THE ORTHO-PARA FORMS OF HYDROGEN, DEUTERIUM, AND TRITIUM: RADIATION AND SELF-INDUCED CONVERSION KINETICS AND EQUILIBRIA

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June 16, 1977

Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

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UCRL-52278

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Abstract

The theory of the ortho-para transitions in H_2 , D_2 , and T_2 is developed. Experimental and calculated values of the ortho-para compositions of the three hydrogen isotopes mentioned in the literature are correlated as a function of temperature, and are discussed critically. The kinetics of the radiation and self-induced ortho-para transitions are reviewed. In

general, the radiation-induced transitions are more rapid than the self-induced transitions. We estimate (based on data for other systems) that the self-induced ortho-para transitions in liquid D_2 or T_2 would be fast, with a half time on the order of a few minutes. Experiments are proposed to study these transitions in the liquid phase using infrared spectroscopy.

Introduction

As part of the quest for new sources of energy, various laboratories throughout the world are trying to find the most practical method of harnessing nuclear fusion. One of the critical problems is selection of the appropriate fusion fuel. The fuel of choice is a mixture of D_2 , HD , and T_2 (hereafter referred to as DT) that fuses at the lowest temperature. Many of the fusion reactor designs include fuel targets of liquid or frozen DT. Since there is little data on T-containing isotopic molecules of hydrogen at temperatures near the triple point,

we have begun an extensive program to characterize the physical and chemical properties of DT at cryogenic temperatures. This program consists of review articles covering the literature, theoretical modeling and calculations, and numerous experiments to measure the various physical and chemical properties of all the isotopic hydrogen molecules (H_2 , HD , D_2 , HT , DT , and T_2). This report concentrates on the effect of the ortho and para forms of H_2 , D_2 , and T_2 on our proposed measurements, and reviews the literature relative to the radiation

and self-induced ortho-para conversions in the homonuclear diatomic hydrogen molecules.

There is considerable literature on ortho-para conversion in hydrogen in the gas phase. This reaction has been especially attractive to physicists who desired tests of the postulates of quantum mechanics, and to chemists who used this system for studies of catalysis and kinetics. There are several helpful articles with extensive literature reviews to

which we refer for general surveys of the field. An exhaustive review of the early literature (up to 1935) is provided by Farkas.¹ Schmauch and Singleton² in 1964 gave a straightforward review of the various methods of catalysis of the ortho-para transition. Scalapino and Pelzinger³ furnish a recent (1974) mathematically rigorous review of surface catalysis by magnetic materials. Our review is necessarily limited by our interest in the radiation and self-induced processes.

Theory of Ortho-Para Transitions

The prediction of the ortho-para forms of homonuclear diatomic molecules (including H_2 , D_2 , and T_2), and the subsequent experimental verification, was one of the early triumphs of quantum statistical mechanics.⁴ The properties of the molecules that lead to the ortho-para forms are the nuclear spin of the nucleus and the rotation of the molecule.⁵ All other properties such as translation, vibration, etc., are the same for the two forms. The combined nuclear spin-rotational partition function^{6,7} is given by

$$Z_r = \sum_{J=0,1,2,\dots} g_J (2J+1) \times e^{-\frac{J(J+1)\theta_r}{T}} \quad (1)$$

in the gas phase, where g_J is the nuclear spin degeneracy, J is the rotational quantum number, and T is the absolute temperature. In Eq. (1), θ_r is the so-called rotational temperature which is equal to hcB_e/kT , where h is Planck's constant, c is the speed of light, k is Boltzmann's constant, and B_e is the rotational constant which is different for each isotopic molecule and is proportional to the moment of inertia.

According to the rules of the quantum theory, homonuclear diatomic molecules can exist in states with even J or odd J but not both. Hence the two forms of hydrogen—one represented by an even series, the other by an odd series. Associated with these two series are certain g_i values, which

are the same for H_2 and T_2 since they have the same nuclear spin, but are different for D_2 since its nuclear spin differs from the other two. The ortho-para properties for H_2 , D_2 , and T_2 are listed in Table 1. Note that some confusion arises since the even (symmetric) series for H_2 and T_2 is called para, while the even series for D_2 is called ortho. The name ortho was applied to the species of H_2 , D_2 , or T_2 that were most abundant at room temperature.⁸ This designation was applied before the correlation with rotational properties was discovered; it persists until the present. The use of the terms symmetric and antisymmetric can be used to eliminate this confusion.

