

The Thermal Conductivity of Solid and Liquid Parahydrogen

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The thermal conductivity of both solid and liquid parahydrogen has been measured for the first time at pressures greater than saturation, and found to be essentially constant within the experimental error over the range of conditions covered. The thermal conductivity of the solid was 0.0092 ± 0.0010 watt per cm. $^{\circ}$ K. over the temperature range 15° to 17° K. at pressures between 88 and 200 atm. The thermal conductivity of the liquid was estimated from the experimental measurements to be 0.0026 ± 0.0015 watt per cm. $^{\circ}$ K. in the temperature range 15.4° to 21.4° K. and from vapor pressure to 216 atm. The measurements were not sufficiently accurate to establish the minor effects of variations in temperature or pressure on the thermal conductivity of either the solid or the liquid.

DATA for the thermal conductivity of solid and liquid hydrogen have been published previously only for saturation pressure. In view of the current importance of hydrogen as a fuel and the possibility of using hydrogen as a working fluid in rocket technology, it was of interest to measure the thermal conductivity at higher pressures.

GENERAL METHOD

The sample of hydrogen was contained in a small cylindrical high-pressure cell. A steady thermal gradient was set up by heating the cell and its contents from the top, and by cooling the bottom through contact with a bath of liquid or slush hydrogen. The temperature profile of the cell was determined by means of three germanium thermometers calibrated by use of the cell as a vapor pressure thermometer with liquid parahydrogen as the fluid. The thermal conductivity of the sample was calculated from the power supplied to the top of the cell (suitably corrected for heat leak and for heat transmitted by the cell walls), from the cross section of the interior of the cell, and from the change in temperature per unit length of the cell.

APPARATUS

The design and size of the thermal conductivity cell was based largely upon the descriptions of apparatus published by Hill and Schneidmeyer (3), Gerritsen and Van der Star (2), and Webb, Wilkinson, and Wilks (6). The cell (Figure 1) was made of a piece of 0.430-inch I.D. stainless steel tubing with side walls 0.035 inch thick and an interior height of approximately 1.5 inches. The top and bottom of the cell consisted of copper plugs. The cell was given a hydrostatic test at 7000 p.s.i. before use. The cell was mounted inside a gas-tight brass can.

For use in determining the temperature profile of the hydrogen sample, three 24-gage copper wires were mounted through the walls of the cell as shown in Figure 1, exactly 0.375 ± 0.005 inch apart. The wires were brazed to the cell wall with an absolute minimum quantity of silver solder, and were wrapped around the germanium thermometers outside the cell. The exact positioning of the three copper wires, their insertion through the cell wall, and the soldering to give leak-tight joints were the most difficult steps in fabrication of the apparatus.

Hydrogen was supplied to the cell through a $\frac{1}{4}$ -inch O.D. stainless steel tube welded to the side of the cell near the

top. The hydrogen was pressurized in a separate "pump vessel" submerged in the same bath as the brass can containing the cell. The pump vessel and its operation have been described previously (1).

Direct current electrical power was supplied to the copper top of the cell from two 12-volt storage batteries. The power was accurately measured with the help of calibrated resistors in a previously used (1) power-measuring circuit. The wires for the heater and for the thermometer were led through the top of the can and outside of the cryostat through stainless steel tubes.

The brass can containing the cell was submerged in a bath of liquid or slush hydrogen inside a glass Dewar 4.75 inches in I.D. and 44.5 inches deep.

As shown in Figure 1, the cell inside the can was provided with a copper heat switch which was manipulated from outside and above the apparatus by a long rod. The purpose of the switch was to establish thermal contact, when desired, between the cell and a copper block brazed to the inner wall of the brass can, to hasten the rate with which the liquid hydrogen in the cell could be cooled and frozen. Unfor-

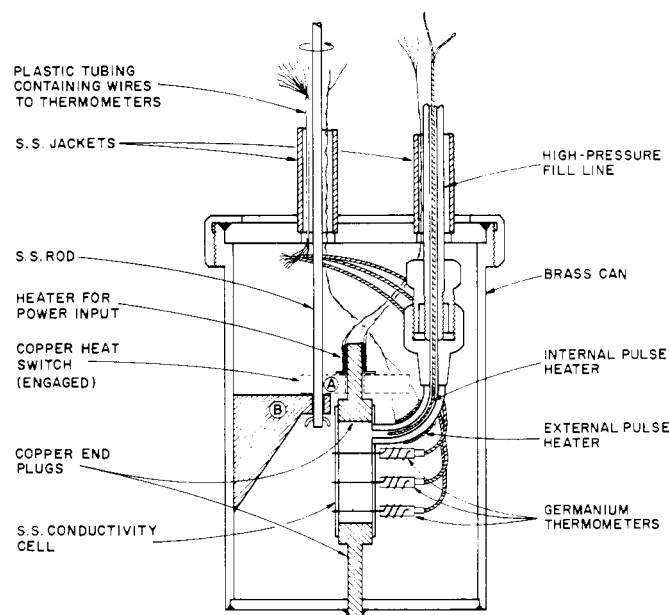


Figure 1. Thermal conductivity cell assembly

unately, the heat switch did not work as intended. Too much heat from outside apparently was conducted down the rod; the result was that closing the switch had a heating instead of a cooling effect. In practice, therefore, the heat switch had to be left in the open position and served no useful purpose.

