

**Registry No.** Cd(NO<sub>3</sub>)<sub>2</sub>, 10325-94-7; Co(NO<sub>3</sub>)<sub>2</sub>, 10141-05-6; H<sub>2</sub>SIF<sub>6</sub>, 16961-83-4; K<sub>3</sub>Fe(CN)<sub>6</sub>, 13746-86-2; KMnO<sub>4</sub>, 7722-84-7; KNO<sub>3</sub>, 7758-09-0; Mg(ClO<sub>4</sub>)<sub>2</sub>, 13770-16-8; NaH<sub>2</sub>PO<sub>4</sub>, 7558-80-7; Na<sub>2</sub>HPO<sub>4</sub>, 7558-79-4; Na<sub>2</sub>MoO<sub>4</sub>, 7631-95-0; Na<sub>3</sub>PO<sub>4</sub>, 7601-54-9; Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, 7722-88-5; Na<sub>2</sub>SO<sub>3</sub>, 7757-83-7; Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 7772-98-7; Na<sub>2</sub>WO<sub>4</sub>, 13472-45-2; NH<sub>4</sub>Al(SO<sub>4</sub>)<sub>2</sub>, 7784-25-0; (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 1113-38-8; NH<sub>4</sub>CH<sub>3</sub>COO, 631-61-8.

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## Thermal Conductivity of Parahydrogen

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The paper presents new experimental measurements of the thermal conductivity of parahydrogen for eight isotherms at temperatures from 100 to 275 K with intervals of 25 K, pressures to 12 MPa, and densities from 0 to 12 mol/L. Three additional isotherms at 150, 250, and 275 K cover para-rich compositions with para percentages varying from 86% to 73%. For these three isotherms the pressures reach 70 MPa and the density a maximum of 30 mol/L. The data for all compositions are represented by a single thermal conductivity surface in which the differences in thermal conductivity for different ortho-para compositions are accounted for in the dilute-gas term. The new measurements are compared with previous data on parahydrogen through the new correlation. It is estimated that the overall uncertainty of both experimental and correlated thermal conductivity is 1.5% at the 3 $\sigma$  level.

#### Introduction

For the H<sub>2</sub> molecule, two spin isomers exist—orthohydrogen and parahydrogen. The differentiating feature is the relative orientation of the two nuclear spins of the molecule. The spins may be either parallel or antiparallel. Parahydrogen molecules have antiparallel nuclear spins, and even rotational quantum numbers; they are therefore in the lowest rotational energy state ( $J = 0$ ) at low temperatures. In the absence of a catalyst, the rate of conversion between the two species is slow; hence, hydrogen can be thought of as a binary mixture of two different species of molecules differing from each other in physical properties. The equilibrium ortho-para composition in the mixture is temperature dependent. For example, at a temperature of about 20 K, the equilibrium composition is 99.79% para and 0.21% ortho. Near room temperature the composition is about 25% para and 75% ortho. This 25-75 composition is called normal hydrogen.

A search of the literature reveals a relative abundance of papers on the thermal conductivity of hydrogen (1). However, measurements on parahydrogen are rare (2, 3). It is, therefore, not surprising that efforts to correlate the thermal conductivity surface of parahydrogen (4) are beset with difficulties and that the correlations are of doubtful accuracy. In this paper new experimental measurements are presented that cover the range 0-8 mol/L for every isotherm with a para percentage of

99.79%. Additional isotherms at 150, 250, and 275 K cover densities up to 30 mol/L at para-rich compositions with para percentages varying from 86% to 73%. For these three isotherms the pressures reach 70 MPa and the density a maximum of 30 mol/L. The results overlap our earlier measurements (2) and extend them to 300 K. The earlier measurements were done primarily at temperatures below 100 K. The present results are described by a new correlation for the thermal conductivity surface of hydrogen between 78 and 300 K for pressures up to 70 MPa (5). In this new correlation (5) differences in thermal conductivity for varying ortho-para compositions are accounted for in the dilute-gas term (6).

