

## **Measurements of the Thermal Conductivity of R11 and R12 in the Temperature Range 250–340 K at Pressures Up to 30 MPa**

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This paper reports new, absolute measurements of the thermal conductivity of liquid refrigerants R11 and R12 in the temperature range 250–340 K at pressures from saturation up to 30 MPa. The measurements, performed in a new transient hot-wire instrument employing two anodized tantalum wires, have an estimated uncertainty of  $\pm 0.5\%$ . Measurements of the thermal conductivity of toluene in the temperature range 250–340 K at pressures up to 30 MPa are also reported.

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**KEY WORDS:** high pressure; R11; R12; refrigerants; thermal conductivity; toluene; transient hot-wire technique.

### **1. INTRODUCTION**

The introduction of new refrigerant fluids, to reduce the harmful effects of the previous generation of materials in the upper atmosphere, has prompted a worldwide program of measurements of the properties of such fluids.

There have been a number of reports of the measurements of the thermal conductivity of the new refrigerants, but a recent analysis demonstrates that there are discrepancies between the authors that exceed the estimated uncertainties [1]. Since the experimental techniques for the measurement of the thermal conductivity of fluids have been greatly refined in the last decade [2], this observation is, at first sight, somewhat alarming. However,

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the findings of Ross et al. [3] and Johns [4] concerning the application of one particular method to fluorocarbon materials indicate that there are unforeseen difficulties that may explain some of the discrepancies.

The transient hot-wire technique is generally the preferred method of thermal-conductivity measurements far removed from the critical region and, for that reason, has been adopted in a number of studies of refrigerant materials. In this technique, the temperature rise of a thin metallic wire immersed in the fluid is determined as a function of the time following initiation of a heat pulse within it. In most cases, the wire employed has been pure platinum. However, measurements in polar materials such as fluorocarbon refrigerants have revealed unexpected electrical effects, as well as chemical effects leading to polymerization [3].

For these reasons, it is though preferable to avoid the use of metallic wires in direct contact with the polar fluid. To that end, the instrument described in this work makes use of tantalum wires insulated by an anodic oxide film in the transient hot-wire technique which was first adopted for measurements in electrically conducting liquids [5].

In this paper we report measurements of the thermal conductivity in the liquid phase of two fluids of the older generation of refrigerants, R11 and R12, to prove the applicability of the present technique. In subsequent work the same method will be applied to the replacement refrigerants.

## 2. EXPERIMENTS

The theory of the transient hot-wire technique for liquid thermal-conductivity measurements has been given in detail elsewhere [2]. Consequently we confine ourselves here to a description of the present experimental installation, except to say that the technique involves the measurement of the temperature rise of a thin wire, by means of its resistance, over a period of 1 s after the initiation of an ohmic dissipation in it when surrounded by the liquid under test.

Following the aforementioned discussion, one of the most important constraints imposed on the choice of the wires is their insulation from the liquid to be measured. Thus, based on our previous experience [6], we chose two 25- $\mu\text{m}$ -diameter tantalum wires (14.5 and 5 cm in length) anodized *in situ* to form a layer of insulating tantalum pentoxide on their surface. In Fig. 1 the tantalum wires (1), the cell (2), and the pressure vessel (3) employed for the measurements are shown. All electrical connections to the wires (4) are made of 0.5-mm-diameter tantalum wire which extends outside of the pressure vessel. The wires, mounted in the cells, and the electrical connections were all together anodized *in situ* [6]. PTFE sleaving (see inset a in Fig. 1) ensures electrical insulation between the wires and the

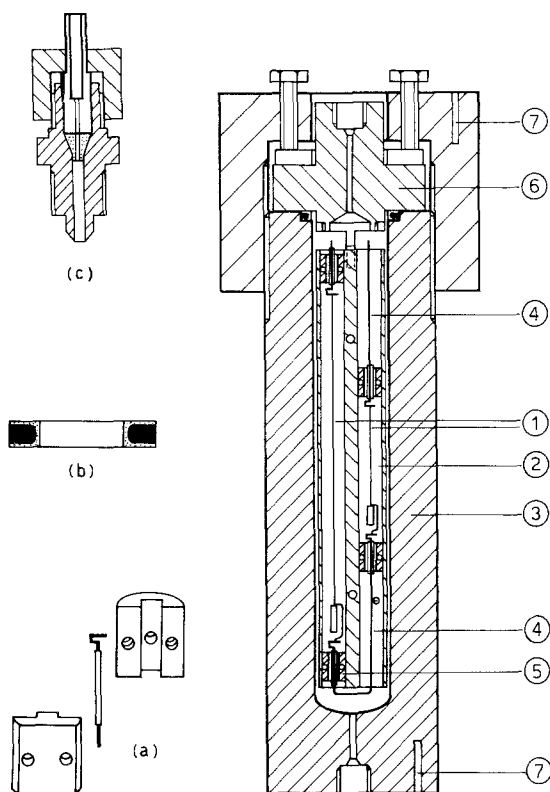


Fig. 1. The thermal conductivity vessel assembly.

supports (5). Constant tensioning and verticality of the wires are achieved by a tantalum weight at the bottom of each wire. The cell (2), in which the wires are mounted, is composed to two cylindrical compartments formed by machining two cylindrical holes centered on the split diameter of a cylinder and parallel to its axis. The half of the cylinder shown in Fig. 1 carries the four wire supports and is itself supported by the top plate (6) of the pressure vessel.

