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THE THERMAL CONDUCTIVITY OF HEAVY WATER BETWEEN 75° AND 260°C AT PRESSURES UP TO 300 ATM

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Abstract—The thermal conductivity of heavy water having an isotopic purity of 99·85 per cent was measured with a vertical coaxial cylinder apparatus at pressures between 24 and 294 atm in the temperature range 75° to 260°C. The pressure range of the experiments included the critical pressure (218 atm).

Identical with the trend exhibited by water, the thermal conductivity of heavy water was found to increase with rising temperature to a shallow maximum near 110°C and to fall with a further rise in temperature. The influence of pressure on thermal conductivity was small, and at 75°C amounted to an increase of 0·77 per cent for a pressure rise from 1 to 100 atm. This is similar to the values reported for natural water by previous investigators [9, 11].

In comparison with natural water, the thermal conductivity of heavy water, in the range investigated, was always lower. According to these tests the ratio k_{H_2O}/k_{D_2O} increased almost linearly from 1·045 at 75°C to a value of 1·134 at 260°C.

No measurements of the thermal conductivity of heavy water have previously been reported at temperatures above 82°C. Below this temperature the present data are in good agreement with earlier work.

Résumé—La conductivité thermique de l'eau lourde ayant une pureté isotopique de 99,85 pour cent a été mesurée avec un appareillage à cylindres coaxiaux verticaux à des pressions variant de 24 à 294 atmosphères et à des températures variant de 75° à 260°C; le domaine des pressions utilisé dans l'expérience comprenanit la pression critique (218 atm).

Suivant la tendance montrée par l'eau, la conductivité thermique de l'eau lourde augmentait avec la température, jusqu'à un maximum aplati à 110°C environ et décroissait quand la température augmentait encore. L'influence de la pression sur la conductivité thermique était faible et, à 75°C, correspondait à une augmentation de 0,77 pour cent pour une augmentation de pression de 1 à 100 atm. Ces résultats sont analogues à ceux trouvés pour l'eau naturelle par les auteurs précédents [9, 11].

Comparée à celle de l'eau naturelle, la conductivité thermique de l'eau lourde était toujours inférieure, dans le domaine étudié. D'après ces expériences, le rapport k_{H_2O}/k_{D_2O} augmentait presque linéairement de 1,045 à 75°C à 1,134 à 260°C.

Jusqu'à présent, il n'existait pas de résultats connus de mesures de conductibilité thermique de l'eau lourde à des températures dépassant 82°C. Au-dessous de cette température, les résultats présents sont en bon accord avec les études précédentes.

Zusammenfassung—Die Wärmeleitfähigkeit von schwerem Wasser mit einer Isotopenreinheit von 99,85 Prozent wurde in einer Apparatur mit senkrechten koaxialen Zylindern bei Drücken von 24 bis 294 atm und Temperaturen von 75° bis 260 °C gemessen (kritischer Druck 218 atm).

Ähnlich wie bei leichtem Wasser hat auch die Wärmeleitfähigkeit von schwerem Wasser ein flaches Maximum bei 110 °C. Der Druckeinfluss ist gering; bei 75 °C erhöht sich die Wärmeleitfähigkeit um 0,77 Prozent bei Druckerhöhung von 0 auf 100 atm. Für leichtes Wasser wurde ähnliches beobachtet [9, 11].

Im Versuchsbereich war die Wärmeleitfähigkeit von schwerem Wasser geringer als die von leichtem Wasser. Das Verhältnis k_{H_2O}/k_{D_2O} steigt linear von 1,045 bei 75 °C zu 1,134 bei 260 °C an.

Für den Bereich oberhalb 82 °C wurden bisher keine Ergebnisse mitgeteilt. Unterhalb dieser Temperatur stimmen die Werte dieser Arbeit gut mit früher veröffentlichten überein.

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Abstract—«Исследование теплопроводности тяжелой воды в интервале температур от 75° до 260°C и давления до 300 ат.»

Коэффициент теплопроводности тяжелой воды с изотопной чистотой 99,85% определяется обычным методом в диапозоне температуры от 75° до 260°C и давлений от 24 до 294 ат, включая и критическое давление (218 ат).

Было установлено, что с повышением температуры коэффициент теплопроводности тяжелой воды увеличивается, при температуре 110°C достигает максимума, а затем уменьшается. Повышение давления мало влияет на величину коэффициента теплопроводности, например, при увеличении давления от 1 до 100 ат. при 75°C изменение теплопроводности составляет 0,77%. Аналогичные данные были получены другими исследователями [9,11] для обычной воды.

Коэффициент теплопроводности тяжелой воды k_{D_2O} при исследованных режимных параметрах меньше коэффициента теплопроводности обычной воды k_{H_2O}. Ожижение $\frac{k_{H_2O}}{k_{D_2O}}$ является линейной функцией температуры, при 75°C это ожижение равно 1,045, а при 260°C — 1,134. Экспериментальные данные по коэффициенту теплопроводности тяжелой воды при температурах выше 82°C впервые приведены в этой статье, при температурах ниже 82°C данные авторов совпадают с ранее опубликованными.

LIST OF SYMBOLS AND DIMENSIONS

k = thermal conductivity (cal cm^{-1} °C^{-1} sec^{-1});
k_0 = thermal conductivity at zero pressure (cal cm^{-1} °C^{-1} sec^{-1});
L = length of emitting cylinder (cm);
P = absolute pressure (atm);*
Q = heat flow (cal sec^{-1});†
r_1, r_2 = radii of emitting and receiving cylinders, respectively (cm);
t_1, t_2 = surface temperatures of emitting and receiving cylinders, respectively (°C);
T = absolute temperature (°K);
α = pressure coefficient of thermal conductivity (atm^{-1}).