It has been shown experimentally that the two forms of H_2 , D_2 , and T_2 are quite stable and require some kind of catalytic process to convert from one form to another.^{1,2} There are two fundamental catalytic mechanisms that

cause the symmetric-antisymmetric transitions: (1) the chemical mechanism in which the molecule is dissociated into atoms or ions and is allowed to recombine, and (2) the physical mechanism in which the nuclear spin of the atoms interacts with an inhomogeneous magnetic field.² These mechanisms will be discussed in the last section. At room temperature, the equilibrium symmetric-antisymmetric composition of H_2 , D_2 and T_2 has a characteristic value that is close to the high-temperature compositions shown in Table 1. Any symmetric-antisymmetric mix that has this composition is known as normal (n); at any other temperature, the equilibrium mixture of the forms is designated as equilibrium (e). In the absence of a catalyst, a room temperature equilibrium mixture of H_2 , D_2 , or T_2 can be cooled to low temperatures and still have a normal composition. On the other hand, the pure symmetric forms

Table 1. Characteristics of ortho and para forms of H_2 , D_2 , and T_2 .

Characteristic	H_2	D_2	T_2
Number of nuclear spin states	2	2	2
Number of rotational states	1	1	1
Number of translational states	1	1	1
Number of vibrational states	1	1	1
Number of electronic states	1	1	1
Number of total states	2	2	2
Number of symmetric states	1	1	1
Number of antisymmetric states	1	1	1
Number of ortho states	1	1	1
Number of para states	1	1	1
Number of normal states	1	1	1
Number of equilibrium states	1	1	1
Number of total states	2	2	2

of H_2 , D_2 , and T_2 can be prepared by cooling a normal mixture of the isotope to very low temperature in the presence of a catalyst, then removing the catalyst.

The symmetric-antisymmetric transition can be written in an analogous form to a chemical reaction. Let X_2 be any of the hydrogen isotopic species H_2 , D_2 , or T_2 . Then the ortho-para transition can be written

$$X_2(\text{ODD SERIES}) \rightleftharpoons X_2(\text{EVEN SERIES}). \quad (2)$$

In a fashion analogous to a chemical equilibrium constant, we can designate a composition ratio R in the gas phase

$$R(X_2) = \frac{[X_2(\text{EVEN SERIES})]}{[X_2(\text{ODD SERIES})]}. \quad (3)$$

Using this formalism, Eq. (1), and the restrictions given in Table 1, we can define the following relationships:

$$R(H_2) = \frac{1}{3} \left[\frac{\sum_{j=0,2,4,\dots} (2j+1)e^{-\frac{j(j+1)}{2} \frac{h^2}{8\pi^2 I k T}}}{\sum_{j=1,3,5,\dots} (2j+1)e^{-\frac{j(j+1)}{2} \frac{h^2}{8\pi^2 I k T}}} \right]; \quad (4)$$

$$R(D_2) = \frac{1}{6} \left[\frac{\sum_{j=0,2,4,\dots} (2j+1)e^{-\frac{j(j+1)}{2} \frac{h^2}{8\pi^2 I k T}}}{\sum_{j=1,3,5,\dots} (2j+1)e^{-\frac{j(j+1)}{2} \frac{h^2}{8\pi^2 I k T}}} \right];$$

$$R(T_2) = \frac{1}{6} \left[\frac{\sum_{j=0,2,4,\dots} (2j+1)e^{-\frac{j(j+1)}{2} \frac{h^2}{8\pi^2 I k T}}}{\sum_{j=1,3,5,\dots} (2j+1)e^{-\frac{j(j+1)}{2} \frac{h^2}{8\pi^2 I k T}}} \right]. \quad (6)$$

Note that the g_j factors have been removed from inside the summations, and cancellations have been as appropriate. It is a simple matter to calculate the $R(X_2)$ values using g_r values from molecular spectroscopy.⁹ This has been done by other workers for the gas phase; we will compare these results with experiment in the next section.

Usually in the literature, the compositions of ortho and para species are given in terms of % ortho or % para rather than $R(X_2)$ values. The % EVEN SERIES is calculated by

$$\%(\text{EVEN SERIES}) = \frac{[X_2(\text{EVEN SERIES})]}{[X_2(\text{EVEN SERIES})] + [X_2(\text{ODD SERIES})]} \times 100,$$

with an analogous expression for the % (ODD SERIES).