#### Experimental Section

The measurements were made with a new transient hot wire thermal conductivity apparatus (7). In the transient hot wire technique, a thin platinum wire, immersed in the fluid and initially in thermal equilibrium with it, is subjected at time  $t = 0$  to a step voltage. The wire behaves as a line source of heat with constant heat generation. The physical arrangement closely models an ideal line source, and the working equation for the temperature increase in the wire,  $\Delta T$ , is given by

$$\Delta T = \frac{q}{4\pi\lambda} \ln \left( \frac{4K}{a^2 C} t \right) \quad (1)$$

where  $q$  is the heat generated per unit length of wire of radius  $a$ ,  $K = \lambda/(\rho C_p)$  is the thermal diffusivity of the fluid at the reference temperature, and  $\ln C = \gamma$ , where  $\gamma$  is Euler's constant.  $K$  is nearly constant since the fluid properties do not change drastically with a small increase in temperature. Corrections to eq 1 have been fully described elsewhere (8), the most important one being the effect of the finite heat capacity of the wire.

Use of a Wheatstone bridge with both a long and a short hot wire provides end-effect compensation. Voltages are measured directly with a fast response digital voltmeter (DVM). The DVM is controlled by a minicomputer, which also handles the switching of the power and the logging of the data. The measurement of thermal conductivity for a single point is accomplished by balancing the bridge as close to null as is practical at the cell or reference temperature. The lead resistance, the hot wire resistances, and the ballast resistors are read first; then the power supply is set to the desired power and the voltage developed across the bridge as a function of time is read and

Table I. Representative Set of Experimental Thermal Conductivity Values for Parahydrogen

$P,^a$ MPa	$T,^b$ K	$\rho,^c$ mol/L	$x_{\text{para}}^d$	power, W/m	$\lambda,^e$ W/(m K)	STAT, <sup>f</sup> %	exptl - calcd, %
67.238	148.553	29.649	0.839 53	0.809 88	0.234 43	0.10	-0.07
67.237	148.823	29.618	0.839 41	0.902 93	0.234 95	0.10	0.15
67.236	149.427	29.551	0.839 29	1.104 76	0.234 55	0.10	-0.04
67.233	149.774	29.512	0.839 17	1.212 90	0.234 30	0.10	-0.16
67.236	149.144	29.583	0.839 4		0.234 6	0.13	-0.03

<sup>a</sup> Pressure. <sup>b</sup> Temperature. <sup>c</sup> Density. <sup>d</sup> Mole fraction of parahydrogen. <sup>e</sup> Thermal conductivity. <sup>f</sup> Experimental precision.

stored. The basic data form a set of 250 voltage readings taken at 3-ms intervals. The other variables measured include the applied power, the cell temperature, and the pressure. All of the pertinent data are written by the minicomputer onto a magnetic tape for subsequent evaluation.

For each run, the data on the magnetic tape are processed on a large computer. In addition to the reduction of the raw data, i.e., the conversion of bridge offset voltages to resistance changes and then to temperature changes, the large computer also handles the wire calibration data, evaluates the best straight line for the  $\Delta T - \ln(t)$  data, and determines the thermal conductivity. For the present measurements a new set of hot wires had to be mounted. The new wires are virtually identical with the old ones in material, length, and diameter. The new wire calibration is obtained from some 918 values collected for each wire in the temperature range 100–320 K during remeasurements of normal hydrogen (5) and the present measurements on parahydrogen.