1. INTRODUCTION

The thermal conductivity of heavy water in its liquid phase at 1 atm pressure has been studied by three investigators.

Bonilla and Wang [1] measured the thermal conductivity of 93 per cent pure heavy water relative to natural water in a two-gap horizontal plate apparatus between 15° and 60°C. According to these authors' observations the ratio of the respective conductivities k_{H_2O}/k_{D_2O} varied linearly with temperature, rising from 1·016 at 10°C to 1·033 at 60°C.

Meyer and Eigen [2] investigated a sample of heavy water of 95 per cent purity using a modification of the flat plate apparatus characterized by an unusually wide gap (5 cm) and a small cross-section (3 cm^2).

The most extensive measurements are due to Challoner and Powell [3] who studied the thermal conductivity of 99·95 per cent pure heavy water in a guarded hot-plate apparatus over the range from 2° to 82°C.

Despite the good numerical agreement between the results of the various authors—the deviation of individual data from a mean curve was rarely more than 1 per cent—some characteristic trends and differences became apparent during a recent survey of these three investigations, on the basis of which new values were proposed for the thermal conductivity of heavy water in the temperature interval from 10° to 80°C [11].

Heavy water is used in atomic power plants as a reactor coolant and moderator, and it was chiefly because of the former application that more data on its thermal conductivity were required covering a wide range of temperature and pressure.

2. DESCRIPTION OF METHOD

The vertical co-axial cylinder method with guard rings, which had been successfully employed in two previous investigations on the thermal conductivity of liquefied gases [4, 5], was also chosen for the determination of the thermal conductivity of heavy water. In this method, heat is generated in an inner emitting cylinder, and conducted radially through the narrow fluid-filled annulus to a co-axial receiving cylinder. From the measured surface

* 1 atm = 660 mm Hg.
† 1 cal = 4·184 J.

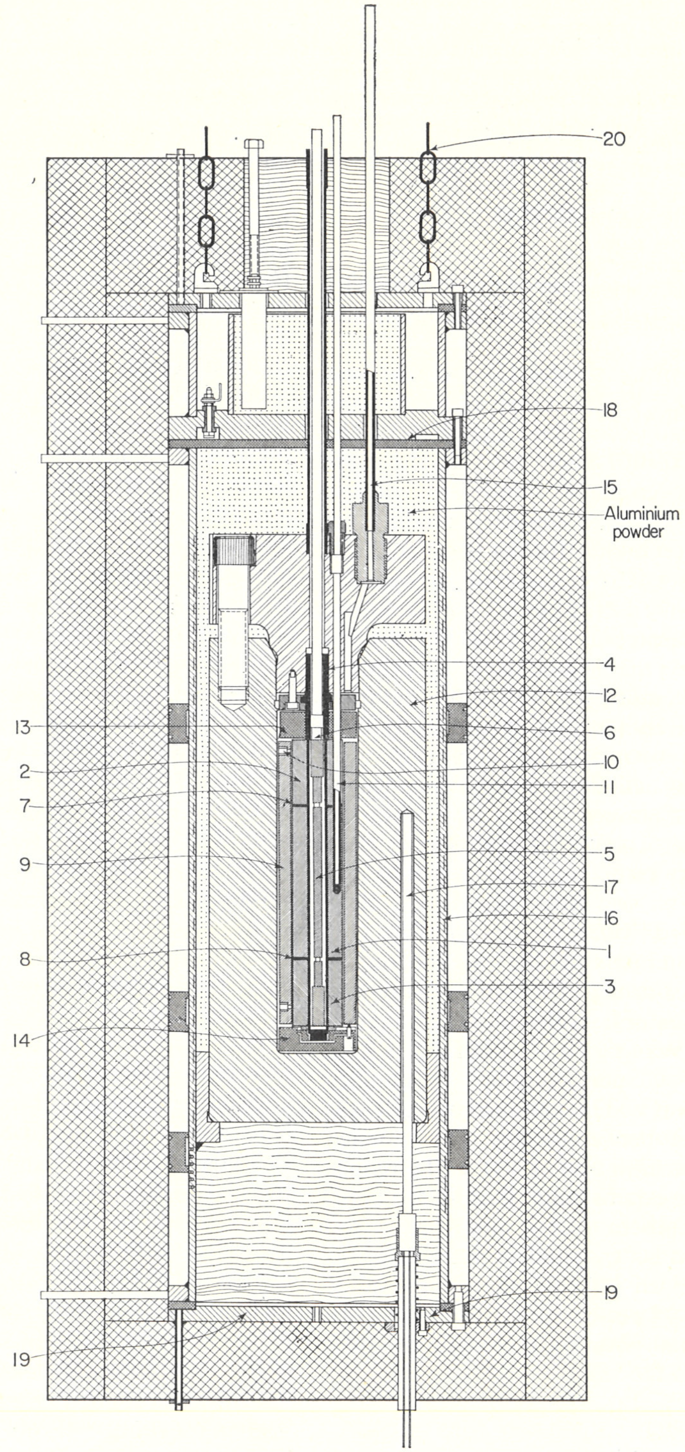

FIG. 1. Cross-section of autoclave and thermostat.

temperature of the emitting and receiving cylinders, the amount of heat conducted radially through the annulus, and the dimensions of the apparatus, the thermal conductivity can be evaluated from the following equation:

$$k = Q \ln (r_2/r_1)/2\pi L(t_2 - t_1).$$

3. EXPERIMENTAL

3.1 *The conductivity cell*

An annotated cross-section of the conductivity cell, the retaining autoclave and the thermostat is shown in Fig. 1.