Equilibrium Ratios

Giauque¹⁰ was the first to calculate the symmetric-antisymmetric com-

position of hydrogen using the method described in the preceding section.

By the same method, Harkness and Deming¹¹ extended the symmetric-antisymmetric compositions of hydrogen to other temperatures.

In 1934, Johnston and Long¹² performed similar calculations for D_2 , and in 1948 Jones¹³ did the same for T_2 . Albers *et al.*¹⁴ also report a table of ortho-para compositions for T_2 . In the context of their papers, these data could be mistaken for experimental values. Careful reading, however, indicates they cannot be. These data therefore must be results of theoretical calculations, but no source is given for them nor details of the calculations. Because of the uncertainty of source, we have omitted these data from our compilation. In 1965, Frauenfelder *et al.*¹⁵ reported a complete set of the calculated values of the symmetric-antisymmetric compositions of H_2 , D_2 , and T_2 in the gas phase; and the measured symmetric-antisymmetric compositions desorbed from a CeO_2 catalyst. All of the foregoing results are summarized in Tables 2-4. Table 2 compares the calculated and experimental values of the percentage of the even series (symmetric form) and the calculated and experimental values of $R(X_2)$ for hydrogen. We have included all the data from Giauque,¹⁰ all the data of Ref. 15 (calculated and experimental) and the data of Harkness and Deming¹¹ at certain temperatures. Only part

of the data from Harkness and Deming¹¹ was retained because we wanted to keep the table smaller and to include all the more recent data of Ref. 15.

Table 3 makes the same comparison as just listed in Table 2, but for all the data we found for deuterium. Table 4 also makes the same comparison as Tables 2 and 3, but includes all the data we found for tritium with the exception of Ref. 14 which we discussed previously. In Fig. 1, all the even-series forms for the three isotopes of hydrogen are plotted versus the absolute temperatures. As is evident, the experimental measurements and the calculated percentages agree very well for H_2 and D_2 . Agreement between the calculated and measured percentages is not as good for T_2 . The authors attribute this disagreement to the effect of the tritium β -ray which causes locally high temperatures along its path, thereby shifting the symmetric-antisymmetric percentages toward the high-temperature values. Error is also attributed to small amounts of HI and DT in the T_2 samples. Note also that the large values of $R(X_2)$ are not accurate. The reason is that an accurately known large number is divided by an inaccurately known small number. For purposes of extrapolating data, we recommend the symmetric-antisymmetric compositions calculated by Frauenfelder *et al.*¹⁵ for all three

Table 2. Percentage symmetric forms and R(H₂) values for hydrogen.

Form 1	Symmetric calculations		Symmetric exptl.		Asymmetric calculations		Asymmetric exptl.	
	Harkness and Demin ¹⁰	Fraumfelder ¹¹	Fraumfelder ¹¹	Harkness and Demin ¹⁰	Harkness and Demin ¹¹	Fraumfelder ¹¹	Harkness and Demin ¹¹	Fraumfelder ¹¹
0	100							
100	99.989			99.989				
200	99.815	99.82		99.815	99.82			
300			99.5			100.0		99.5
400			99.1			99.0		99.0
500	98.996	99.91		98.996	99.91			98.9
600			98.2			97.0		97.0
700	96.951	96.98		96.951	96.98			96.9
800			95.9			94.0		94.0
900			94.6			91.9		91.9
1000			92.7			88.3		88.3
1100	88.557	88.61		88.557	88.61			88.5
1200			88.0			86.5		86.5
1300			87.5			85.0		85.0
1400			84.0			83.6		83.6
1500			81.9			80.5		80.5
1600	76.798	76.89		76.798	76.89			76.7
1700			76.9			76.6		76.6
1800			74.5			74.3		74.3
1900			71.2			70.6		70.6
2000			70.2			68.6		68.6
2100			67.9			64.7		64.7
2200			65.7			63.2		63.2
2300			64.8			62.9		62.9
2400			58.2			58.2		58.2
2500			56.1			54.2		54.2
2600			53.3			51.1		51.1
2700	51.776	51.86		51.776	51.86			51.7
2800			50.6			50.2		50.2
2900			50.8			50.7		50.7
3000			49.7			50.5		50.5
3100			45.3			44.9		44.9
3200			40.4			39.4		39.4
3300	38.467	38.51		38.467	38.51			38.4
3400			36.2			36.0		36.0
3500			34.5			34.0		34.0
3600			33.6			33.4		33.4
3700	31.871			31.871				31.8
3800			31.0			30.6		30.6
3900			29.3			29.3		29.3
4000			28.8			28.7		28.7
4100	28.524	28.55		28.524	28.55			28.5
4200			27.6			27.4		27.4
4300			26.9			27.4		27.4
4400						26.6		26.6
4500	26.836			26.836				26.8
4600	25.953			25.953				25.9
4700			25.9			26.2		26.2
4800			25.3			25.9		25.9
4900			25.3			25.7		25.7
5000	25.257	25.29		25.257	25.29			25.2
5100						24.8		24.8
5200	25.141	25.13		25.141	25.13			25.1
5300						24.7		24.7
5400	25.072			25.072				25.0