The samples used are research-grade hydrogen stated by the supplier to be a minimum of 99.999 mol % hydrogen. Nominally pure parahydrogen, i.e., a 20.4 K equilibrium composition of 99.79% para, was obtained by running the samples from the supply bottle through an ortho-para catalyst directly into the system. The catalyst was cooled with liquid parahydrogen at approximately 20 K. Completion of the conversion was verified with an ortho-para analyzer (9). For these measurements the maximum pressure is about 12 MPa (1800 psia). The measurements to higher pressures were made by running the parahydrogen from the ortho-para catalyst through a small diaphragm compressor which operated at ambient temperature. The compressor converted some of the para back to ortho, yielding an initial para concentration in the 80–90% range. Additional conversion occurs while the sample is in the experimental cell so that the final para concentrations were in the 70–80% para range. The assignment of composition to a particular point is discussed in detail in ref 5.

## Results

Approximately 510 points were measured. The measurements are distributed among eight pseudoisotherms where the nominal isotherm temperatures are 100, 125, 150, 175, 200, 225, 250, and 275 K. For the eight short isotherms with a para percentage of 99.79% measurements were taken at eight or nine different pressures. For the three extended isotherms with varying para percentages measurements were taken at 24 different pressure levels. At each pressure replicate measurements were made at four different applied powers. The total range of powers is from 0.21 to 1.3 W/m. Table I shows a representative set of actual experimental thermal conductivity values. The pressure, temperature, and applied power are measured directly; the thermal conductivity, the ortho-para percentage, and the associated regression error (STAT) are obtained through the data reduction program; and the density is calculated from an equation of state (10) using the measured pressure and temperature. The entire set of data is shown in thermal conductivity vs. density coordinates in Figure 1. Shown as lines in Figure 1 are the isotherms calculated from the correlating equation for a para percentage of 99.79%. Since the temperature of measurement varies with the applied power,

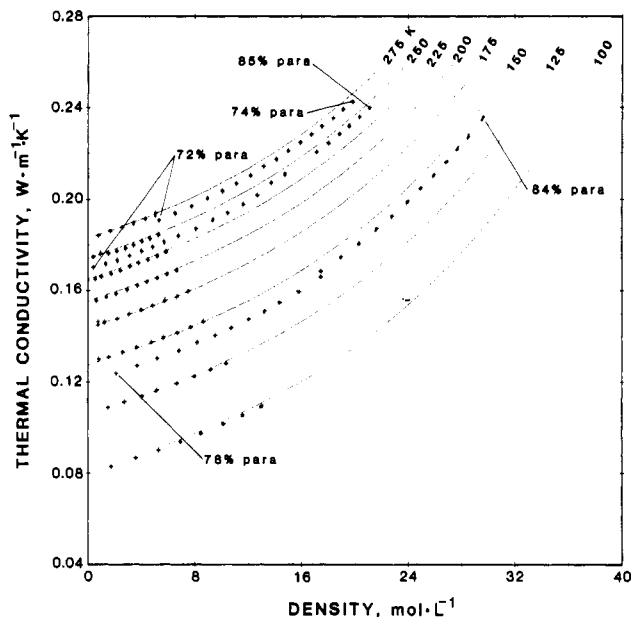


Figure 1. Thermal conductivity of parahydrogen along isotherms: (+) experimental results, (—) correlation.

each experimental point had to be adjusted slightly to obtain values on even isotherms.

A complete table which includes all 510 experimental measurements is given in ref 11. In this paper, to conserve space, Table II gives a summary of the thermal conductivity values. Replicate measurements for any given pressure obtained by varying the applied power are averaged to yield a single line. An example is shown in the last line of Table I. Unfortunately the column giving the applied power becomes meaningless. The column STAT becomes a nominal reproducibility which is calculated as the rms percentage from the adjusted thermal conductivity values.

