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Spin-Diffusion Measurements in Hydrogen between 20 and 55°K*

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The spin-diffusion coefficient D of hydrogen has been measured as a function of the density ρ up to a maximum density of 850 amagats for various ortho-para hydrogen concentrations in the range 20–75% of orthohydrogen between 20 and 55°K by the spin echo technique. Within the experimental error of ±10%, the absolute value of D for the dilute gas is in agreement with the calculations of Buckingham *et al.* over this entire temperature range. Within this accuracy, no dependence on orthohydrogen concentration (at constant total density) is observed. The experimental results tend to confirm the conclusion of Emery, deduced from a detailed analysis of the Boltzmann diffusion equation, that symmetry effects cannot be observed in the diffusion process.

INTRODUCTION

THE self-diffusion coefficient D_0 for hydrogen at low density may be calculated from the Chapman-Enskog theory, using a well-known relation that we write in the following form[1]:

$$D_0 = 3kT/8\rho m\Omega^{(1,1)}, \tag{1}$$

where ρm is the mass density, k is Boltzmann's constant, T is the absolute temperature, and $\Omega^{(1,1)}$ is a temperature-dependent average cross section for the collision of two hydrogen molecules, and is a weighted average over all values of the energy of relative motion. Cohen *et al.*[1] and Buckingham *et al.*[2] have assumed a spherically symmetric intermolecular potential, that inhibits transitions between the rotational levels of ortho and parahydrogen in order to calculate values of $\Omega^{(1,1)}$. We shall assume this approach to be valid, since the degree of thermal excitation of the $J=2$ level at 60°K is only 2.6×10^{-2}. Hydrogen gas may then be considered a quantum-mechanical system with nine substates for orthohydrogen molecules ($I=1$ $J=1$) and one substate for parahydrogen molecules ($I=0$ $J=0$).

The process of diffusion implies that one molecule is distinguishable relative to another. In our experiments the molecules are labeled by their spin states ("spin diffusion") and, as has been shown by Emery,[3] orthomolecules in different quantum substates are to be treated as *distinguishable* particles, while collisions of orthomolecules in the same substate do not contribute at all to the diffusion cross section. Cohen *et al.*,[1] however, treat all orthomolecules as indistinguishable particles and define partial cross sections $\Omega_s^{(1,1)}$, $\Omega_a^{(1,1)}$ and $\Omega_{ns}^{(1,1)}$, as follows: $\Omega_s^{(1,1)}$ is the "symmetrized" cross section, calculated using only spatial wave functions which are symmetric in the internal coordinates of the two molecules. $\Omega_a^{(1,1)}$ is the "antisymmetrized" cross section, calculated using antisymmetric wave functions. $\Omega_{ns}^{(1,1)}$ is the "nonsymmetrized" cross section applicable for a system of distinguishable particles.

In our measurements, we only "observe" the orthohydrogen molecules and measure their diffusion relative to both orthohydrogen and parahydrogen molecules. It follows from Emery's paper,[3] that $\Omega_s^{(1,1)}$ and $\Omega_a^{(1,1)}$ have no physical reality and that symmetry effects are not observed in the diffusion process. Since only the nonsymmetrized cross section $\Omega_{ns}^{(1,1)}$ is relevant and since the *total* mass density appears in Eq. (1), the coefficient of diffusion should be independent of the ortho-para concentration of the gas. Thus, the value of D measured in our experiments should equal the mutual diffusion coefficient D_{op} of orthohydrogen in parahydrogen.

In this paper we present absolute values for $D\rho$ as a function of ρ, of T, and of the orthohydrogen concentration.

EXPERIMENTAL

We have used the well-known nuclear magnetic resonance (NMR) pulse technique[4,5] to measure D. Hydrogen gas (or liquid) samples prepared from a Matheson ultrahigh purity hydrogen gas cylinder, at all temperatures other than the boiling point (20.35°K) were contained in a beryllium-copper high-pressure bomb placed inside a metal cryostat. Temperatures were measured with a platinum resistance thermometer. The cryostat, high pressure, and electronic arrangements have been previously described.[5,6] The only addition to the outside of the cryostat for this work was a pair of coils coaxial with the static magnetic field and supplying a linear field gradient G (of up to a maximum value of 20G/cm) to the region of the sample. D was then deduced from the expression

$$A(2\tau) \propto \exp[(-2\tau/T_2) - \tfrac{2}{3}\gamma^2 G^2 D\tau^3], \tag{2}$$

