Diffusion and ortho-para conversion in solid hydrogen

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The ortho-para conversion in solid hydrogen is investigated at 12, 4.2, and 1.57 K in long-term experiments up to 1200 h. The results are discussed in the light of the influence of molecular diffusion on the conversion rate. At 4.2 and 1.57 K, the conversion rate shows that the diffusion coefficient is $D \approx 10^{-20}$ cm^2 sec^{-1}. This value is much larger than those predicted from an extrapolation of experimental results at higher temperatures and from recent theoretical predictions. At 1.57 K, an increase of the conversion rate with decreasing o-H$_2$ concentration is observed. Calculations show this increase is due to clustering of o-H$_2$ molecules caused by electric quadrupole-quadrupole interactions between them. The estimated diffusion rate is consistent with that found previously from the rate of clustering.

Soon after the discovery of the two hydrogen modifications, the ortho-para (o-p) conversion in the liquid state as well as in the solid state was investigated. The reaction was found to be autocatalytic and thus of second order[1,2]:

$$\frac{dX}{dt} = -KX^2 ,$$

where X is the o-H$_2$ concentration, and K is the rate constant.

In liquid hydrogen the conversion reaction always follows this equation. In solid hydrogen, however, it was observed at temperatures between 11 and 14 K that with decreasing o-H$_2$ concentration the conversion rate decreased more than predicted by Eq. (1). This deviation was explained by a change in the distribution of the o-H$_2$ molecules, that is, an increase in the number of isolated o-H$_2$ molecules, whereas K was assumed to remain constant.[3]

Essential for the autocatalytic reaction is the mean number of nearest o-H$_2$ neighbors M surrounding each o-H$_2$ molecule. That means the rate of conversion dX/dt is proportional to MX.

Normally, the equilibrium distribution of o-H$_2$ molecules is a binomial distribution. So the number of o-H$_2$ molecules with n neighbors is given by $W_n = X^n (1 - X)^{12-n} \binom{12}{n}$. The mean number of o-H$_2$ molecules surrounding each o-H$_2$ molecule is then given by

$$M_0 = \sum_{n=0}^{12} n W_n = 12X . \qquad (2)$$

For the normal equilibrium distribution, Eq. (1) can thus be written

$$\frac{dX}{dt} = -K \frac{M_0}{12} X . \qquad (3)$$

For other distributions, that is, $M \neq M_0$, different values of K result from Eq. (1).

The o-p conversion causes a deviation from the equilibrium distribution which at sufficiently high temperatures is balanced by the diffusion of o-H$_2$ molecules. If at lower temperatures the rate of diffusion becomes small compared to the rate of conversion, however, the deviation from the equilibrium distribution will increase with decrease of the o-H$_2$ concentration.

Accordingly the observed deviations mentioned above were used to calculate the upper limiting value of the diffusion coefficient, which was found to be $D = 3 \times 10^{-22}$ cm^2 sec^{-1} at 12 K.[4] Later NMR measurements between 9 and 14 K yielded a value of $D = 10^{-10}$ cm^2 sec^{-1} at 12 K,[5,6] which means that no deviation from Eq. (1) should occur at this temperature. An extrapolation of D to lower temperatures shows, however, that a deviation should be expected at temperatures below 4.5 K (curve 1 in Fig. 1). Calculations of D considering tunneling mechanisms lead to yet higher values of D (curve 2 in Fig. 1),[7] and accordingly deviations from the equilibrium distribution should occur only below 3 K.

Besides being influenced by the o-H$_2$ diffusion, the equilibrium distribution can be altered by the electric quadrupole-quadrupole (EQQ) interaction between o-H$_2$ molecules. With decreasing temperature this interaction leads to the formation of "clusters" of o-H$_2$ molecules. That means the equilibrium distribution changes as a function of the temperature, and the mean number of o-H$_2$ molecules surrounding each o-H$_2$ molecule exceeds M_0.[8]