## Correlation of the Data

It is generally accepted that the thermal conductivity should be correlated in terms of density and temperature rather than temperature and pressure because over a wide range of experimental conditions the behavior of thermal conductivity is dominated by its density dependence. This preferred technique requires an equation of state (10) to translate measured pressures into equivalent densities. The dependence of thermal conductivity on temperature and density is normally expressed as

$$\lambda(\rho, T) = \lambda_0(T, x) + \lambda_{\text{excess}}(\rho, T) + \Delta\lambda_{\text{critical}}(\rho, T) \quad (2)$$

The dilute-gas term,  $\lambda_0(T, x)$ , in the case of hydrogen is a function of both temperature and ortho-para composition. For a given temperature the relationship is linear in the difference between ortho- and parahydrogen. It is expressed in eq 3 in

$$\lambda_0(T, x) = \lambda_0(T, 0.25) + [\lambda_0(T, 1.0) - \lambda_0(T, 0.25)](x - 0.25)/0.75 \quad (3)$$

terms of the dilute-gas conductivities of normal and parahydrogen. For the dilute gas we use the values of  $\lambda_0$  calculated

Table II. Summary of Thermal Conductivity Values for Parahydrogen

$P_{av},^a$ MPa	$T_{av},^b$ K	$\rho_{av},^c$ mol/L	$x_{para,av}^d$	$\lambda_{adj},^e$ W/(m K)	STAT $_{adj},^f$ %	exptl - calcd, %
11.522	99.373	12.991	0.9979	0.1087	0.40	-1.40
10.079	99.391	11.576	0.9979	0.1047	0.28	-1.31
8.670	99.495	10.107	0.9979	0.1010	0.10	-1.18
7.145	99.368	8.464	0.9979	0.0968	0.13	-1.08
5.790	99.470	6.921	0.9979	0.0932	0.13	-1.01
4.370	99.278	5.275	0.9979	0.0895	0.08	-0.81
2.958	99.453	3.580	0.9979	0.0861	0.10	-0.70
1.442	99.390	1.748	0.9979	0.0823	0.07	-0.79
11.634	124.232	10.318	0.9979	0.1274	0.16	-0.59
10.210	124.351	9.182	0.9979	0.1248	0.07	-0.36
8.722	124.475	7.949	0.9979	0.1219	0.17	-0.32
7.187	124.586	6.634	0.9979	0.1190	0.12	-0.20
5.440	124.330	5.104	0.9979	0.1156	0.21	0.08
4.223	124.501	3.990	0.9979	0.1133	0.32	-0.06
2.848	124.672	2.710	0.9979	0.1109	0.09	0.02
1.531	124.528	1.469	0.9979	0.1083	0.15	-0.04
11.718	148.898	8.634	0.9979	0.1456	0.07	0.13
10.293	148.950	7.681	0.9979	0.1432	0.22	0.05
8.821	149.044	6.665	0.9979	0.1408	0.12	0.08
7.343	149.123	5.615	0.9979	0.1388	0.21	0.31
6.100	148.834	4.722	0.9979	0.1364	0.14	0.21
4.633	148.955	3.624	0.9979	0.1343	0.10	0.31
3.251	149.059	2.567	0.9979	0.1323	0.06	0.38
1.909	148.883	1.524	0.9979	0.1299	0.07	0.27