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where $A(2\tau)$ is the amplitude of the spin echo formed at time 2τ, and τ is the time spacing between the $\pi/2$ and π rf pulses applied to the coil surrounding the sample. T_2 is the spin-spin relaxation time, which in our case is equal to T_1, the spin-lattice relaxation time, and γ is the gyromagnetic ratio for the proton. The plot of $\ln A(2\tau)\exp(2\tau/T_1)$ versus τ^3 gives a straight line of slope $k(=\frac{2}{3}\gamma^2G^2D)$, from which D can be calculated if G is known. The value of G, which was made as large as practicable so that the second term in the exponential of Eq. (2) dominated over the relaxation term, was found by measuring k at 55°K where the value of D has been measured.[5] At 20.35°K an absolute determination of G was possible, since at this temperature the sample was enclosed in a cylindrical glass tube whose diameter was accurately measured and G could then be calculated from the properties of the "wiggles" which characterize the shape of the echo.[5]

At 20.35°K, in an attempt to reduce convection effects to a minimum, we surrounded the glass sample holder with a tube containing helium gas at one atmosphere pressure, the whole assembly being placed in a single Dewar containing the coolant, liquid hydrogen.

To obtain various concentrations of orthohydrogen, we mixed normal hydrogen with hydrogen containing approximately 5% of orthohydrogen. This had been prepared by converting normal hydrogen at 20°K in a stainless steel high-pressure bomb containing a catalyst (anhydrous iron oxide) and surrounded by liquid hydrogen. The amplitude of the NMR signal (corrected for detector nonlinearity) following a single $\pi/2$ pulse was used to measure the orthohydrogen concentration of our samples, calibration being provided by a similar measurement on a sample of normal hydrogen.

We estimate our accuracy in the product $D\rho$ at all temperatures to be ±10% or slightly better. The determination of the percentage of orthohydrogen was ±3%. The density was determined to ±2%, and the maximum error in our absolute temperature measurements was of the order 0.5°K below 35°K and of order 0.7% at all other temperatures. The temperature stability during a measurement was of the order of 0.1°K.

RESULTS AND DISCUSSION

Figure 1 shows $D\rho$ plotted as a function of ρ in normal hydrogen gas at 36.2°K up to a maximum density of 840 amagats. It is observed that $D\rho$ remains constant up to about 550 amagats and decreases rapidly thereafter. This effect has been previously observed[5,7] and is typical of all our results at all temperatures where measurements over the complete range of densities (i.e., up to 850 amagats) are feasible. Figure 1 also shows some measurements taken at 25.6°K in the normal liquid under pressure, and in a sample of liquid containing 22.2% of orthohydrogen. We find in all cases, within the experimental error of 10%, D is independent of the concentration of orthohydrogen at constant temperature and density. This confirms Emery's conclusion[3] that symmetry effects are not observed in the diffusion process. Furthermore, the fact that D is independent of orthohydrogen concentration even at high density would indicate that second-order terms neglected in Emery's paper are indeed quite small. It is also observed that the rate of change of $D\rho$ with ρ in the high-density region is roughly the same at 36.2 and 25.6°K as, indeed, it is at all temperatures where we have made measurements.

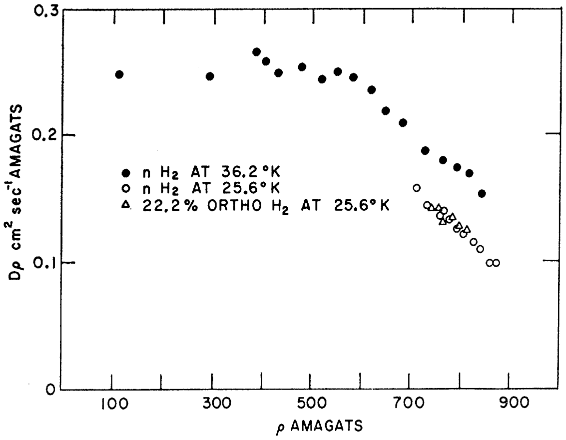

FIG. 1. Density dependence of $D\rho$.

In Fig. 2. we plot values of $D\rho$ for the density region $\rho<450$ amagats, as a function of the temperature.

