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Thermal Conductivity of Condensed Gases. II. The Thermal Conductivities of Liquid Normal and of Liquid Parahydrogen from 15 to 27°K.

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The thermal conductivities of liquid normal and liquid parahydrogen have been measured over the temperature interval 15–27°K. They were found to be independent of the ortho–para composition and can be expressed by the equation $K = (1.702 + 0.05573T) \times 10^{-4}$, cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$. It is believed that our probable error is within 2%.

Introduction

The thermal conductivity of liquid hydrogen has not been reported previously. Since such information is useful in the calculation of heat transfer at very low temperatures and may thereby be of theoretical interest in the field of liquid state, we have carried out measurements over the temperature interval 15–27°K. in a parallel plate type of cell described previously.[1]

The correction for the heat flow through the wall of the cell was determined with the measuring chamber filled with helium at 200 mm. of pressure. The rates of heat flow thus obtained were corrected for helium heat flow from the conductivity data of Ubbink and deHaas.[2] We find it convenient to express this wall correction in the form of K_{wall}, the product of the rate of heat flow per degree through the wall, and l/A, the dimensional constant of the cell. Because K_{wall} changes rapidly with temperature, we have plotted in Fig. 1 the deviation of K_{wall} from the arbitrary function $9 \times 10^{-6}\,T$.

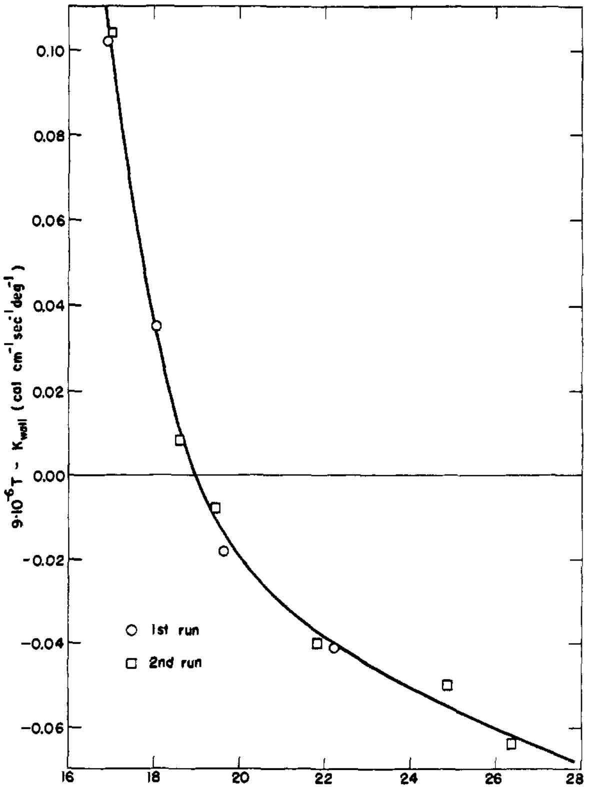

Fig. 1.—Cell-wall calibration curve.

Another important correction which we found it necessary to apply in this temperature range was one arising from the fact that it was not possible, at small values of ΔT, to cool the block to the temperature of the chamber heater. This resulted in a flow of heat from the block to the heater and necessitated a correction. The correction factor was determined by noting the effect on ΔT of keeping the block several degrees warmer than the heater, and at most it amounted to 5%.

For normal hydrogen, it was necessary to take account of the energy liberated in the conversion of orthohydrogen to parahydrogen. Unlike the heat that is generated at the top of the cell by resistance heating, this is evolved uniformly throughout the liquid under test. However, it can be shown that the effect is equivalent to that produced when one-half of this rate of heat evolution is liberated at the top of the liquid chamber.

Let us consider an element of cell volume, $A\mathrm{d}l$, where A is the cross-sectional area and l is the distance along the axis of the cell measured from bottom to top. Now the rate of heat flowing across the upper boundary of this volume element is

$$KA(\mathrm{d}T/\mathrm{d}l)$$

where K is the thermal conductivity coefficient of liquid hydrogen and is known with sufficient accuracy from the uncorrected data. That flowing across the lower boundary is

$$KA\left[\left(\frac{\mathrm{d}T}{\mathrm{d}l}\right) + \frac{\mathrm{d}}{\mathrm{d}l}\left(\frac{\mathrm{d}T}{\mathrm{d}l}\right)\mathrm{d}l\right]$$

The difference represents the rate of heat evolution from the ortho–para reaction. Therefore

$$KA\left(\frac{\mathrm{d}T}{\mathrm{d}l}\right) - KA\left[\left(\frac{\mathrm{d}T}{\mathrm{d}l}\right) + \frac{\mathrm{d}}{\mathrm{d}l}\left(\frac{\mathrm{d}T}{\mathrm{d}l}\right)\mathrm{d}l\right] = A\mathrm{d}l\rho H$$

or

$$\frac{\mathrm{d}^2T}{\mathrm{d}l^2} = -\frac{\rho H}{K}$$

where ρ is the density and H is the rate of heat evolution per gram of hydrogen per second. Our boundary conditions are that

$$T = T_l \text{ at } l = 0 \text{ and } \frac{\mathrm{d}T}{\mathrm{d}l} = 0$$

at $l = L$, where L is the total length of the cell. The solution of this differential equation is

$$T_u - T_l = \frac{\rho H}{2K}L^2$$

where T_u and T_l are the temperatures of the top and bottom of the cell, respectively. On the other

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(1) R. W. Powers, R. W. Mattox and H. L. Johnston, THIS JOURNAL, **76**, 5968 (1954).

