putting the diffusion chamber in a liquid hydrogen bath boiling under constant pressure.

The concentration analyses of neon or deuterium in hydrogen were performed with an Italelectronica SP21Fπ/3 sector analyzer mass spectrometer,<sup>9</sup> and those of HT in hydrogen with a system of internal gas Geiger-Müller counters.<sup>10</sup> Each analysis was repeated at least three times.

The experimental results are listed in Tables I-III. The errors in the temperatures are given by the fluctuations of the controlled pressure of the hydrogen bath. The errors in  $D$  are determined, taking into account the errors due to the concentration measurements and to the length of the capillary.<sup>6</sup>

The reproducibility of experimental data is within experimental error, except for one point of HT at the highest temperature. We believe that this could be due to turbulence occurring for a short period of time during run No. 2.

Turbulence might very well happen at 20.25°K, because the bath is freely boiling at atmospheric pressure and so the temperature is not under differential oil manometer control. But for completeness in Tables I, II, and III, we report all the experimental runs performed, including the somewhat suspect point discussed above. Incidentally we want to stress that we have searched many times<sup>5-7</sup> for systematic errors in our technique by changing the various experimental features such as the capillary length or the time of diffusion. We have never found any systematic dependence on these variables.

In Fig. 1 the experimental data of the present investigation are shown together with those previously obtained by Careri *et al.*,<sup>2</sup> for diffusion of deuterium in liquid hydrogen, which agree satisfactorily with our point at a higher temperature.

The experimental results can be represented by the

TABLE III. Experimental results for D<sub>2</sub>-H<sub>2</sub> diffusion.

Run No.	Length $L$ (cm)	Time $t$ (sec)	Temperature (°K)	$D$ (10 <sup>-5</sup> cm <sup>2</sup> /sec)
1	2.23±0.05	10.980	20.25±0.05	4.95±0.10
2	2.23±0.05	5.280	20.25±0.05	4.60±0.20

<sup>8</sup> G. Cini-Castagnoli, F. Duprè, and F. P. Ricci, *Nuovo cimento* **13**, 464 (1959).

<sup>9</sup> A. Giardini-Guidoni and G. G. Volpi, *Nuovo cimento* **17**, 919 (1960).

<sup>10</sup> G. Cini-Castagnoli, A. Giardini, and F. P. Ricci, *Nuovo cimento* **13**, 916 (1959).

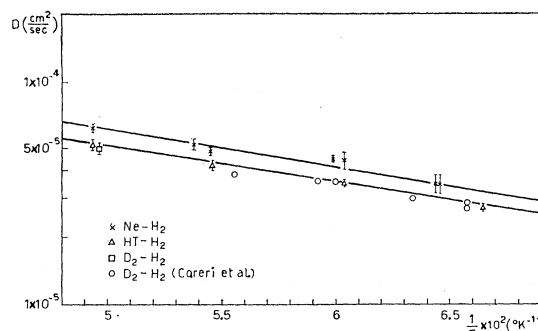


FIG. 1. Diffusion coefficient as a function of temperature.

following equations:

$$D(\text{Ne}-\text{H}_2) = 36e^{-36/T} \times 10^{-5} \text{ cm}^2/\text{sec}, \quad (1)$$

$$\begin{aligned} D(\text{HT}-\text{H}_2) &= D(\text{D}_2-\text{H}_2) \\ &= 30.5e^{-36/T} \times 10^{-5} \text{ cm}^2/\text{sec}. \end{aligned} \quad (2)$$

#### DISCUSSION

As pointed out previously, a very powerful method to investigate the aspects of the quantum deviations in the liquid state is that of the corresponding state principle, as already shown in the case of equilibrium properties.<sup>11</sup> Strictly speaking it is correct to apply the corresponding state principle only to the rare gases, but it is possible to verify that it holds with quite good approximation ( $\sim 10\%$ ) also for some simple diatomic molecules.<sup>11,12</sup>

So we think it useful to treat our experimental data according to this scheme. In this case, the experimental relationship  $D=D(T)$  must be transformed into  $D^*=D^*(T^*)$ , where  $D^*$  and  $T^*$  are dimensionless quantities and therefore independent of the substance with which we are dealing.

In the case of self-diffusion, just by means of dimensional analysis one derives<sup>11</sup>

$$D^* = D(1/\sigma)(m/\epsilon)^{\frac{1}{2}}, \quad (3)$$

and

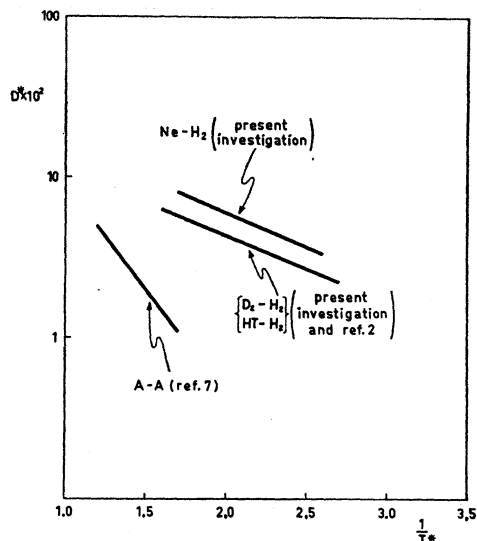
$$T^* = kT/\epsilon. \quad (4)$$

In the case of isotopic diffusion (i.e., when the substances involved have the same intermolecular force parameters), using the previous reduced expressions, the only ambiguity could arise in Eq. (3) from the difference between the masses of the tracers and the atoms of the solvent liquid.