HYDROGEN

The hydrogen used was obtained from a superinsulated container of commercial liquid which consisted of about 99% parahydrogen and 1% orthohydrogen. Information from previously published literature (3, 5) made it quite certain that, in the temperature range of the authors' measurements, the presence of about 1% orthohydrogen would make no measurable difference in the thermal conductivity.

SAFETY

Extensive precautions were taken to prevent fire or explosion that could occur if hydrogen were allowed to escape into the air of the room. The glass Dewar containing the bath of liquid hydrogen was surrounded by a heavy steel pipe 12 inches in O. D. This pipe was contained in a hollow cube, 3 feet on edge, with transparent Plexiglas walls. From the cube a 6-inch pipe passed outdoors through the roof of the building. A continuous small purge of nitrogen kept air out of the Plexiglas cube. The room in which the experiments were conducted had two large blowers in the ceiling which were operated continuously while experiments with hydrogen were in progress. The room was also equipped with automatic hydrogen-concentration monitors which would have sounded an alarm had any appreciable quantity of hydrogen escaped from the apparatus.

Had the thermal conductivity cell ruptured (which it did not) while under pressure, the walls of the glass Dewar might have been broken. Flying pieces of glass would have been stopped by the heavy steel pipe, and hydrogen from the cell and from the bath would have flowed out of the Plexiglas cube through the 6-inch pipe.

OPERATION

To measure the heat leak,—i.e., the heat which flowed from the outside of the apparatus down through the tubing into the brass can and to the cell,—the temperature profile was determined on the empty cell with no power on the heater. This was done by reading the temperatures of the three accurately spaced thermometers after a steady state was established in the cell. These measurements showed that the heat leak flowed from the top of the cell down to the bottom plug, in the same direction as the power applied while measurements of thermal conductivity were being made. This fact enabled us to make a relatively simple correction for the heat leak.

There were two parallel paths for the flow of heat in the cell; one was the cylindrical cell wall, and the other was the cell contents. The quantity of heat flowing through the cell wall was the same for a given temperature gradient, whether the cell was full or empty; this quantity was measured with no hydrogen in the cell, and was then subtracted from the quantity of heat which flowed down the cell when the cell was full of hydrogen.

In the actual runs, measured electrical d. c. power was applied to the top heater with the cell full of hydrogen at a known pressure. When a steady state was reached, the temperature profile was determined by reading the three thermometers. After suitable corrections were made for the heat leak and for the heat that flowed down through the cell walls, the thermal conductivity was calculated from the power applied, the cross section of the cell, and the change in temperature per unit length of the cell.

Table I. Experimental Values for the Thermal Conductivity of Parahydrogen

Temp., ° K.	Pressure, Atm.	Thermal Conductivity, Watt/Cm. ° K.
SOLID		
15.08	88.1	0.010
15.18	162	0.0091
17.11	201	0.0086
LIQUID		
15.41	0.16 ^a	0.0034
17.44	0.39 ^a	0.0030
17.60	0.41 ^a	0.0027
17.615	59.9	0.0021
21.37	1.70	0.0024
21.35	10.3	0.0036
21.36	102	0.0029
21.38	213	0.0023
21.37	216	0.0014

^a Saturation pressure.

RESULTS AND ACCURACY

The experimental results are given in Table I. Consideration of all sources of error leads to the conclusion that the accuracy of the values given in the table is about ± 0.001 watt per cm. ° K. for the solid and ± 0.0015 watt per cm. ° K. for the liquid. This corresponds to $\pm 11\%$ of the mean value for solid hydrogen, and $\pm 57\%$ of the mean value for the liquid. The principal sources of error lay in the facts that condensed hydrogen has a low thermal conductivity and that the wall thickness of the cell had to be sufficiently great to withstand a pressure of several hundred atmospheres. As a result, in the liquid runs 92% of the total heat flow down the cell was transmitted by the walls, and only 8% through the liquid parahydrogen sample. In the case of the solid, the situation was better: only about 68% of the heat flowed through the cell walls, and 32% through the solid parahydrogen. Calculation showed that there would have been no gain in making the diameter of the cell larger, as the wall thickness would have had to be correspondingly increased to withstand the pressure.

COMPARISON WITH EARLIER WORK

Solid Parahydrogen. The present measurements fit very well with those in the literature, as can be seen in Figure 2, in which the data of Hill and Schneidmesser (3) are plotted in circles, and the authors' in squares.