The uppermost curve of Fig. 2 is a plot of Eq. (1). The values of Ω have been taken from the calculations of Buckingham *et al.*[2] which are limited to the nonsymmetrized cross section $\Omega_{ns}^{(1,1)}$ and this curve is, therefore, appropriate to the mutual diffusion of orthohydrogen in parahydrogen. The absolute values of $D\rho$ deduced from our measurements are seen to be in quite good agreement with these calculations.

Cohen *et al.*[1] have assumed that orthomolecules are indistinguishable particles and they write the cross section for ortho-ortho collisions:

$$\Omega_{oo}=5/9\Omega_s^{(1,1)}+4/9\Omega_a^{(1,1)}. \tag{3}$$

Equation (1) would then read:

$$D\rho=(3kT/8m)[1/n_o\Omega_{oo}+1/n_p\Omega_{ns}^{(1,1)}], \tag{4}$$

where n_o and n_p are the respective fractions of orthohydrogen and parahydrogen molecules ($n_o+n_p=1$). Unfortunately, $\Omega_s^{(1,1)}$ and $\Omega_a^{(1,1)}$ have not been calculated above 22°K. However, comparison of the data given in Refs. 1 and 2 suggests that it is safe to assume that $\Omega_s^{(1,1)}/\Omega_{ns}^{(1,1)}=\Omega_a^{(1,1)}/\Omega_{ns}^{(1,1)}=3.3$, to within an accuracy of 10% over the temperature range 20–55°K. Equation (4) for normal hydrogen ($n_o=0.75$) is plotted as the lowermost curve in Fig. 2. This curve is clearly

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[7] M. Lipsicas and M. Bloom, Can. J. Phys, **39**, 881 (1961).

in complete disagreement with our experimental results and, moreover, Eq. (4) would predict a relatively strong dependence on orthohydrogen concentration, which has not been observed.

In a recent letter[8] published prior to the work of Emery,[3] we suggested that the cross section for ortho-ortho collisions (allowing for the fact that one-ninth of the orthomolecules are in identical spin states) be written:

$$\Omega_{oo}=(1/9)\Omega_s^{(1,1)}+(8/9)\Omega_{ns}^{(1,1)}. \qquad (5)$$

Assuming, again, $\Omega_s^{(1,1)}/\Omega_{ns}^{(1,1)}=3.3$, this leads to a diffusion coefficient (for normal hydrogen) given by

$$D\rho=(3kT/8m)(5/6\Omega_{ns}^{(1,1)}). \qquad (6)$$

Equation (6) is plotted in Fig. 2 and our experimental points are seen to be bounded by this curve and the curve for ρD_{op}. The experimental accuracy, of approximately ±10%, is, unfortunately, not good enough to distinguish between Eqs. (1) and (6).

CONCLUSIONS

The experimental data lie close to the curve for ρD_{op}, i.e., to the curve obtained on the assumption that in the diffusion process only collisions of distinguishable particles are considered. The absence of any significant dependence of D on the relative concentration of orthohydrogen (at constant total density) further substantiates Emery's conclusion, that symmetry effects cannot be observed in diffusion. Furthermore, the high-density results indicate that the second-order corrections to Emery's analysis are quite small.

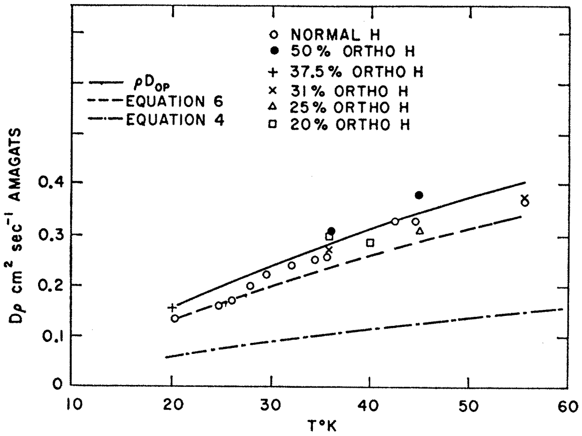

Fig. 2. Temperature dependence of $D\rho$ for $\rho<450$ amagats.

It has previously[5] been observed that the experimental results at high densities are in conflict with the Enskog dense gas theory, and we do not attempt to make further comparison here between theory and experiment. When computer calculations are complete, it should be possible to correlate the diffusion values in the high-density region with the spin-lattice relaxation time in a manner suggested elsewhere.[6]

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