(2) J. B. Ubbink and W. J. deHaas, *Physica*, **10**, 465 (1943).

hand, if all this energy were introduced at the top of the cell, then

$$AL\rho H = KA\frac{(T_u - T_l)}{L}$$

or

$$T_u - T_l = \frac{\rho HL^2}{K}$$

which proves the relationship stated above. H was calculated on the assumptions that the reaction proceeds entirely by the homogeneous mechanism and that the heat of reaction and the rate of reaction are temperature-independent in the temperature range over which this investigation extends. The most that this correction affected our final results, under any circumstances, was 4%.

The gas used in the first and second runs on normal hydrogen was of electrolytic grade. That used in all other runs was triply distilled material with an oxygen content of less than 1 p.p.m. By a run we mean a single filling of the cell, during which 2–5 points were obtained. Parahydrogen was prepared by condensing about 150 ml. of the liquid around 50 g. of chromic oxide gel ($t_{1/2} <$ 5 min.), contained in a copper bomb immersed in liquid hydrogen. It was allowed to remain in contact with this catalyst for more than half an hour, when it was immediately distilled into the measuring chamber.

TABLE I

THE THERMAL CONDUCTIVITIES OF LIQUID NORMAL AND OF LIQUID PARAHYDROGEN AT SEVERAL TEMPERATURES

Run no.	Material	Mean temp., °K.	ΔT	$K \times 10^4$, cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$
1	Normal H_2	16.84	4.31	2.69
		18.16	4.71	2.70
		19.88	5.51	2.83
		21.46	6.45	2.93
		22.79	6.22	3.02
2	Normal H_2	16.81	3.90	2.62
		19.08	4.63	2.70
		23.84	6.43	3.02
		24.29	7.20	3.02
3	Normal H_2	17.00	4.42	2.59
		18.58	4.80	2.68
		22.72	4.47	2.94
4	Para H_2	16.83	4.50	2.81
		18.97	4.76	2.81
		21.16	4.84	2.87
5	Para H_2	17.85	4.55	2.76
		19.66	4.52	2.86
		21.69	4.55	2.84
		23.23	5.42	3.05

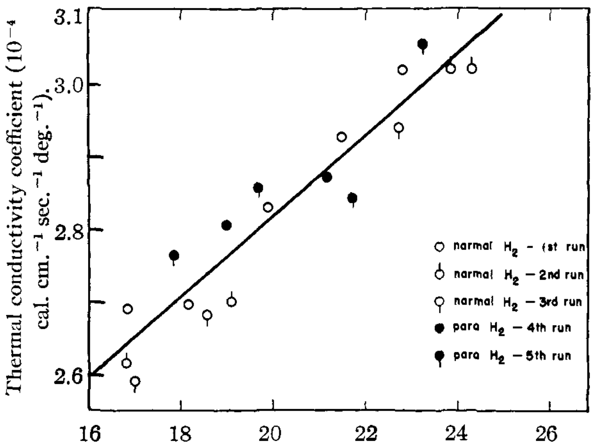

Fig. 2.—Thermal conductivity of liquid hydrogen as a function of temperature.

Our experimental data are shown in Table I and are shown graphically in Fig. 2. It is apparent from the figure that the conductivity of liquid parahydrogen is the same as that for the normal, within the limits of our experimental error. Furthermore, the thermal conductivity of liquid hydrogen increases with temperature; whereas it decreases for other low boiling liquids N_2, CO, CH_4, C_2H_4, which have been hitherto investigated.[1,3]

Our data have been fitted to the equation for a straight line by the method of least squares. The expression

$$K = (1.702 + 0.05573T)10^{-4}, \text{ cal. cm.}^{-1} \text{ sec.}^{-1} \text{ deg.}^{-1}$$

represents the data within an r.m.s. deviation of 1.6%.

We believe that the combined error in the dimensional constant of our cell and the calibration factor for the difference couple, the only sources of systematic error likely to be appreciable, is less than 2%. We consider that our error limit lies near 3.5%, and that the probable error is about 2%.

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(3) E. Borovik, A. Matveev and E. Panin, *J. Tech. Phys.* (*U.S.S.R.*), **10**, 998 (1940).