The inner emitting cylinder (1) and two heat guards (2) and (3) of the same diameter were mounted on a stainless steel sheath (4). The emitting cylinder and each heat guard were heated by independently controlled electric heaters (5), consisting of uniform windings of constantan wire on a glass former (6). Each heat guard was separated from the emitting cylinder by mica washers (7) and (8) of 0·1 cm thickness. Current for the heaters was drawn from a large nickel–iron battery. An outer receiving cylinder (9) was arranged coaxially about the emitting cylinder to form an annulus of nominally 0·02 cm width. Accurate coaxial alignment was achieved by three uniformly spaced mica leaves of equal thickness, inserted into each end of the annulus and held in place by grub screws (10).

Holes were drilled through the emitting and receiving cylinders, and into these holes, close fitting thin walled stainless steel sheaths (11) were inserted, to protect the thermocouples placed in them from the effects of pressure and the chemical action of the substance investigated.

The cylinders were made of Hidural 5, a high conductivity copper alloy, supplied by Langley Alloys, Ltd., Slough. The conductivity cell was placed within a monel autoclave (12) designed for pressures up to 300 atm at 400°C. To reduce convection in the experimental fluid in the autoclave, the free spaces above and below the emitting and receiving cylinders were filled as far as possible with suitably shaped pieces of fired pyrophillite (wonderstone) (13) and (14). The autoclave was filled by means of the inlet connexion (15) in the lid.

3.2. *The thermostat*

The assembled autoclave was placed in a heavy gauge steel tube (16) which carried on its external surface an electric heater. To ensure good thermal contact, whilst at the same time providing for the differential thermal expansion, the inter-space between the heat tube and the autoclave was filled with aluminium powder. The temperature of the conductivity cell was maintained by a Sunvic Resistance Thermometer Controller, Type RT 2, which controlled the current in the thermostat heater. The temperature-sensing element, a platinum resistance thermometer (17), was placed in a hole drilled in the body of the autoclave.

In addition, manually controlled electric heaters (18) and (19) were fitted to the top and bottom of the heater tube to compensate for end losses. All thermostat heaters were fed from the electric mains via a common voltage stabilizer and individual variable transformers. Chromel–alumel thermocouples were attached to various parts of the thermostat, so that axial temperatures could be checked and the heater controls adjusted accordingly (see Fig. 2).

The complete assembly of autoclave and thermostat was suspended on four chains (20) and was thermally insulated. The temperature stability with this arrangement was very good. Variations from a chosen value over a period of several hours were less than 0·01°C, and in some cases this stability was maintained for several days.

3.3. *The pressure transmitter and expansion vessel (Fig. 2)*

Part of the investigation was conducted at elevated pressures not only because of the increasing saturation pressure with increasing temperature, but also because it was intended to study in general the effect of pressure on the thermal conductivity in the temperature region above 100°C. In view of the wide range of experimental conditions (pressure, temperature), some expansion of the test fluid, filled initially at ambient conditions into the autoclave, will take place. To allow for these changes in volume, and at the same time separate the heavy water from the pressurizing fluid, an expansion and pressure transmitting vessel *PT* was arranged between the autoclave containing the conductivity cell and

Table 5. The ratio $k_{H_2O}k/_{D_2O}$. Values for k_{H_2O} derived from Timrot's and Vargaftik's paper [9], those for k_{D_2O} from Table 4

Pressure (atm)	Temperature (°C)									
	80	100	120	140	160	180	200	220	240	260
100	1·0453	1·0522	1·0611	1·0727	1·0839	1·0936	1·1047	1·1121	1·1230	1·1315
200	1·0463	1·0520	1·0621	1·0727	1·0830	1·0917	1·1015	1·1116	1·1253	1·1325
300	1·0450	1·0518	1·0631	1·0728	1·0839	1·0915	1·1040	1·1149	1·1275	1·1356
400	1·0482	1·0516	1·0640	1·0746	1·0848	1·0950	1·1064	1·1162	1·1297	1·1386
Mean value	1·0462	1·0519	1·0626	1·0732	1·0839	1·0929	1·1041	1·1137	1·1264	1·1345
Standard deviation	0·0012	0·0002	0·0011	0·0008	0·0006	0·0014	0·0018	0·0019	0·0025	0·0028

to that of heavy water, k_{H_2O}/k_{D_2O}, as a quantity for checking the internal consistency of experimental results was demonstrated. This quantity was computed using the smoothed experimental results contained in Table 4 for heavy water and Timrot's and Vargaftik's smoothed values of the thermal conductivity of light water. These k_{H_2O}/k_{D_2O}-values were compiled in Table 5 and two facts worth mentioning can be observed, viz.:

(a) the ratio k_{H_2O}/k_{D_2O} appears to be independent of pressure within the ranges of pressure and temperature covered in this investigation.

(b) between 100° and 260°C all values can be satisfactorily correlated by the following linear expression

$$k_{H_2O}/k_{D_2O} = 5{\cdot}3 \times 10^{-4} \times t + 1{\cdot}00 \quad (4)$$

where t is the temperature in degrees Centigrade. At the lower end of the temperature range of this work, i.e. between 80° and 100°C, the experimental k_{H_2O}/k_{D_2O}-values begin to deviate slightly from the linear equation (4), but are in good agreement with the corresponding values derived from the analysis of the results of earlier workers [10].

Preparations are in hand to extend the range of this work to the critical temperature of heavy water with an improved apparatus. The opportunity may then be taken to redetermine the conductivity of light water between 260° and 400°C, which so far has been investigated only once, viz. by Timrot and Vargaftik [9] in 1940. The remarkable consistency of certain properties of heavy and light water, derived from this work and from Timrot and Vargaftik's experiments, appears to lend support for the validity of the latter authors' data on light water within the ranges of temperature and pressure covered in this research.

