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Author
Ahlers, Guenter.

Publication Date
1963-10-01

UCRL-11042

University of California

Ernest O. Lawrence Radiation Laboratory

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AEC Contract No. W-7405-eng-48

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Guenter Ahlers

October 1963

ON THE ORTHO-PARA CONVERSION IN SOLID HYDROGEN[*] [+]

Guenter Ahlers[‡§]

Inorganic Materials Research Division
of Lawrence Radiation Laboratory
and Department of Chemistry
University of California, Berkeley, California

The homogeneous conversion of ortho hydrogen to para hydrogen in the liquid and solid state at zero pressure has been studied experimentally by a number of investigators.[1,2,3] It is generally agreed that the conversion follows a second order rate law with a temperature independent rate constant. Recently some theoretical interest developed in the interactions which are responsible for the conversion, and Motizuki and Nagamiya calculated the rate constant for the ortho-para conversion in the solid.[4] They obtained excellent agreement with the experimental value at zero pressure. Similar calculations have been performed for solid deuterium.[5,6]

Hydrogen because of its large compressibility offers the opportunity to study intermolecular interactions over a large volume range, and experimental data on the ortho-para conversion at small molar volumes would provide a further check on theoretical derivations. There is at this time only one determination of the rate constant at a volume smaller than the zero pressure volume.[7] It is the purpose of this note to report determinations of the rate constant at three molar volumes, and to discuss the volume dependence of the ortho-para conversion.

The rate constant for the ortho-para conversion was determined at 22.6, 19.0 and 16.4 cc/M from the initial and final ortho hydrogen concentrations of samples which had been kept at constant volume for a number of hours. It was assumed that the conversion followed a second order rate law. Details of the apparatus and procedures used are described elsewhere.[8,9] The final concentrations were always high enough to cause the formation of isolated ortho molecules to be negligible.[1] The rate constants together with some of those determined by others are given in Table I.

There appears to be some confusion in the literature about the value of the rate constant in the solid at zero pressure. Cremer[1] and earlier workers obtained a value of 17.5 x 10^{-5} (% hr)$^{-1}$. Motizuki and Nagamiya[4] claimed that Hill and Ricketson[10] found the conversion to be only about half as fast, but Hill and Ricketson quoted a rate of heat generation which corresponds to a rate constant of 17.4 x 10^{-5} (% hr)$^{-1}$. It is not clear whether Hill and Ricketson measured this rate or whether they calculated it from Cremer's rate constant. The rate constant determined by Smith and Housley[11] is well in line with Cremer's value, and with the work reported here. Only the results obtained by Sugawara, et. al.[3] appear to be considerably higher. In view of the good agreement between all the other determinations their value must be considered in error.

There is also some question about the interpretation of McCormick's value at 13.7 cc/M[7]. McCormick reports that "the measured rate of ortho-para conversion was 7.5 % per hour." Since McCormick did not report his concentration, it is assumed that his rate was quoted for 100 % ortho hydrogen, and that the rate constant was 75 x 10^{-5} (% hr)$^{-1}$. If, however, McCormick's rate was that in approximately normal hydrogen, then his rate constant may be twice as large.

The relative rates of conversion in two samples of molar volumes of

19 and 16 cc were also determined from the heat evolution in the samples between 1.6 and 2.7°K and between 1.6 and 3.6°K respectively. No temperature dependence was observed. This confirms the results of Hill and Ricketson at zero pressure.

Cremer[1] first suggested on the basis of theoretical calculations by Wigner[12] that the rate constant should depend on R^{-8}. The calculations by Motizuki and Nagamiya indicate a more complicated volume dependence.[4] They assumed that the energy of the transition was converted into lattice vibrations, and the emission of phonons due to the conversion was considered in the Debye approximation. Because of the relative magnitudes of the Debye theta and the difference between the J=0 and J=1 rotational levels, at least two phonons had to be emitted at the zero pressure volume. Two phonon emission was found to be about ten times as efficient as three phonon emission. In the case of deuterium one phonon emission was possible,[6] and was found to be about ten times as efficient as two phonon emission.[5] Whereas the basic volume dependence of the interaction is proportional to R^{-8}, an additional dependence on the volume is introduced through the Debye approximation in the form of the sound velocity. McCormick estimated that the overall dependence of Motizuki and Nagamiya's rate constant on the intermolecular separation should follow an R^{-12} relation.[7] Figure 1 shows that experimentally this is not realized and that the rate constant depends on R^{-8}. It must thus be considered fortuitous that the theoretical rate constant agrees so well with experiment at zero pressure.