0.989	148.897	0.794	0.9979	0.1291	0.17	0.70
67.236	149.144	29.583	0.8394	0.2346	0.13	-0.03
62.547	149.232	28.506	0.8378	0.2269	0.19	-0.02
59.172	149.280	27.689	0.8363	0.2217	0.10	0.13
55.842	149.026	26.876	0.8350	0.2156	0.11	-0.11
52.250	149.140	25.905	0.8337	0.2098	0.07	0.03
48.868	149.244	24.938	0.8323	0.2042	0.11	0.07
45.356	148.940	23.918	0.8310	0.1981	0.16	0.05
41.810	149.048	22.772	0.8295	0.1918	0.12	-0.06
38.363	149.145	21.582	0.8280	0.1862	0.14	0.13
34.822	148.937	20.303	0.8267	0.1797	0.13	-0.02
31.398	149.043	18.935	0.8254	0.1740	0.06	0.16
27.892	149.174	17.421	0.8074	0.1666	0.46	-0.23
24.287	148.860	15.774	0.7896	0.1588	0.16	-0.72
21.443	148.941	14.337	0.7884	0.1541	0.20	-0.51
19.316	148.875	13.206	0.7871	0.1501	0.19	-0.68
17.231	148.934	12.029	0.7859	0.1467	0.07	-0.48
15.027	149.086	10.713	0.7844	0.1430	0.10	-0.45
13.084	149.185	9.499	0.7831	0.1398	0.04	-0.38
11.011	148.904	8.166	0.7820	0.1364	0.12	-0.11
9.014	149.018	6.800	0.7808	0.1329	0.16	-0.27
6.705	149.170	5.153	0.7795	0.1297	0.14	0.11
4.660	148.935	3.645	0.7783	0.1262	0.06	0.10
2.627	149.198	2.082	0.7773	0.1232	0.09	0.06
11.849	173.581	7.493	0.9979	0.1591	0.21	0.13
10.398	173.635	6.653	0.9979	0.1569	0.20	0.03
8.859	173.641	5.740	0.9979	0.1553	0.35	0.38
7.333	173.753	4.806	0.9979	0.1528	0.12	0.14
5.971	173.857	3.953	0.9979	0.1510	0.18	0.11
4.560	173.954	3.050	0.9979	0.1492	0.06	0.16
3.199	174.159	2.159	0.9979	0.1473	0.08	0.00
1.781	173.545	1.219	0.9979	0.1455	0.29	0.26
1.059	173.316	0.729	0.9979	0.1448	0.57	0.57
12.020	199.473	6.631	0.9979	0.1688	0.20	-0.39
10.561	199.533	5.890	0.9979	0.1671	0.24	-0.33
9.147	199.581	5.155	0.9979	0.1654	0.06	-0.36
7.723	199.648	4.398	0.9979	0.1639	0.06	-0.27
6.403	199.314	3.688	0.9979	0.1620	0.11	-0.37
5.000	199.409	2.909	0.9979	0.1602	0.15	-0.48
3.533	199.473	2.077	0.9979	0.1586	0.16	-0.46
2.244	199.117	1.334	0.9979	0.1569	0.19	-0.53
1.002	199.081	0.601	0.9979	0.1554	0.29	-0.51
11.781	224.014	5.824	0.9979	0.1767	0.14	-0.19
10.369	224.031	5.176	0.9979	0.1749	0.23	-0.37
8.850	224.107	4.464	0.9979	0.1733	0.07	-0.36
7.361	224.144	3.752	0.9979	0.1718	0.12	-0.34
6.059	224.244	3.115	0.9979	0.1704	0.16	-0.41
4.628	224.332	2.402	0.9979	0.1686	0.17	-0.56
3.269	223.967	1.716	0.9979	0.1672	0.22	-0.53
1.842	223.866	0.977	0.9979	0.1658	0.19	-0.43
0.987	223.904	0.526	0.9979	0.1649	0.25	-0.49
66.948	254.747	21.097	0.8473	0.2420	0.03	-0.02
63.432	255.019	20.345	0.8443	0.2380	0.13	-0.09

Table II (Continued)