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of light and heavy water. The results of this research on the latter substance were correlated by the empirical relation

$$\alpha = 1{\cdot}81 \times 10^{-3}\, T \exp(4{\cdot}264 \times 10^{-9}\, T^3) \quad (3)$$

In view of the scatter of the α-values derived from these experiments, it does not seem justified to attach any physical significance to the small difference in the pressure coefficients for light and heavy water. This opinion is supported by the results of a recent study by Lawson *et al.* on the thermal conductivity of light

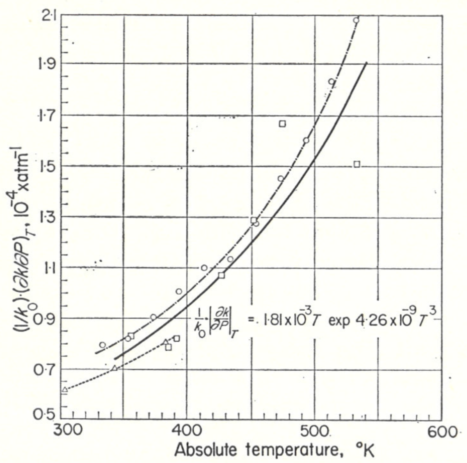

FIG. 4. Experimental values of the pressure coefficient of the thermal conductivity of light and heavy water:
····△···· H_2O, Lawson *et al.*[11];
—·—○—·— H_2O, Timrot and Vargaftik[9];
—□— D_2O, this research.

water at pressures up to 8000 kg/cm² and temperatures from 30° to 130°C [11]. The analysis of the data of these authors within the pressure range of linear dependence between pressure and thermal conductivity, yielded α-values which are distinctly lower than those derived from Timrot's and Vargaftik's measurements, and even fall below those for heavy water.

In view of this discrepancy it was not possible to decide with certainty whether the pressure coefficients of light and heavy are different.

Values of the pressure coefficient α for heavy water were computed from equation (3) and were compiled in Table 3. With the aid of these values the thermal conductivity of heavy water was calculated up to 500 atm and 260°C. These data can be found in Table 4.

In a previous paper [10] the usefulness of the ratio of the thermal conductivity of light water

Table 3. *The pressure coefficient of the thermal conductivity of heavy water.*

$$\left[\alpha = 1/k_0 \times \left(\frac{\partial k}{\partial P}\right)_T\right].$$

t (°C)	$\alpha \times 10^4$ (atm^{-1})	t (°C)	$\alpha \times 10^4$ (atm^{-1})
80	0·77	180	1·22
100	0·84	200	1·35
120	0·92	220	1·49
140	1·01	240	1·65
160	1·11	260	1·84

Table 4. *Thermal conductivity of heavy water* (10^{-4} cal cm^{-1} °C^{-1} sec^{-1})*
(Smoothed data)

Pressure (atm)	Temperature (°C)									
	80	100	120	140	160	180	200	220	240	260
100	15·52	15·66	15·60	15·43	15·20	14·91	14·53	14·09	13·53	12·91
200	15·64	15·79	15·74	15·59	15·36	15·09	14·73	14·29	13·75	13·15
300	15·76	15·93	15·89	15·74	15·53	15·27	14·92	14·50	13·97	13·38
400	15·87	16·06	16·03	15·90	15·70	15·45	15·11	14·71	14·19	13·61
500	15·99	16·20	16·17	16·05	15·86	15·63	15·31	14·91	14·41	13·85

* To convert cal cm^{-1} °C^{-1} sec^{-1} into W cm^{-1} °C^{-1} multiply by 0·2389.

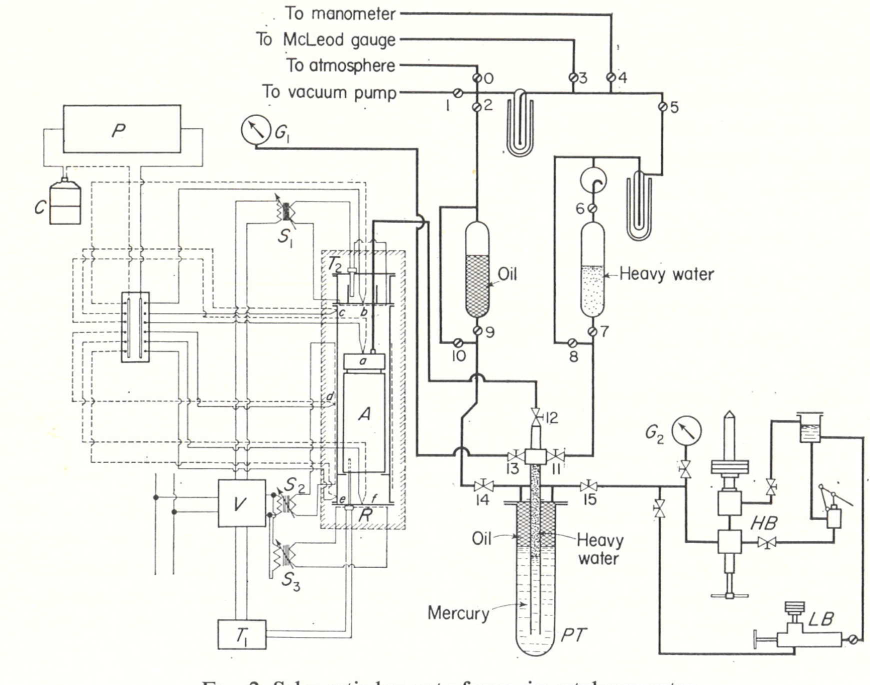

FIG. 2. Schematic lay-out of experimental apparatus.