In view of these differing results and theoretical predictions, new long-term measurements of the o-p conversion in solid hydrogen seemed to be of interest. Temperatures above 4.2 K were obtained with a continuous flow cryostat, whereas at lower temperatures a bath cryostat with an automatic refilling device was used.[9,10] The o-H$_2$ concentra-
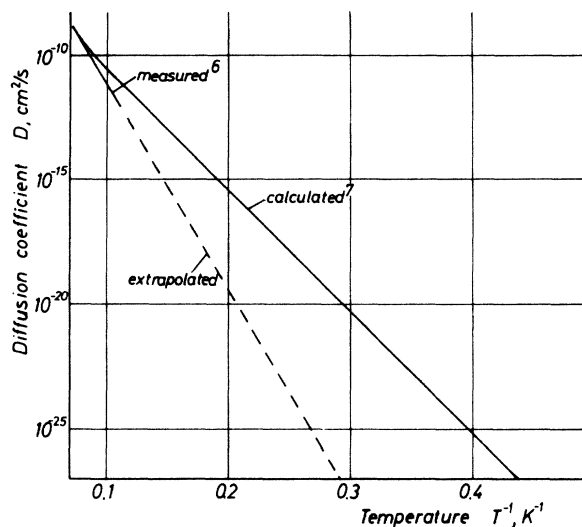
FIG. 1. Diffusion coefficient of solid hydrogen as a function of temperature according to the literature (Refs. 6 and 7).

tion was measured by NMR, which allows continuous measurements without influencing the sample. A commercial NMR system for magnetic field measurements with a high-frequency coil of four windings and a magnetic field sweep of 50 Hz was used. The measurements were performed at a frequency of about 29 MHz. It was found to be necessary to calibrate the analyzing system with samples of known o-H_2 concentration.[11] For the samples (about 1 cm^3), pure n-H_2 gas (75% o-H_2) was condensed, which took about 1 min.

The integration of Eq. (1) leads to the expression

$$\frac{1}{X} - \frac{1}{X_0} = Kt, \tag{4}$$

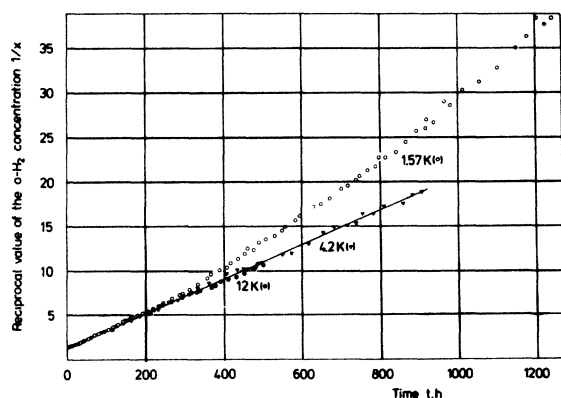which can be used for plotting the experimental results. As Fig. 2 shows, the values measured at 12

and 4.2 K can be represented by the same straight line. At 1.57 K, however, only the values obtained during the first 200 h, which means at high o-H_2 concentrations, can be fitted by this straight line. With further decreasing o-H_2 concentration, deviating values are obtained.

From the slope of the straight line, the rate constant results as $K = 0.019 \pm 0.0003$ h^{-1}. As Table I shows, this result is in good agreement with most of the values given in the literature. It should be noted that most of these values were obtained by analyzing gaseous probes taken from the sample. This method yields values of the o-H_2 concentration which are somewhat too high owing to the different vapor pressures of o-H_2 and p-H_2, or owing to a conversion to higher o-H_2 concentrations in the gaseous state. The discrepancy of one of the results obtained by NMR measurements[15] must probably be explained by the fact that the analyzing system was not calibrated. Impurities can scarcely be assumed to be the reason, since the solubility of O_2 in liquid H_2 is less than 0.2 ppm,[17] and since during condensation of solid H_2 from the gaseous phase, O_2 and other impurities will be solidified at temperatures far above the triple point of H_2. An acceleration of the o-p conversion in the presence of O_2 impurities[18] can only be explained by a reaction during the evaporation of the solid H_2. To be sure of the influence of O_2 experiments with amounts of up to 20% O_2 were performed during this investigation. They yielded no acceleration of the conversion.

The straight line obtained for measurements at 12 K and 4.2 K indicates that the o-p conversion is not influenced by the o-H_2 diffusion at these temperatures. Thus the lower limiting value of the diffusion coefficient D can be estimated.

Figure 3 shows a number of curves which were calculated assuming the indicated different values between 10^{-19} and 10^{-23} cm^2 sec^{-1} for the diffusion

FIG. 2. Experimental results for the o-p conversion in solid hydrogen at 12, 4.2, and 1.57 K.

TABLE I. Rate constant K for the o-p conversion in solid hydrogen.