$P_{av}$ , <sup>a</sup> MPa	$T_{av}$ , <sup>b</sup> K	$\rho_{av}$ , <sup>c</sup> mol/L	$x_{para,av}$ <sup>d</sup>	$\lambda_{adj}$ , <sup>e</sup> W/(m K)	STAT <sub>adj</sub> , <sup>f</sup> %	exptl - calcd, %
59.924	254.808	19.594	0.8415	0.2341	0.12	-0.05
56.564	254.820	18.836	0.8367	0.2307	0.11	0.09
53.104	254.952	18.019	0.8337	0.2265	0.13	-0.06
49.499	254.991	17.139	0.8310	0.2227	0.03	0.02
40.368	254.698	14.755	0.8278	0.2129	0.22	0.06
36.796	254.731	13.740	0.8250	0.2091	0.08	0.09
33.258	254.778	12.688	0.7507	0.2036	0.10	-0.16
29.811	254.664	11.622	0.7484	0.1997	0.17	-0.29
26.240	254.288	10.475	0.7460	0.1957	0.20	-0.41
22.939	254.326	9.349	0.7438	0.1927	0.21	-0.21
19.376	254.463	8.074	0.7412	0.1888	0.08	-0.39
15.866	254.491	6.762	0.7383	0.1857	0.18	-0.21
13.128	254.570	5.693	0.7337	0.1830	0.24	-0.20
10.997	254.412	4.838	0.7315	0.1808	0.16	-0.25
8.987	254.549	4.003	0.7291	0.1789	0.15	-0.26
6.828	254.596	3.084	0.7269	0.1769	0.05	-0.26
4.790	254.691	2.192	0.7245	0.1749	0.22	-0.31
2.781	254.730	1.289	0.7219	0.1734	0.22	-0.09
0.841	254.329	0.395	0.7185	0.1718	0.12	0.11
12.019	253.514	5.270	0.9979	0.1858	0.13	-0.41
10.479	253.351	4.644	0.9979	0.1841	0.18	-0.52
9.030	253.356	4.040	0.9979	0.1829	0.09	-0.42
7.516	253.391	3.395	0.9979	0.1811	0.13	-0.61
6.123	253.446	2.791	0.9979	0.1798	0.18	-0.64
4.688	253.554	2.156	0.9979	0.1786	0.13	-0.59
3.308	253.614	1.535	0.9979	0.1776	0.10	-0.47
1.979	253.491	0.927	0.9979	0.1776	0.25	0.25
0.862	253.195	0.407	0.9979	0.1760	0.15	0.00
65.617	273.045	19.836	0.7423	0.2420	0.18	-0.06
62.102	273.135	19.102	0.7405	0.2387	0.06	0.08
58.808	273.675	18.368	0.7386	0.2350	0.05	-0.05
55.037	273.467	17.539	0.7368	0.2313	0.05	0.07
51.613	273.495	16.747	0.7351	0.2278	0.05	0.08
48.124	273.555	15.908	0.7333	0.2244	0.08	0.13
44.581	273.602	15.022	0.7315	0.2206	0.04	0.08
41.043	273.203	14.121	0.7297	0.2169	0.13	0.06
37.571	273.241	13.181	0.7280	0.2137	0.04	0.17
33.984	273.378	12.165	0.7262	0.2097	0.17	-0.05
30.463	273.468	11.126	0.7244	0.2064	0.13	0.01
27.069	273.502	10.084	0.7227	0.2031	0.19	-0.02
23.528	273.617	8.948	0.7210	0.2000	0.13	0.07
19.962	273.210	7.767	0.7193	0.1964	0.07	0.01
16.434	273.329	6.529	0.7175	0.1933	0.14	0.10
13.092	273.464	5.306	0.7159	0.1903	0.06	0.10
12.398	272.730	5.059	0.9979	0.1929	0.39	-0.07
10.365	272.794	4.282	0.9979	0.1909	0.09	-0.17
8.092	272.846	3.390	0.9979	0.1887	0.19	-0.28
6.029	272.895	2.558	0.9979	0.1870	0.08	-0.23
3.888	273.211	1.670	0.9979	0.1856	0.12	-0.08
1.836	272.652	0.800	0.9979	0.1834	0.37	-0.28

<sup>a</sup> Average pressure. <sup>b</sup> Average temperature. <sup>c</sup> Average density. <sup>d</sup> Average mole fraction of parahydrogen. <sup>e</sup> Adjusted thermal conductivity. <sup>f</sup> Adjusted experimental precision.