A	Conductivity cell.	R	Resistance thermometer
P	Potentiometer	S_1, S_2, S_3	Variable transformer
C	Cold junction	G_1, G_2	Pressure gauges
a—f	Thermocouples	HB	High pressure balance
V	Voltage stabilizer	LB	Low pressure blance
T_1, T_2	Thermostat controller	PT	Pressure transmitter.

the high pressure and low pressure balances *HB* and *LB*.

The lower half of this vessel was filled with mercury as a separating fluid between the oil from the pressure balance and the heavy water that rested in the immersion tube above the mercury. The volume of the immersion tube was sufficiently large to allow for the expansion of the quantity of liquid contained in the autoclave. The pressure of the test fluid in the autoclave was kept constant at a desired value by occasionally operating the oil presses of the high or the low pressure balances *HB* or *LB*, respectively.

3.4. *Temperature measurement and calibration of thermocouples*

All temperatures were measured with copper–constantan thermocouples, and an ice bath was used to provide a reference temperature. The e.m.f.s generated by the couples were measured with a Diesselhorst potentiometer having a least count of 0·1 μV. With these thermocouples a temperature variation of 0·0025°C could be detected.

The thermocouples were made of multi-stranded wires to minimize the effects of inhomogeneities on thermal e.m.f.s; twelve wires, 44 s.w.g. formed the constantan member, and four wires, 40 s.w.g. the copper member. The junctions were silver-soldered into small copper cylinders which, in turn, were hard-soldered to the ends of thin-walled stainless steel tubes. Electrical insulation inside the stainless steel tube was provided by twin-bore alumina tubing. The cold junctions were made in an identical way, with the exception that the wires were supported by twin-bore silica tubes and the soldered junctions at the ends were electrically insulated by a thermo-setting resin. The upper ends of the hot junctions contained in the stainless steel tubes were also sealed by a thermosetting resin after they had been dried by heating to about 300°C. This construction eliminated slow oxidation of the thermocouples and the ensuing effects on the thermal e.m.f.s.

The two thermocouples for measuring the important temperature difference across the fluid-filled annulus were located in the middle of the emitting and receiving cylinders, respectively. For the control of the heat guards, a thermocouple was placed in each guard cylinder about 3 mm from the separating mica washer. By means of steel springs, which pressed the thermal junctions against the closed end of the retaining sheaths, good thermal contact was ensured.

The calibration was performed by replacing the autoclave shown in Fig. 1 by a block of copper of the same dimensions. A central hole was drilled in the block to accommodate a NPL-calibrated platinum resistance thermometer, and the thermocouples were placed in holes drilled on a pitch circle round it. The temperature was then controlled by the same thermostat that was used when making conductivity measurements. An ice bath provided the reference temperature. Over the temperature range from 20° to 385°C the e.m.f.–temperature relationship could be represented by a cubic equation.

Although multistranded wires were used in the construction of the couples, small differences of the order of 1 μV were observed for the same temperature between individual couples. The thermocouples were therefore frequently intercalibrated *in situ* in the thermal conductivity cell with the emitter heaters switched off, as explained later.

3.5. *The geometric constant, and its dependence on temperature*

The equation for the evaluation of the thermal conductivity given in Section 2 contains the term $\ln (r_2/r_1)/2\pi L$ which is solely dependent on the linear dimensions of the apparatus used. It is usually referred to as the geometric constant of the conductivity cell.

To obtain a high degree of absolute accuracy, precision machining of the emitting and receiving cylinders was essential. The construction of the cell used in this research was carried out by Pitter Gauge and Precision Tool Company, Ltd., Woolwich, who also determined the dimensions contained in the geometric constant.

It was found that the deviations of the diameters of emitting and receiving cylinders from mean values of 3·3062 cm and 3·3493 cm, respectively, were less than 0·0001 cm at any part of their entire length.

The dimensions of the cylinders at the temperature of the experiments were calculated from the known dimensions at 20°C and the coefficient of thermal expansion of Hidural 5 quoted by Langley Alloys, Ltd., Slough [6]. The geometric constant changes only by 5 per cent over the temperature range from 75° to 360°C, so that, even if the data for Hidural 5 were somewhat in error, the effect on the accuracy of the reported data on the thermal conductivity of heavy water would be almost negligible.

Because of the low compressibility of metals, pressure had an insignificant effect on the dimensions of the cylinders.

3.6. *The heater and electrical energy measurement*

The emitting cylinder and the two guard sections were heated by an electrical heating element which consisted of three separate, closely wound sections of 30 s.w.g. glass-covered, oxidized constantan wire.

Various configurations of this kind of heater were constructed and tried; the one described below was found to be the most satisfactory for use at elevated temperatures.

It consisted of a central, 2 ft long, thin-walled, stainless steel tube of 0·25 cm external diameter as structural support, on the surface of which, alternately, glass tubes and glass rods of 0·2 cm diameter and a total length equal to that of the heater were fastened. Over this assembly the three heater sections were wound and hard-soldered to 22 s.w.g. pure silver leads, which were brought down to the requisite position inside the glass tubes. In addition to the current-carrying leads, a pair of potential leads was connected to the centre section of the heater. Several layers of glass tape wound over all sections provided additional protection against mechanical and electrical hazards, and also ensured a close fit in the heater sheath.

the precipitation of the alloying constituents. The material for the receiver which had been annealed and slowly cooled to ambient temperature was therefore in a more stable condition.