Table 3. Percentage symmetric forms and $R(D_2)$ values for deuterium.

Temp, K	<u>Symmetric Calculation</u>		Symmetric expt, % Frauenfelder <i>et al.</i> ¹⁵	<u>$R(F_2)$ Calculation</u>		$R(D_2)$ expt Frauenfelder <i>et al.</i> ¹⁵
	Johnston and Long ¹²	Frauenfelder <i>et al.</i> ¹⁵		Johnston and Long ¹²	Frauenfelder <i>et al.</i> ¹⁵	
0	100.00					
10	99.97			3332.		
15	99.51			203.1		
20	97.97			48.26		
21.87		97.1	97.2		33.5	34.7
21.87		95.5	95.8		21.2	22.8
25	95.29			20.23		
28.02		93.5	93.4		14.4	14.2
30	92.07			11.61		
30.96		91.5	91.5		10.8	10.8
35.00		88.6	88.4		7.77	7.62
39.75		85.4	85.4		5.85	5.85
40	85.12			5.72		
42.87		83.4	83.0		5.02	4.88
50	79.19			3.81		
51.95		78.3	77.9		3.61	3.52
54.97		76.9	76.5		3.33	3.26
58.71		75.3	74.7		3.05	2.95
60	74.79			2.97		
63.04		73.8	73.2		2.82	2.73
67.06		72.6	72.0		2.65	2.57
70	71.78			2.54		
72.00		71.4	70.9		2.50	2.44
76.87		70.4	70.0		2.38	2.33
80	69.82			2.31		
82.88		69.4	69.1		2.27	2.24
89.99		68.6	68.4		2.18	2.16
90	68.58			2.18		
99.66		67.8	67.6		2.11	2.09
100	67.82			2.11		
115.3		67.2	66.9		2.05	2.02
120	67.07			2.04		
132.0		66.9	66.7		2.02	2.00
140	66.81			2.01		
160	66.72			2.00		
190	66.68			2.00		
220	66.67			2.00		
260	66.67			2.00		
300	66.67			2.00		

Table 4. Percentage symmetric form and $R(T_2)$ values for tritium.

Temp, K	Symmetric calculation		Symmetric expt, %		$R(T_2)$ Calculation		$R(T_2)$ expt	
	Jones ¹³	Frauenfelder et al. ¹⁵	Frauenfelder et al. ¹⁵	Jones ¹³	Frauenfelder et al. ¹⁵	Frauenfelder et al. ¹⁵	Frauenfelder et al. ¹⁵	Frauenfelder et al. ¹⁵
10	97.18			34.4				
15	83.57			5.09				
20	66.19			1.96				
20.85		63.9	63.2		1.77		1.73	
22.24		59.7	57.2		1.48		1.34	
24.06		55.0	53.1		1.22		1.13	
25	52.55			1.11				
25.37		52.0	49.3		1.08		0.972	
27.04		48.6	43.9		0.946		0.783	
28.65		45.6	39.9		0.838		0.664	
30	43.31			0.764				
30.79		42.4	37.1		0.736		0.590	
32.87		39.7	35.6		0.658		0.553	
34.73		37.6	33.5		0.603		0.504	
35	37.22			0.593				
37.68		35.0	33.6		0.538		0.506	
40	33.20			0.497				
40.83		32.8	32.0		0.488		0.471	
43.71		31.3	29.7		0.456		0.422	
47.76		29.5	28.2		0.418		0.393	
50	28.73			0.403				
51.77		28.2	28.4		0.393		0.397	
61.87		26.6	25.0		0.362		0.334	
66.55		26.0	26.5		0.351		0.361	
72.33		25.6	26.8		0.344		0.366	
75	25.52			0.343				
76.88		25.4	24.3		0.340		0.321	
100	25.07			0.335				
125	25.01			0.334				
150	25.00			0.333				
175	25.00			0.333

Fig. 1. Symmetric-antisymmetric equilibrium percentages of hydrogen isotopes as a function of temperature.

species since they are based on more recent values of the rotational constants.