by Hanley et al. (6). An abbreviated set of values from ref 6 appears in Chart I in arrays TNZ and TPZ for the temperatures in array TT. However, the zero-density extrapolations for both normal and parahydrogen obtained from the experiment (5, 12) are lower than the values calculated by Hanley et al. (6). To match the experiment we lower the calculated values by a factor which is temperature dependent and given by

$$R = 1.0 - 0.028484 + 0.000070588T \quad (4)$$

The functional form used to describe the excess thermal conductivity is similar to the one used for oxygen (13).

$$\lambda_{\text{excess}}(\rho, T) = \alpha\rho + \delta[e^{\beta\rho^\gamma} - 1.0] \quad (5)$$

The coefficients of eq 5 are

$$\alpha = 0.17316 \times 10^{-2}$$

$$\beta = 2.5$$

$$\gamma = 0.34$$

$$\delta = 0.15811 \times 10^{-4} + 0.48207 \times 10^{-7}T$$

with  $\lambda$  in W/(m K) and  $\rho$  in mol/L.

We neglect the last term in eq 2, the critical contribution,  $\Delta\lambda_{\text{critical}}(\rho, T)$ , because the new data for parahydrogen are not close enough to the critical point to display a critical enhancement.

A listing of a short computer program to calculate the thermal conductivity of hydrogen for temperatures from 78 to 310 K and pressures to 70 MPa, provided that the density and the ortho-para composition are known, is given in Chart I.

## Discussion

The precision of the measurements can be established from several considerations. These are the linear regression statistics for a single point (the column STAT in Table I), the variation in the measured thermal conductivity with applied power, and the variation obtained in a curve fit of the thermal conductivity surface considering different densities, different ortho-para compositions, and different temperatures. All of these lead to a value of precision or reproducibility of a single measurement between  $\pm 0.6\%$  and  $\pm 1.0\%$ . The accuracy

Chart I

```

FUNCTION TCOPM2(DD,TIN,DP)
C INPUT, DENSITY MOL/L, TEMPERATURE K, DP PARA FRACTION
C OUTPUT, THERMAL CONDUCTIVITY OF HYDROGEN, W/M.K, & FERR 84
DIMENSION TNZ(26),TPZ(26),TT(26),G(3)
DATA(TNZ(I),I=1,26)/.0505,.0568,.0632,.0695,.0763,.0829,.0896,
1 .0962,.1026,.1092,.1157,.1220,.1282,.1342,.1401,.1458,.1514,
2 .1569,.1622,.1674,.1725,.1774,.1823,.1870,.1917,.1962/
DATA(TPZ(I),I=1,26)/.0529,.0617,.0714,.0816,.0924,.1028,.1125,
1 .1212,.1294,.1365,.1427,.1497,.1570,.1644,.1714,.1787,
2 .1723,.1758,.1791,.1828,.1863,.1899,.1935,.1972,.2010/
DATA(TT(I),I=1,26)/70.,90.,9C.,100.,110.,120.,130.,140.,150.,
1 160.,170.,180.,190.,200.,210.,220.,230.,240.,250.,260.,270.,
2 280.,290.,300.,310.,320./
DATA G/.1984312604E-02 , .3961103193E-04 , .1066433014E-06/
DD 3 I=1,26
IF(TIN.LT.TT(I)) GO TO 4
3 CONTINUE
4 CONTINUE
TCZN=TNZ(I-1)+(TNZ(I)-TNZ(I-1))*(TIN-TT(I-1))/(TT(I)-TT(I-1))
TCZP=TPZ(I-1)+(TPZ(I)-TPZ(I-1))*(TIN-TT(I-1))/(TT(I)-TT(I-1))
OPDIFF=TCZP-TCZN
TCZADJ=OPDIFF/0.75*(DP-C.25)
FACTOR=1.0-0.028484+0.000070588*TIN
TCZ=TCZN*FACTOR+TCZADJ*CRITH2(DD,TIN)
TCOPM2=TCZ+G(1)*DD+G(2)+G(3)*TIN*(EXP(2.1*DD**0.36)-1.0)
RETURN
END

FUNCTION CRITH2(RHO,TEMP)
C ADAPTED FROM D2 FOR HIGH TEMPERATURE H2
C VALID FROM 78 K UP, AMPL IS LINEAR
DATA (TC=32.938), (RHOC=15.556)
T=TEMP
DEN=RHO
IF(T.GT.77. AND. T.LT.108.25459) GO TO 4
CRITH2=0.
RETURN
4 CONTINUE
AMPL=0.00635363-0.00005843*T
DELTA=T-TC
RHOCENT=RHOC-0.008229*DELTA**1.5
DELRHO=DEN-RHOCENT
X1=.138*DELRHO
CRITH2=AMPL*EXP(-X1**2)
RETURN
END