From the reproducibility of these experiments, demonstrated by the results of test (30) to (37), it can be concluded that no irreversible change of the dimensions of the emitter assembly took place below an operating temperature of 260°C. Above this temperature, the linear dimensions of the emitter continually and irreversibly increased. It was thus impossible to apply the appropriate corrections to the individual results obtained during this phase and they were consequently omitted from this paper. The only result which appeared worthwhile studying was the point obtained immediately before the leak in the apparatus terminated the experimental work. Re-evaluating this result with the cell dimensions obtained after the inspection gave a value of the thermal conductivity which seems to suggest that the ratio of the thermal conductivity of light water to that of heavy water continues to rise with increasing temperature.

5. DISCUSSION

A comparison of the results of this research with those by other authors was confined to the lower end of the temperature range of this work (75°C) which slightly overlapped the range of Challoner and Powell's [3] investigation. The data of the latter authors, together with those by Bonilla and Wang [1], and Meyer and Eigen [2] were reviewed in a recent publication by one of the writers [10] and new mean values between 10° and 80°C for the thermal conductivity of heavy water were proposed. Table 2 contains the individual values and the proposed best average value for the thermal conductivity of heavy water at 75°C and 1 atm. Given in parentheses are the individual deviations from the new mean value. As can be seen the agreement is excellent which is the more noteworthy as different experimental methods were used by the various authors.

Table 2. Thermal conductivity of heavy water at 75°C *and* 1 atm (10^{-4} cal cm^{-1} sec^{-1} °C^{-1}).

(Deviation from proposed average value in parentheses below.)

Challoner and Powell [3]	Bonilla and Wang [1]	This research	Proposed average value
15·21 (−0·39%)	15·32 (+0·33%)	15·27 ±0·00%	15·27

The general trend in the variation of the thermal conductivity of heavy water with temperature, as exhibited in Fig. 3, is analogous to that of light water. There is a rise of thermal conductivity with temperature up to a shallow maximum which occurs at a somewhat lower temperature than for light water, viz. at about 110°C, followed by a gradual fall towards higher temperatures.

The influence of pressure on the thermal conductivity of heavy water was studied over the entire temperature range of these experiments. Analysis of the experimental data showed that over the comparatively narrow range investigated, the effect of pressure on the thermal conductivity can be adequately expressed by a linear equation

$$k = k_0 + (\partial k/\partial P)_T . P \qquad (2)$$

The choice of the fictitious quantity k_0 appeared to be justified as it was immediately obtainable by direct extrapolation of the experimental pressure—thermal conductivity isotherms to zero pressure without further recourse to other physical properties not studied in this investigation. Modifying this equation leads to

$$k = k_0 + k_0 . (1/k_0) . (\partial k/\partial P)_T . P = k_0(1 + \alpha P) \qquad (2a)$$

where $\alpha = (1/k_0)(\partial k/\partial P)_T$, is the pressure coefficient of the thermal conductivity.

The constants required in equation (2a) were found from a least square analysis of the unsmoothed isothermal experimental results. The resultant pressure coefficients were plotted in Fig. 4 where they are compared with the corresponding values on light water obtained from an analysis of the smoothed data of the thermal conductivity of light water by Timrot and Vargaftik [9]. These observers conducted their experiments over ranges of pressure and temperature similar to those on this investigation. Identical trends and similar numerical values were found for the pressure coefficients of the thermal conductivity

Table 1. *Thermal conductivity of heavy water: experimental data*

No.	Temperature (°C)	Pressure (atm)	Thermal conductivity (10^{-4} cal cm^{-1} sec^{-1} °C^{-1})	Number of determinations	Standard deviation 10^{-4} cal cm^{-1} sec^{-1} °C^{-1}
33	75·7	294	15·73	5	0·031
32	75·8	24	15·31	7	0·036
12	82·5	97	15·65	6	0·056
11	82·5	195	15·74	5	0·045
10	82·5	294	15·84	6	0·054
9	82·6	24	15·48	6	0·049
8	112·1	97	15·66	5	0·024
5	112·2	24	15·42	5	0·040
7	112·2	195	15·69	6	0·029
6	112·2	294	15·79	7	0·063
4	118·4	97	15·58	7	0·038
3	118·4	195	15·68	5	0·025
2	118·4	294	15·83	6	0·057
1	118·5	24	15·48	9	0·072
30	137·4	24	15·42	6	0·086
31	137·4	294	15·81	6	0·092
16	153·2	97	15·27	4	0·089
18	153·3	24	15·09	4	0·072
13	153·3	24	14·95	7	0·055
15	153·3	195	15·35	6	0·070
14	153·3	294	15·39	6	0·053
17	153·3	294	15·55	4	0·048
22	178·0	97	15·01	5	0·044
23	178·0	97	15·15	5	0·021
21	178·0	195	15·14	7	0·054
19	178·1	24	14·85	6	0·061
20	178·1	294	15·43	6	0·141
37	200·6	195	14·79	5	0·022
35	200·7	97	14·55	6	0·044
36	200·7	294	14·92	4	0·042
24	212·0	97	14·28	8	0·047
25	212·0	195	14·36	5	0·025
26	212·0	294	14·55	6	0·045
34	228·6	97	13·89	6	0·077
29	259·6	195	13·23	5	0·040
28	259·6	294	13·42	6	0·032
27	259·8	97	13·04	5	0·034

from previously established trends, mainly the dependence of k_{H_2O}/k_{D_2O} on temperature, was noticed. The experimental work was unfortunately terminated by the occurrence of a leak in the lid of the autoclave whilst operating the apparatus at 300 atm and 370°C. The opportunity was taken to inspect the conductivity cell and redetermine its vital dimensions. It was found that the dimensions of the receiver (part (9) in Fig. 1) were virtually unchanged, whereas the average diameter of the emitter and the guard rings (parts (1), (2) and (3), respectively) had increased from their original value of 3·3062 cm to 3·3129 cm. The investigation into the causes of this unexpected phenomenon revealed that the material used for the construction of the receiver had been annealed prior to the final machining operations, whilst the material for the emitter had been used as received from the manufacturers of the alloy.