10^3 K (h^{-1})	Duration of experiment (h)	Experimental method	Source
19	250	HC [a] (gas)	Ref. 2
19.4	...	Theory	Ref. 12
18.3 ± 1	12	HC (gas)	Ref. 13
18.2 ± 0.1	7	HC (gas)	Ref. 14
36 ± 8	7	NMR (solid)	Ref. 15
19 ± 1	...	HC (gas)	Ref. 16
18.5 ± 1	...	HC (gas)	Ref. 8
19.0 ± 0.3	900	NMR (solid)	This investigation

[a] Heat conduction.

FIG. 3. Calculation of the o-p conversion in solid hydrogen assuming different values for the diffusion coefficient D [cm^2 sec^{-1}] given as parameters (Ref. 9).

coefficient D (for details see the Appendix).[9] It can be seen that deviations from a straight line should occur with $D \leqslant 10^{-20}$ cm^2 sec^{-1}. The experimental results indicate a larger value of D down to 4.2 K.

To explain the experimental results at 1.57 K given in Fig. 2, the influence of the EQQ interaction on the equilibrium distribution of the o-H$_2$ molecules at this temperature as well as at 4.2 K was calculated. Such calculations can only be made for low o-H$_2$ concentrations at which mainly clusters of two or three o-H$_2$ molecules must be considered. The neglect of o-H$_2$ molecules with more than two neighbors yields values of M which are too small. The energy levels needed for the calculations as well as the calculation method were taken from the literature.[8,19]

Table II shows the calculated concentrations of single o-H$_2$ molecules (n_s), o-H$_2$ molecules with one neighbor (n_p), and those with two neighbors (n_t) for high temperatures ($T \to 14$ K, no EQQ interaction), for 4.2 K, and for 1.57 K. $m = n_p + 2n_t$ is the mean number of o-H$_2$ molecules surrounding each o-H$_2$ molecule resulting from the calculations. M_0 was evaluated using Eq. (2). A comparison with m_0, the value of m at 14 K, shows agreement of the values only for o-H$_2$ concentrations up to 0.05, whereas at higher concentrations the deviation is increasing. This is due to the neglect of clusters with higher numbers of o-H$_2$ molecules.

To enable an approximation of the mean number of o-H$_2$ molecules in the neighborhood of each o-H$_2$ molecule M for concentrations up to 0.15 at lower temperatures, it was assumed that the deviation

TABLE II. Calculated concentrations of single o-H$_2$ molecules (n_s), o-H$_2$ molecules with one neighbor (n_p), and those with two neighbors (n_t): the mean number of o-H$_2$ molecules surrounding each o-H$_2$ molecule is $m = n_p + 2n_t$ and $M = m(M_0/m_0)$.

Temperature X	M_0	$\to$14 K				4.2 K					1.57 K				
		n_s	n_p	n_t	m_0	n_s	n_p	n_t	m	M	n_s	n_p	n_t	m	M
0.01	0.12	0.886	0.107	0.007	0.121	0.871	0.119	0.011	0.140	0.139	0.740	0.177	0.082	0.341	0.338
0.02	0.24	0.785	0.192	0.023	0.238	0.760	0.206	0.034	0.273	0.276	0.574	0.244	0.182	0.608	0.613
0.03	0.36	0.694	0.258	0.048	0.354	0.663	0.270	0.067	0.404	0.411	0.457	0.266	0.277	0.820	0.834
0.04	0.48	0.613	0.306	0.081	0.468	0.578	0.312	0.109	0.531	0.544	0.371	0.265	0.363	0.991	1.016
0.05	0.6	0.540	0.341	0.119	0.579	0.504	0.341	0.155	0.652	0.675	0.305	0.259	0.435	1.129	1.170
0.07	0.84	0.419	0.378	0.203	0.784	0.384	0.365	0.252	0.868	0.930	0.215	0.236	0.550	1.336	1.431
0.1	1.2	0.282	0.377	0.341	1.059	0 254	0.350	0.398	1.145	1.298	0.130	0.191	0.679	1.549	1.755
0.15	1.8	0.142	0.301	0.557	1.415	0.125	0.265	0.609	1.482	1.886	0.059	0.124	0.816	1.756	2.234

is of the same order at all temperatures, that is,
$M = mM_0/m_0$.

The curves shown in Fig. 4 correspond to the values of M_0 and M given in Table II. As the slope of the experimental curves shown in Fig. 2 is given by $(M/M_0)K$, it is even possible to evaluate M from the experimental results. The points in Fig. 4 represent these values for 1.57 K.