```

of the measurement can be established, in principle, from the measurements and certain theoretical considerations, i.e., the Eucken factor for the rare gases (14). Accuracy can also be estimated by comparison to the results of others. These comparisons run between 1% and 2% for nitrogen and helium (7), argon (14), oxygen (13), propane (15), and normal hydrogen (5, 12).

The deviations of the parahydrogen results from the correlating surface are given in Table II. The average deviation for all hydrogen measurements is 0.37% (5), equivalent to 1.5% at the 3 $\sigma$  level.

Extrapolation of the present results for runs with a 99.79% para composition to zero density yields the values given Table III. The differences between these values and the theoretical

Table III. Extrapolated and Calculated Values of  $\lambda_0$  for Parahydrogen

T, K	$x_{\text{para}}$	$\lambda_0$ , W/(m K)			exptl - calcd, %
		extrapd	$\pm 2\sigma$	calcd (6)	
100.0	0.9979	0.08009	$\pm 0.00052$	0.08157	-1.84
125.0	0.9979	0.10613	$\pm 0.00059$	0.10759	-1.38
150.0	0.9979	0.12824	$\pm 0.00084$	0.12932	-0.85
150.0	0.7772	0.11999	$\pm 0.00039$	0.12144	-1.21
175.0	0.9979	0.14304	$\pm 0.00119$	0.14538	-1.63
200.0	0.9979	0.15434	$\pm 0.00083$	0.15733	-1.94
225.0	0.9979	0.16223	$\pm 0.00288$	0.16685	-2.85
250.0	0.9979	0.17311	$\pm 0.00151$	0.17576	-1.53
250.0	0.7186	0.16852	$\pm 0.00087$	0.17070	-1.29
275.0	0.9979	0.18372	$\pm 0.00460$	0.18452	-0.44
275.0	0.7157	0.18044	$\pm 0.00176$	0.18091	-0.26

calculations by Hanley et al. (6) range from -0.3% to -2.85%, and they were used to establish the offset given in eq 4. These differences are within the combined error estimates.

The comparison of the present results to those of others is limited because measurements of the thermal conductivity of parahydrogen are rare. Our earlier results (2), using a different method and a different apparatus, had an uncertainty of less than 2%. If one uses the computer program given in Chart I, the 17 experimental points given in ref 2 which fall into the present range of measurements show an average departure of 1%; thus, the two sets of measurements agree well within their combined uncertainties.

## Conclusion

The thermal conductivity of parahydrogen has been measured for temperatures from 100 to 275 K with pressures to 12 MPa for a para composition of 99.79%. For para compositions between 73% and 86% the pressures reach 70 MPa. Assuming that the dilute-gas thermal conductivity defines the ortho-para composition, and that the excess thermal conductivity is independent of ortho-para composition, the new measurements on parahydrogen were combined with new measurements on normal hydrogen to produce a new wide-range correlation for thermal conductivity of hydrogen. The estimated uncertainty in the thermal conductivity is  $\pm 1.5\%$  at the 3 $\sigma$  level as established from a fit of this thermal conductivity surface.

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