The material used for the construction of the conductivity cell was a precipitation hardening alloy and according to the manufacturers the dimensional changes observed are associated with

This construction offered a number of advantages over previous designs, the principal one being a considerable reduction, if not elimination, of axial heat exchange between individual heater sections. The heat dissipated in the emitting cylinder was evaluated from measurements of the current flowing through the appropriate heater section and the potential difference across it. The current was determined by measuring the potential difference across a standard resistance of 0·01 Ω; the potential difference across the heater was obtained with the aid of a potential divider having a ratio of 10^4:1. All measurements of potential differences were made with a Diesselhorst-pattern potentiometer, made by H. Tinsley and Co., Ltd., London.

Because of the small currents employed, and the high electrical conductance of the leads, no corrections were required for the small quantity of Joule's heat generated in those portions of the leads which were situated in the centre section of the heater.

A further error could arise through conduction of heat along the 22 s.w.g. silver leads which carried the current to the main heater. The guard ring heaters, however, were always carefully adjusted so that the axial temperature difference between the centre of the emitter and the guard rings was only about 0·045°C. Because of the close contact between the heater and the metallic heater sheath (4), which in turn fitted with a press fit into the emitter cylinder assembly, a similar small axial temperature variation can be assumed for the heater itself. As, furthermore, the leads to the main heater section are exposed over a length of about 5 cm to near isothermal conditions it was considered unlikely that heat conduction along those leads was of any significance.

3.7. *The filling and emptying of autoclave and pressure transmitter*

Just above the pressure transmitter *PT* in Fig. 2, a glass apparatus is shown, the main purpose of which was to ensure gas-free filling of heavy water into the autoclave and the relevant section of the pressure transmitter, and, in view of the high cost of heavy water, also to facilitate its complete recovery from all parts of the experimental apparatus after the tests.

It can be seen from Fig. 2 that the pressure transmitter consists in effect of three chambers, occupied by mercury, oil and heavy water, respectively. To fill this vessel, valve (12) was temporarily removed and mercury admitted through the open connexion up to half the height of the immersion tube. Valve (12) was then replaced, and the oil and heavy water chambers simultaneously evacuated via valves (10) and (8), respectively. A vacuum better than 0·1 mm Hg was attained. The oil chamber was then filled with previously outgassed vacuum oil through valves (9) and (14), valve (15) being kept closed during that operation. After closing of valve (14), the heavy water chambers of the pressure transmitter and the autoclave were evacuated through valves (11) and (12), and previously outgassed heavy water was admitted by opening valve (7). Valve (11) was then closed. On opening valve (15) the pressure of the test fluid in the autoclave could then be adjusted to any desired value by manipulation of the dead-load balance.

The heavy water contained in the pressure transmitter was recovered by opening valve (11), closing valves (12) and (14), and forcing oil from the dead-load balance into the oil chamber of the pressure transmitter until mercury appeared at valve (7). Valve (7) was then closed, and the mercury level was lowered by returning the oil to the dead-load balance or to the oil reservoir, and opening valve (12). The small amount of heavy water (about 50 ml) remaining in the conductivity cell and the inlet pipe was recovered by distillation at reduced pressure through valves (11), (12) and (18) and freezing out in two cold traps.

3.8. *Corrections to thermal conductivity measurements*

3.8.1. *Temperature drop in walls.* Owing to the location of the thermocouples somewhat below the surfaces of the emitting and receiving cylinders, the measured temperature differences between them included the temperature drop through the metal layers between the thermocouples and the surfaces of the cylinders.

On the basis of some thermal conductivity data quoted by Langley Alloys, Ltd. (who state that the measurements were made by Bristol Aeroplane Company, Ltd.), for Hidural 5 [7], the correction for this effect was found to amount to about 9 per cent of the measured total temperature difference.

Thus to a small extent the accuracy of the reported values of the thermal conductivity of heavy water depends on the reliability of the data available for the thermal conductivity of Hidural 5.

3.8.2. *Intercalibration of thermocouples.* In order to determine the temperature difference across the annulus as accurately as possible, it was first necessary to compare carefully the e.m.f.s generated by the emitter and receiver thermocouples under isothermal conditions. This was achieved by operating the thermostat with the emitter and guard ring heaters switched off. It was found that over the temperature range from 75° to 360°C the receiver thermocouple always read 0·3 μV, i.e. about 0·006°C, lower than the emitter thermocouple. The appropriate correction was made to the measured temperatures before evaluating the temperature difference across the annulus, which was between 0·5° and 1°C.

Owing to small axial temperature gradients in the autoclave, the guard ring thermocouples could not be compared *in situ* with the same accuracy as the emitter and receiver thermocouples, since the former are located about 12 cm apart. However, it is considered that the total errors in calibration of the guard ring thermocouples and in the matching of the temperatures of the emitter and guard rings did not exceed 2 μV in any of the experiments. This corresponds to an error of less than 0·4 per cent in the reported values of thermal conductivity.

3.8.3. *Effect of radiation and correction.* When making measurements of thermal conductivity, it is essential that heat transfer by radiation and by convection should either be negligible, or should be accurately determined. It will be shown that convection had no effect, and that radiation had only a negligible effect, on the thermal conductivity data reported here.