A logical extension of the theory of Motizuki and Nagamiya would have to permit one phonon emission at molar volumes smaller than about 19cc because at smaller volumes the Debye theta becomes larger than the energy difference between the J=0 and J=1 rotational levels.[13] From the relative efficiencies of two and three phonon emission in hydrogen[4] and one and two phonon emission in deuterium,[5,6] it can be expected that the theoretical rate constant should increase by perhaps one order of magnitude at 19 cc/mole, although one phonon emission has not yet been considered for hydrogen. No such increase is manifested by the experimental data. The possibility of such an increase at volumes smaller than 16 cc/M cannot be ruled out because of the uncertainty in the interpretation of McCormick's conversion rate.

It is suspected that the differences between the experimental results and the theoretical predictions are primarily due to the use of the Debye theory. For this problem the Debye theory is particularly unsuitable because the high frequency vibrations, which in this case are of primary importance, can be expected to be extremely anharmonic because of the large zero point energy of solid hydrogen.

TABLE I. The Second Order Rate Constant for the Ortho-para Conversion

Investigator	$k \times 10^{-5}$ ($\%$ hrs)$^{-1}$	Volume cc/M	Temperature °K
Cremer[a]	17.5	23.0	11 to 12
Cremer[a]	11.2	28.39 (liquid)	20
Smith & Housley[b]	18.1	22.64	2
Sugawara, et.al[c]	~ 60	22.64	2
McCormick[d]	75	13.7	
This work	18.2	22.64	2 to 4
This work	18.2	22.64	2 to 4
This work	18.1	22.64	2 to 4
This work	29.9	18.98	9 to 20
This work	45.6	16.42	3 to 20

[a] Reference 1
[b] Reference 11
[c] Reference 3
[d] Reference 7

[*] Based on part of a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree, University of California, Berkeley.

[+] This research was supported by the U.S. Atomic Energy Commission.

[‡] National Science Foundation Predoctoral Fellow, 1960-61; and General Electric Company Predoctoral Fellow, 1961-62.

[§] Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.

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Figure Captions

Figure 1 The rate constant k for the homogeneous ortho-para conversion in hydrogen as a function of molar volume.

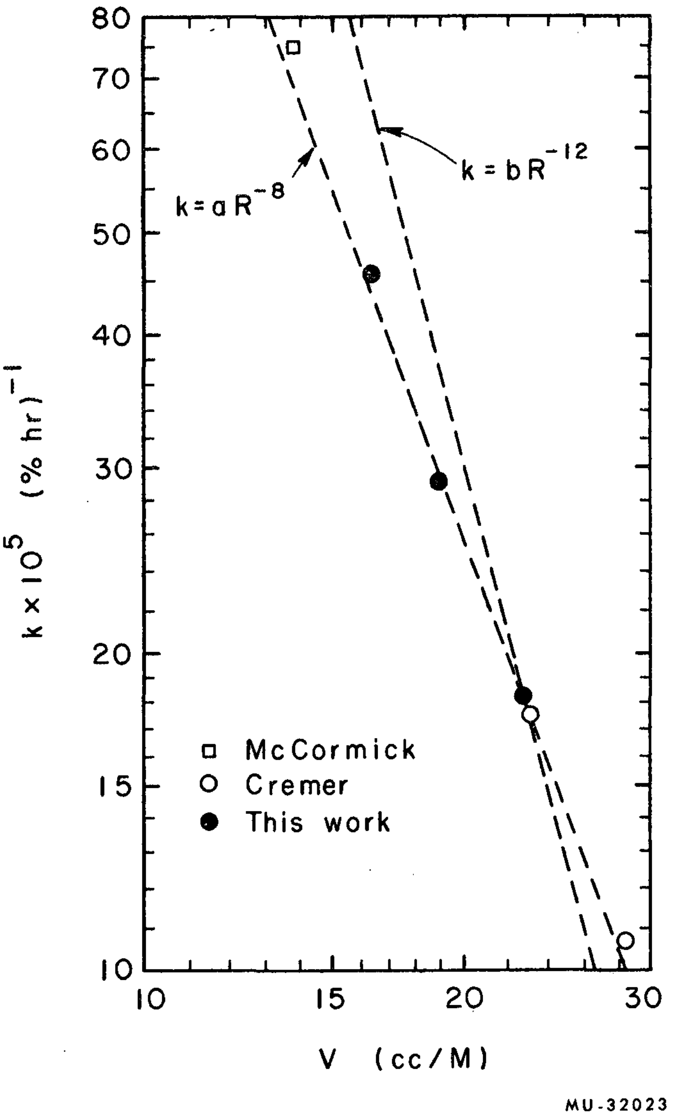
80
70
60
50
40
30
20
15
10
k × 10^5 (% hr)$^{-1}$
10
15
20
30
V (cc/M)
k = aR^{-8}
k = bR^{-12}
□ McCormick
○ Cremer
● This work
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Fig. 1