It can be seen that M_{expt} is smaller than M_{calc}. The calculated curve for 4.2 K, also lies, somewhat higher than the curve for high temperatures, though no such difference can be seen in Fig. 2. This suggests the conclusion that the diffusion velocity is not quite sufficient to compensate completely the deviation from the o-H_2 equilibrium distribution caused by the o-p conversion. It seems reasonable to assume that the above-mentioned lower limiting value $D = 10^{-20}$ cm^2 sec^{-1} is really valid at 4.2 K and even at lower temperatures. According to the results given in Fig. 3, the deviation to a lower conversion rate corresponding to this value of D would just compensate the deviation to a higher conversion rate occurring at 4.2 K according to Fig. 4.

That means that the diffusion coefficient between 1.5 and 4.2 K is of the order of 10^{-20} cm^2 sec^{-1}, which is in contradiction with the strong temperature dependence of the calculated and extrapolated values of D given in Fig. 1. Furthermore, the extrapolated and calculated values of D become lower at temperatures lower than 4.8 and 3.4 K, respectively. Similar results concerning the diffusion in solid hydrogen were found by experimental and theoretical investigations of quantum diffusion.[20, 21] In these experiments the reaction-time constant was measured[20] from which the diffusion coefficient can be calculated using equations assumed by Oyarzum and Kranendonk.[21] One obtains $D = 4 \times 10^{-20}$ cm^2 sec^{-1} at 1.5 K and an o-H_2 content
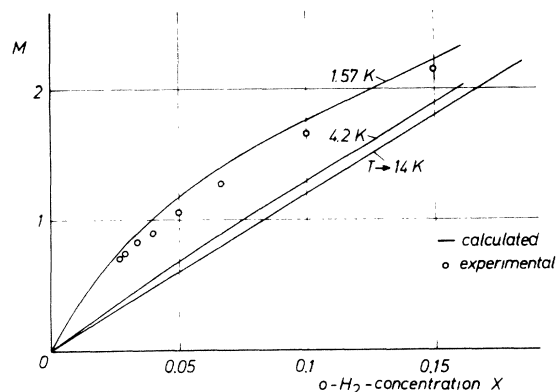

FIG. 4. Calculated values of the mean number of o-H_2 molecules in the neighborhood of each o-H_2 molecule M (see Table II) in comparison with the experimental results.

of 0.05. A weak temperature dependence of a factor of 2 between 1 and 4 K was measured for D, but this is too weak to be measurable using the o-p-H_2 conversion constant as was done with this work.

APPENDIX

The o-p-hydrogen conversion for different rates of diffusion as given in Fig. 3 is now calculated. For this calculation the influence of the EQQ was neglected. Thus the results are valid only for temperatures above 4 K.

As was mentioned before, the conversion follows the equation

$$\frac{dX}{dt} = -K\frac{M}{12}X .$$ (3)

M, the mean number of nearest o-H_2 neighbors surrounding each o-H_2 molecule, is influenced by the conversion as well as by the diffusion of o-H_2.

Since the conversion of a given o-H_2 molecule is proportional to the number of nearest o-H_2 molecules, the conversion itself reduces M to values smaller than M_0, which is the equilibrium distribution. Moreover, the concentration X is changed by the conversion. So the changes in MX must be studied.

By the conversion of one o-H_2 molecule with n nearest o-H_2 neighbors, MX is diminished by $2n$. The probability for such a conversion is $\frac{1}{12}nW_nXK$. Thus it results that

$$\frac{d(MX)}{dt} = -\frac{K}{12} X \sum 2n^2W_n ,$$ (5)

and, considering Eq. (3), it follows that

$$\frac{dM}{dt} = \frac{K}{12} \left(M^2 - 2 \sum n^2 W_n \right) .$$ (6)

This deviation in M is reduced by the diffusion. It can be assumed that the exchange of sites is independent of the ortho or para state of a molecule. The exchange frequency is $2D/d^2$, where D is the diffusion constant and d is the distance between two nearest molecules in solid H_2.

By the exchange of sites between an o-H_2 molecule with n o-H_2 neighbors and one of the surrounding p-H_2 molecules, on the average $14n/11$ o-H_2 molecules lose one neighbor while $14 X$ o-H_2 molecules gain one neighbor. Since the probability for such an exchange of sites is proportional to $W_n(1 - \frac{1}{12}n)$, the change of M due to diffusion results as

$$\frac{dM}{dt} = \frac{2D}{d^2} \sum \left(14X - \frac{n}{11} \right) W_n \left(1 - \frac{n}{12} \right) .$$ (7)

From Eqs. (3), (6), and (7), the numerical values of the curves shown in Fig. 3 can be calculated in small steps.

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