It should be emphasized that all of the preceding measurements and calculations are for the gas phase. We found no specific data on the symmetric-antisymmetric compositions in the hydrogen species in the con-

densed phases. Welsh and his co-workers¹⁶ have pointed the way to such data, however, by their studies of quantum diffusion of ortho-hydrogen in solid para-hydrogen. Using their infrared technique, we should be able to study the ortho-para transition in the liquid and solid phases.

Rate of Radiation-Induced Symmetric-Antisymmetric Transition

As we pointed out in the introduction to the theory, the symmetric-antisymmetric transition in the hydrogen isotopes is not spontaneous; it requires some sort of catalytic process. The transition induced by the tritium β -particle¹⁷ is an example of the chemical mechanism. The requirement for this mechanism is some process that produces hydrogen atoms or ions. Unfortunately, the early and later workers disagree as to whether the mechanism is atomic or ionic. This disagreement cannot be resolved at this time since their data do not overlap, nor do the later workers address the discrepancy. The early work was by Eyring, Hirschfelder, and Taylor¹⁸ who studied the symmetric-antisymmetric transition in hydrogen induced by α -particles. They proposed that a free-hydrogen atom mechanism was more probable than an ionic one:

The α -particles cause dissociation into free-hydrogen atoms followed by a free atom and a bound atom interchanging, causing an ortho-para transition. The latter workers, Albers *et al.*¹⁴ in a tritium study and Conant *et al.*¹⁹ in a study of gamma ray and neutron-induced symmetric-antisymmetric conversion in hydrogen, indicated that an ion-molecule mechanism fit their experimental data better.

The suggested mechanism from Conant *et al.*¹⁹ follows:

where the H_2 molecule can be either a symmetric or antisymmetric hydrogen. The chain-terminating step requires a third body, R:

The physical mechanism, which is the one that predominates at low temperature, requires a collision with a paramagnetic molecule in the gas phase or on a surface. The conversion is caused by the influence of the inhomogeneous magnetic field upon the nuclear magnetic field of the hydrogen molecule. This can be mechanistically represented as

with an oxygen atom, O^* , as the paramagnetic agent. In their review article, Schmauch and Singleton² indicate that an effective low-temperature catalyst must have the following:

(1) a large physical adsorptive capacity for hydrogen, (2) a high concentration of the active catalyst specie, and (3) a high paramagnetic susceptibility. They developed a catalyst designated APACHI-1 that was more effective than those previously

used. Other catalysts used by the workers cited in this review are hydrous ferric oxide gel,² charcoal,^{2,11} chromia on alumina,³ and cerium oxide.¹⁵

We did not find in the literature what we considered to be a complete kinetic study of the radiation-induced symmetric-antisymmetric conversion of the hydrogens. Fessler and Blue^{17(a)} in a study of the conversion in liquid hydrogen caused by a fast neutron irradiation indicated that their data could not be fit by the assumption of a first-order reaction. The mechanism that seemed to fit their data was a two-step process: step one with a lifetime of 8.1 min, which was inactive in causing conversion; and step two with a lifetime of 5.7 min, which caused the conversion. No rate equation or rate constants were given. This mechanism is consistent with that described by Conant *et al.*¹⁹ which we illustrated by Eqs. 10-13 wherein the chain initiation step [Eq. (10)] would be the slow or rate determining step. Nelms and Carter^{17b} also studied the conversion in hydrogen using both gamma and neutron radiation. They give the rate of increase for ortho-hydrogen from irradiated para-hydrogen as

$$\frac{d[o-H_2]}{dt} = \frac{3}{4} k [H^*] [p-H_2] \\ - \frac{1}{4} k [H^*] [o-H_2], \quad (15)$$

where k is the rate constant for hydrogen exchange. The brackets denote concentrations, and $H^{\bullet}$ stands for hydrogen atoms. The first term represents the forward conversion and the second term the back conversion to para-hydrogen. The value of k used was $3.6 \times 10^8 \text{ cm}^3/\text{mole sec}$ at 300 K. This equation is not useful to us because it depends on the hydrogen atom concentration, which is difficult to measure.