Radiation. If the least favourable of the experiments are considered, viz. those at the highest temperature and for the largest temperature differences, and if one assumes an extreme case, viz. that the surface of the emitting and receiving cylinders are black bodies and that heavy water is perfectly transparent to black body radiation at this temperature (both assumptions being unnecessarily conservative), it can be shown by Stefan's law that the heat transferred by radiation must be less than 1·4 per cent of that transferred by thermal conduction. In view of the fact that conditions are much more favourable in reality, heat transfer by radiation will be considerably smaller than the above figure. No corrections were applied therefore for this effect in these tests.

Convection. It has been shown that thermal conductivity measurements are unaffected by convection, provided the product of the Grashof and Prandtl numbers proper to the experimental conditions is less than a certain value known as Rayleigh's criterion, which for vertical cylinders has a value of about 1,000. In the present experiments the product of the Grashof and Prandtl numbers was always considerably less than that value.

3.8.4. *Axial heat losses and gains.* As already stated in Section 3.6 the guard ring heaters were always adjusted with great care so that the temperature difference between the centre of the emitter and the guard rings amounted to not more than the reproducible limit of accuracy established by the calibration of the guard ring thermocouples which amounted to ± 2 μV, or expressed in terms of a temperature difference, to $\pm 0·045$°C.

Using a computed value of overall conductance between the emitting cylinder and the guard rings, a temperature difference of the above magnitude would cause an error in the thermal conductivity of less than $\pm 0·4$ per cent.

Apart from the axial energy exchange between the guard rings and the emitting cylinder due to imperfect matching of their temperatures, there is another possible source of error, viz. an error in the measurement of temperature caused by the axial conduction of heat along the thermocouple leads to, or from the thermal junction. This influence was studied experimentally in some earlier work by the present writers [4]. It was found that deliberate heating of the thin-walled stainless steel tube retaining the thermocouple leads at a point where it emerged from the thermal insulation surrounding the apparatus, had no significant effect on the e.m.f. observed

for that particular thermocouple. This test was applied to the thermocouple with the shortest depth of immersion in a zone of near-uniform temperature, viz. the top guard ring thermocouple. Temperatures of more than 300°C above the temperature of the thermal junction were applied before a measurable change of the e.m.f. was noticed. This observation is perhaps not so surprising when one considers that the vertical distance between the thermal junction and the heated area was about 45 cm and that the thermocouple leads traversed a near-isothermal zone of about 23 cm.

As the geometry and general arrangement of the apparatus used in this research resembles closely the one used in the above-mentioned tests, it was concluded that the same conditions would apply to the present case.

3.9. *Purity of heavy water*

The heavy water used in this research was supplied by A.E.R.E., Harwell, and was stated to have an isotopic purity of 99·85 per cent. Before filling the apparatus, dissolved gases were removed from the heavy water by boiling at reduced pressure.

4. EXPERIMENTAL RESULTS

Thirty-seven determinations were made of the conductivity of heavy water, covering the temperature range from 75° to 260°C at pressures up to 300 atm. Each determination is the mean of up to six complete sets of measurements taken over a period of about 1 hr, the standard deviation of these measurements being of the order of one-third of 1 per cent of the average thermal conductivity. The experimental data are given in Table 1. A smoothed plot of isobars is given in Fig. 3, and smoothed data can be found in Table 4. The numbers in the first column of Table 1 refer to the chronological order in which these experiments were carried out. In the first group of tests (nos. 1 to 29 incl.) experiments were carried out to a maximum temperature of about 260°C, followed by a check on the calibration of all thermocouples used in the conductivity cell. The next group of tests (nos. 30 to 37) was designed to fill some of the rather wide gaps in the preceding series, and at the same time provide a check on the reproducibility of the results of the first group. There is always the possibility that prolonged exposure of the conductivity cell to high pressures and temperatures has led to changes in the geometry of the system and thus affected the geometrical constant of the cell. The plot of experimental points in Fig. 3 shows no difference in trend between the two groups of tests and it can be concluded that no changes affecting the accuracy of these determinations have taken place during these tests.

When the experiments were extended to higher temperatures a progressively increasing deviation

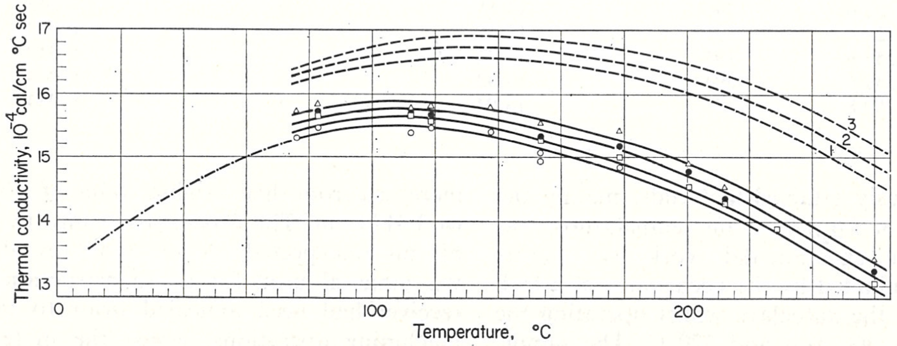

FIG. 3. The thermal conductivity of heavy water. Experimental data and smoothed isobars with the corresponding isobars for light water according to Timrot and Vargaftik [9];

— — Light water, Timrot and Vargaftik[9]; 3. 300 kg/cm^2
—— Heavy water, this research; 2. 200 kg/cm^2
— · — Heavy water, proposed average of previous investigations[10]. 1. 100 kg/cm^2

△ 294 atm ⊗ 195 atm □ 97 atm ⊙ 24 atm.