However, from the analysis of diffusion in classical liquids one clearly derives that the mass appearing in Eq. (3) (in the case of binary diffusion) is the reduced mass  $m_{ij} = 2m_i m_j / (m_i + m_j)$ . Therefore in our cases Eq.

<sup>11</sup> J. de Boer, *Physica* **14**, 139 (1948).

<sup>12</sup> G. Cini-Castagnoli, G. Pizzella, and F. P. Ricci, *Nuovo cimento* **11**, 466 (1959).

FIG. 2.  $D^*$  versus  $1/T^*$ .

(3) can be written as

$$D^* = D(1/\sigma)(m_{ij}/\epsilon)^{1/2}. \quad (5)$$

In Fig. 2,  $D^*$  vs  $1/T^*$  is shown for our data (Ne-H<sub>2</sub>, D<sub>2</sub>-H<sub>2</sub>, HT-H<sub>2</sub>) and for a perfect classical liquid (i.e., argon).<sup>13</sup>

If quantum effects were not present, all the systems would behave in the same way as the perfect classical liquid.

The essential features of the quantum effects in the diffusion process can be summarized as follows (see Fig. 2):

(a) The diffusivity increases strongly going from diffusions in liquid argon to those in liquid hydrogen, and at the same time the temperature dependence decreases.

(b) Considering the diffusion of various tracers in liquid hydrogen, one notices that the diffusivity of neon is higher than that of deuterium. The temperature dependence seems to be the same for both the tracers.

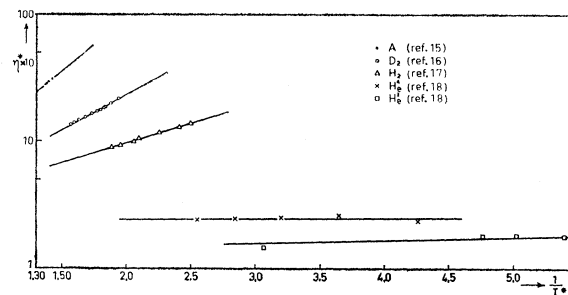
(c) HT and D<sub>2</sub> behave in the same way, within the experimental errors. It seems, therefore, that the diffusion process is not appreciably affected by the internal configuration of the molecules. [In vapor pressure measurements<sup>14</sup> a small effect (8%) was detected and ascribed to the different mass configuration.]

With respect to point (a) one could say that both the effects are due to the more relaxed structure of the quantum liquids.

It is interesting to see that the viscosity shows this

<sup>13</sup> The experimental values of  $D$  refer to diffusion under constant pressure. The value of the reduced pressure  $p^* = p(\sigma^3/\epsilon)$  is almost the same; moreover, the value of  $(\partial D/\partial p)_{T=\text{const}}$  seems to be small [See H. Watts, B. J. Alder, and J. H. Hildebrand, *J. Chem. Phys.* **23**, 659 (1955)], and anyway this effect would tend to increase the absolute value of the deviations. For the values of  $\epsilon$  and  $\sigma$  see reference 11.

<sup>14</sup> A. Bellemans, *Suppl. Nuovo cimento* **9**, 181 (1958).

FIG. 3.  $\eta^*$  versus  $1/T^*$ .

same behavior of the diffusion coefficient. This is illustrated in Fig. 3 where  $\eta^* = \eta[\sigma^2/(m\epsilon)^{1/2}]$  is reported as a function of  $1/T^*$  for argon, deuterium, hydrogen, and helium.<sup>15-18</sup>

Point (b) has no simple explanation. The effect, however, is clearly outside the experimental error. One could object that this is not a quantum effect but that it is due to the biatomicity of deuterium compared with the monatomicity of neon. We do not believe that this fact could account for this discrepancy as large as 30%. In fact, with regard to equilibrium properties,<sup>11</sup> we can see that in the liquid state the hydrogen isotopes fit well on the curve drawn for the monatomic substances, and furthermore the same thing happens if we consider the reduced viscosity at the same reduced temperature as a function of the quantum parameter.

We would like to mention one more thing: As pointed out, for each tracer it is possible to fit the experimental data with an Arrhenius law in which the activation energy of the diffusion process seems to be independent of the tracer. This is quite similar to what is found in the case of classical liquids.<sup>7</sup> (See work cited in reference 13.)

So it seems that the basic mechanism of the diffusion process in quantum liquids (at least up to hydrogen) could remain the same as in classical liquids.<sup>7</sup> This is in agreement with two considerations based on the viscosity results: first, London's suggestion<sup>19</sup> that the classical liquid-like behavior is only a matter of density; and second, considering the results on the viscosity of argon and nitrogen<sup>20</sup> at various densities, one finds that in the transport processes the liquid-like behavior is retained until  $\rho \geq 2\rho_c$ , where  $\rho_c$  is the critical density (in our case  $\rho = 2.3\rho_c$ ).

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<sup>15</sup> N. S. Rudenko and L. W. Schubnikow, *Physik. Z. Sowjetunion* **6**, 470 (1934); **7**, 179 (1935).

<sup>16</sup> W. H. Keesom, *Physica* **5**, 745 (1938).

<sup>17</sup> A. Van Itterbeek, *Physica* **7**, 208 (1940).

<sup>18</sup> R. D. Taylor and J. G. Dash, *Phys. Rev.* **106**, 398 (1957).

<sup>19</sup> F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1954), Vol. II.

<sup>20</sup> N. F. Zhdanova, *Soviet Phys.—JETP* **4**, 19 (1957); **4**, 749 (1957).