Other workers have given kinetic data in terms of conversion half times without specifying mechanisms or giving a rate equation. Jones¹³ has estimated the half time of β -catalyzed

ortho-para transition in tritium gas to be a few days, presumably at room temperatures. Albers *et al.*¹⁴ reported the conversion half time for tritium on coconut charcoal as 0.92 min at 27.2 K and 1.0 min at 77.4 K; the conversion half time for deuterium on the same catalyst was 19 min at 27.2 K. The tritium conversion in the solid at 4.2 K had a half time of 17 min. Conant *et al.*¹⁹ in a study of $p\text{-H}_2$ conversion induced by gamma and neutron radiation saw appreciable conversion at 300 K and 195 K but very little at 77 K. Albers *et al.*¹⁴ also noted very slow conversion in tritium gas at 27.2 K.

Self-Induced Symmetric-Antisymmetric Conversion Kinetics

In the gas phase, the self-induced symmetric-antisymmetric conversion rate of the hydrogen isotopes is very slow. On the other hand, the self-induced conversion in the liquid and solid phases may be appreciable. In liquid and solid tritium, we would expect that the self-induced conversion would be overshadowed by the radiation-induced process.

Much of the data on the self-induced ortho-para conversion in liquid hydrogen and deuterium dates from early measurements in the 1930's.

Woolley, Scott, and Brickwedde²⁰ have reviewed this early work; the discussion that follows is based on their paper. The self-conversion depends upon a magnetic interaction on a molecular scale, and, since symmetric hydrogen has no nuclear magnetic moment (spin opposed), the self-conversion of symmetric-antisymmetric mixtures depends only on the interaction of antisymmetric molecules with each other and with symmetric molecules. The symmetric-symmetric interaction does not cause conversion.

The rate equation is therefore written

$$-\frac{d[\text{asym-H}_2]}{dt} = k_1 [\text{asym-H}_2]^2 - k_2 [\text{asym-H}_2] [\text{sym-H}_2]. \quad (16)$$

The rate constant k_2 is much smaller than k_1 and the second term is omitted by the earlier workers.²¹ For liquid hydrogen, the second-order rate constant k_1 is equal to 0.0114 per hour when concentrations are expressed as mole fractions. The value of k_1 for solid H_2 , 0.019 per hour, is larger than that for liquid H_2 but decreases with time due to immobility of the molecules in the solid. The initial value of k_1 is restored by melting and freezing.

The self conversion of ortho and para D_2 in the liquid phase proceeds at a much slower rate than the H_2 rate. This is due to the much smaller magnetic moment of the deuteron as compared with that of the proton. Brickwedde, Scott, and Taylor²¹ showed by means of a theoretical analysis that

$$\frac{d[\text{asym-H}_2]}{dt} / \frac{d[\text{asym-D}_2]}{dt} = 340. \quad (17)$$

Their analysis also showed that

$$-\frac{d[\text{asym-D}_2]}{dt} = k_p [\text{asym-D}_2], \quad (18)$$

instead of the square of the concentration as it is for the corresponding change in hydrogen.

A number of calculations and experiments giving the rate of the self-induced symmetric-antisymmetric conversion in liquid and solid hydrogen have been reported. These results have been compared for solid hydrogen by Schmidt²² and for liquid hydrogen by Milenko and Sibileva²³. For hydrogen, all the values are essentially in agreement with those reported for Eq. (16), $k_1 = 0.0114$ per hour for liquid hydrogen and 0.019 per hour for solid hydrogen. Schmidt²² discusses the effect of molar diffusion and electric quadruple-quadruple interaction on the conversion rate in solid hydrogen at temperatures below 4.2 K and at times longer than 300 hours. Under these conditions, the simple bimolecular model does not hold, and an increase of the conversion rate with decreasing antisymmetric hydrogen is seen.