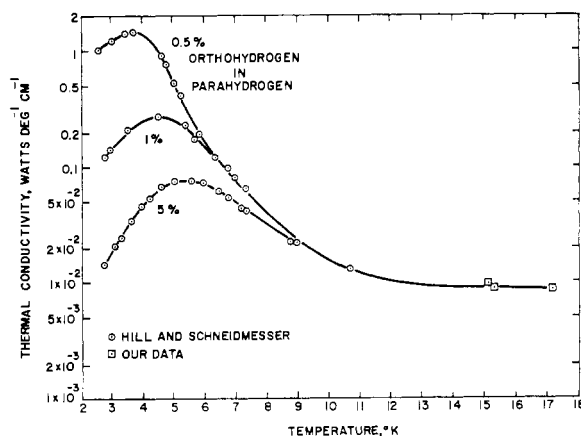


Figure 2. Thermal conductivity of solid parahydrogen

Liquid Parahydrogen. There are two sets of earlier measurements on liquid parahydrogen at saturation pressures. Powers, Mattox, and Johnston (5) obtained values ranging from 0.00118 at 16.83° K. to 0.00128 watt per cm. ° K. at 23.23° K. The other set of data is from unpublished (4) results of work carried out by McCall at the University of St. Andrews in Scotland; the values obtained there range from 0.00146 at 18.0° K. to 0.00166 at 25.6° K. The authors' mean value at saturation pressure is 0.0030 ± 0.0015 ; it agrees with McCall's results within the authors' estimated experimental error, but is slightly larger than the measurements made by Johnston and his associates. Considering the necessity of having the walls of the cell relatively thick to withstand higher pressures, the agreement of the present results with those previously published for the liquid at saturation pressure are considered to be fairly good.

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Salt Effect on Liquid-Liquid Equilibria in the Ethyl Acetate-Ethyl Alcohol-Water System

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Salt effect on the liquid-liquid equilibria of the ternary ethyl acetate-ethyl alcohol-water system has been investigated at 30° C. with potassium acetate and sodium acetate, respectively. Solubility and tie-line data of the two quaternaries have been determined at salt saturation in each case, as well as in the basic ternary in the absence of salt at that temperature. Salt effect is discussed. Certain features of the potassium acetate system indicate its advantage over sodium acetate. Data on the effect of some electrolytes on mutual solubilities of ethyl acetate and water at salt saturation at 30° C. also are presented here.

THE RECOVERY of anhydrous, technically pure ethyl acetate from its mixtures with ethyl alcohol generally involves an aqueous extraction step to remove the latter. The ternary system ethyl acetate-ethyl alcohol-water is, thus, of considerable industrial importance. Concurrent with separation of ethanol from the ester, lowering the mutual solubilities of the ester and water in presence of ethanol is important to minimize the loss of ester in the aqueous phase and to obtain a drier ester. The latter is particularly essential in certain organic processes requiring anhydrous conditions as in the production of ethyl acetoacetate. Each part of water is accompanied by about 10 parts of ester in the ternary azeotrope on distillation (5); even more ester is removed per part of water when the ethyl acetate-water binary is fractionated (5).

Although the industrial use of potassium acetate solution has been reported (2) for this system, no phase data seem to be available in literature. Such data have been published only for a few systems until now, although salt effect on binary liquid systems seems to have been investigated more extensively. The present work deals mainly with the effect of potassium acetate and sodium acetate on this ternary at 30° C.

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EXPERIMENTAL

Materials. ETHYL ALCOHOL. Absolute ethyl alcohol was purified by the method recommended by Vogel (10) (B.P. at 710 mm. of Hg, 76° C., d_4^{30} 0.7810). ETHYL ACETATE. Technical grade ester was treated with potassium carbonate and then fractionated (B.P. at 710 mm. of Hg, 75.4° C., d_4^{30} 0.8877). WATER. Pure double-distilled. SALTS. Anhydrous potassium acetate and sodium acetate and other salts, all of C.P. grade were used.

Procedure. The binodal curve and the tie lines for the ternary system at 30° C. were determined by the method of Othmer, White, and Trueger (4). About 3 hours' settling time, after 30 minutes of vigorous shaking, was sufficient for complete phase separation in tie-line determinations. The tie-line data were checked by the addition-point method.

The binodal curve of the quaternary system ethyl acetate-ethyl alcohol-salt-water at complete salt saturation was determined essentially by the trial and error procedure adopted by Swabb and Mongan (8). Known mixtures of ethyl acetate and fine dry salt crystals were titrated carefully with water and ethanol in 125-ml. stoppered glass conical flasks maintained at 30° C. in a thermostat (30° + 0.1° C.). The titrations were so adjusted that the disappearance of the two liquid phases closely coincided with the dissolution of all but a couple of salt crystals. This then was