The theoretical calculations of the rate of symmetric-antisymmetric conversion in solid deuterium have been compared with the experimental rate by Grenier and White.²⁴ They give a rate equation analogous to Eq. (16):

$$-\frac{d[\text{asym-D}_2]}{dt} = k_1 [\text{asym-D}_2]^2 + k_2 [\text{asym-D}_2] [\text{sym-D}_2], \quad (19)$$

with $k_1 = 1.27 \times 10^{-3} \text{h}^{-1}$ and $k_2 = 1.78 \times 10^{-3} \text{h}^{-1}$. The agreement between their data and experiment was considered to be good taking account of the experimental error. Milenko and Sibileva²³ report an analysis in disagreement with that of Grenier and White. They report an extensive experimental study of the conversion rates in both liquid and solid hydrogen and liquid and solid deuterium. As mentioned earlier, their hydrogen data agrees well with that of previous workers. They show that their deuterium data can be fit by Eq. (18)

rather than Eq. (19). They report values of $k_D = 3.3 \pm 0.1 \times 10^{-4} \text{h}^{-1}$ for liquid D_2 at 20.4 K; and $k_D = 5.3 \pm 0.3 \times 10^{-4} \text{h}^{-1}$ at 4.2 K.

Their data in solid deuterium disagrees with that of the theory and with Grenier and White.²⁴ We also found some data for liquid and solid deuterium in Ref. 25, which likewise disagrees with Milenko and Sibileva.²³ Because of the precision of their experimental data and their straightforward analysis, we recommend the values of k_D given by Milenko and Sibileva.²³

Summary and Conclusions

For our purposes, it is of interest to compare the rates of the various mechanisms of symmetric-antisymmetric conversions as a function of isotopic hydrogen and phase. In Table 5, we list the half times of some conversion reactions under different conditions. Some of the half times were taken directly from the literature, such as those from Refs. 13 and 14. Others, such as those from Refs. 17b, 20, and 23, were calculated from rate constants or taken from graphs. No extensive efforts were made to find rate constants for different processes using various catalysts, as pointed out before. The catalytic conversion for D_2 and T_2 from Ref. 14 were in-

cluded for comparison with the author's other data. The transition half times are also plotted as a function of $\log T$ in Fig. 2. The data from Table 5 and Fig. 2 indicate that in general the catalytic process even in the gas phase is the most rapid, although the combination of the tritium β -ray and catalyst gives the fastest rate listed in the table. Also the radiation-induced conversion (liquid H_2 at 20 K, gas T_2 at 300 K, and solid T_2 at 4.2 K) is more rapid than the self-induced conversion in the liquid or solid state.

One of our proposed measurements is the equilibrium constant for the reaction $D_2 + T_2 = 2DT$ in the gas and

Fig. 2. Plot of symmetric-antisymmetric half times of H₂, D₂, and T₂ as a function of log₁₀ T.

Table 5. Comparison of symmetric-antisymmetric conversion rates for H₂, D₂, and T₂, for some catalyzed (C), radiation-induced (RI), and self-induced (SI) processes. Rates are expressed as half times in minutes and temperatures in kelvins.

Species	H ₂	H ₂	D ₂	D ₂	T ₂	T ₂
Process	(RI)	(SI)	(C)	(SI)	(C)	(RI)
Phase						
Gas	—		19 at 27.2 K (coconut charcoal) (Ref. 14)	—	0.92 at 27.2 K 1.0 at 77.4 K (coconut charcoal) (Ref. 14)	Approx 1540 at 300 K (x-ray from Ti) (Ref. 13)
Liquid	6 at 20 K (Ref. 17b)	7020 at 20.4 K (Ref. 20)	—	2.1 × 10 ³ at 20.4 K (Ref. 23)		—
Solid	—	4210 at 12 K (Ref. 20)	—	1.3 × 10 ³ at 4.2 K (Ref. 23)		17 at 4.2 K (x-ray from Ti) (Ref. 14)

liquid phases. If we hope to compare the experimental results with our calculations from spectroscopic data,⁷ we need to know the symmetric-antisymmetric states of the tritium and deuterium. The radiation-induced conversion in liquid hydrogen from Ref. 17b indicates that the radiation-induced rate in liquid D_2 and T_2 may be fairly rapid—on the order of a few minutes. In any case, we plan to measure $R(T_2)$ and $R(D_2)$ and the conversion rate in a liquid-phase mixture of D_2 , DT , and T_2 using infrared spectroscopy.

Acknowledgments

We thank Robert Epple and others of the Division of Physical Research, Energy Research and Development Administration Washington, D. C., for their support of basic DT studies at cryogenic temperatures. We also thank Clark Souers who had the original idea for this cryogenic program and under whose direction it proceeds.

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