The pressure vessel (3) is made of stainless steel 304 and designed for an operating pressure of 70 MPa and an operating temperature range of 240–350 K. Sealing the pressure vessel at low temperatures and in the presence of the refrigerants, which react with the usual Viton o-rings, is problematic. The seal develop for this application, shown in inset in Fig. 1, is in essence a very thin-walled hollow PTFE o-ring with the external side cut out and a Viton o-ring in it. This seal was found to behave perfectly under all experimental conditions, i.e., 250–335 K and up to 30 MPa, and

chromatographic analysis of the fluids after long exposures to the seal showed no sign of contamination.

To take the three electrical contacts (0.5-mm tantalum wire) out of the pressure vessel at the aforementioned experimental ranges, the arrangement show in inset c in Fig. 1 was designed. By screwing the cup, the metal tube compresses the PTFE cone through which the three wires come out, and thus sealing is achieved. Two holes (7) were also drilled in the top and bottom of the pressure vessel for the platinum resistance thermometers. These thermometers were calibrated over the whole temperature range to an uncertainty of  $\pm 20$  mK. The whole pressure vessel was placed in a closed, insulated, 60-L water + ethylene glycol bath (60%, by weight, ethylene glycol). Temperature stability was controlled via a PID thermostat (Techne TE-8D) coupled with a refrigeration unit (Haake EK 51-1).

Filling of the pressure vessel was accomplished via an air-driven pump (Stansted Fluid Power A0612). Prior to filling the system, evacuation was carried out for a long period of time. The pressure of the system was registered via an electronic transducer (Druck PTX 520), calibrated to  $\pm 1$  bar.

The calibration of the wires to determine the temperature coefficient of resistance of tantalum was carried out *in situ*, as no values were available in the literature for the low-temperature region. The result was represented by a polynomial function of the resistance,  $R$  ( $\Omega$ ), of tantalum vs the absolute temperature  $T$  (in K), over the temperature range 240–350 K, as

$$R(T) = R(273.15)[1 + 3.4345 \cdot 10^{-3}(T - 273.15) - 4.8844 \cdot 10^{-7}(T - 273.15)^2] \quad (1)$$

The above equation is in full agreement with both our previously reported calibration [6] and that carried out by Zalaf [7], both in the temperature range 290–350 K.

The resistance change, and thus the temperature rise of the wires, is recorded by incorporating the two wires in the arms of a Wheatstone-type computer-controlled bridge [6, 8]. One arm of the bridge is arranged to provide a preset sequence of balance points at the resistance difference of the two wires in the bridge increases. The times at which these preset balances occur yield a series of temperature rise-time data for the regression analysis [6, 8]. In order to ensure stability of the oxide layer on both wires, a bias was applied to them by means of a DC supply so that the wires are positive with respect to the vessel, which is itself maintained at ground potential. This arrangement also provides the means of registering the leakage current from the wires to the vessel through the refrigerant at

all times. This registered leakage current through the refrigerant was always less than  $1 \mu\text{A}$ .

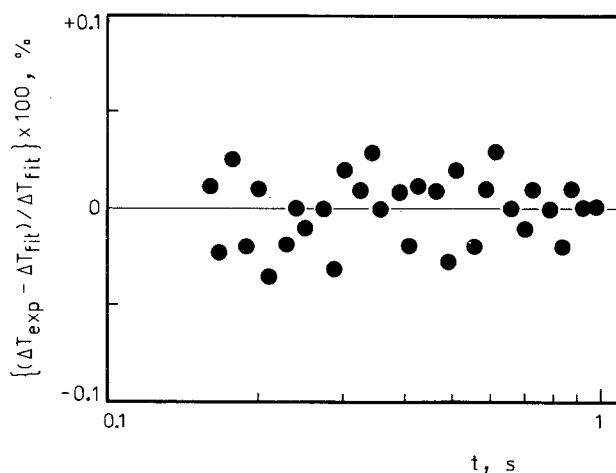
The samples of R11 and R12 were supplied by SICNG Chemical Industries of Northern Greece SA, both at stated purities better than 99.95%. The sample of toluene was supplied by BDH Ltd. at a nominal purity of better than 99.9% (HiperSolv grade).

### 3. WORKING EQUATION

According to the theory of the transient hot-wire technique the thermal conductivity,  $\lambda$ , of the liquid at a reference temperature  $T_r$  and a density  $\rho_r$ , can be derived from the equation [2, 9]

$$\Delta T_{\text{id}} = \Delta T_w + \sum_i \delta T_i = \frac{q}{4\pi\lambda(T_r, \rho_r)} \ln \left[ \frac{4kt}{a^2 C} \right] \quad (2)$$

in which  $q$  is the heat input per unit length of the wires,  $a$  the wire radius, and  $C$  a numerical constant. The symbol  $k$  represents the thermal diffusivity of the fluid surrounding the wires. The various correction terms  $\delta T_i$  have been identified [9] and are all rendered  $< 0.5$  of  $\Delta T_{\text{id}}$  by the design of the wire and the operation of the instrument. It follows from Eq. (2) that an essential feature of the correct operation of the instrument is that the measured data  $\Delta T_{\text{id}}$  should be a linear function of  $\ln t$ . In Fig. 2 the



**Fig. 2.** Percentage deviations of the measured temperature rise as a function of the logarithm of time, from linearity for a typical run of R11 at 273 K and 13-MPa pressure.

percentage deviations of the experimental temperature rise from this linearity as a function of time are shown for a typical run of R11 at 273 K and 13-MPa pressure. It can be seen not only that no curvature or systematic trend is apparent but also that the maximum deviation is less than  $\pm 0.04\%$ . Similar deviation plots were obtained for all measurements described in this paper. The lack of any curvature or systematic trend as well as the magnitude of the maximum deviation indicates that, for the temperature range considered, no radiation correction is necessary [15, 23].

#### 4. CONFIRMATION OF OPERATION AND ACCURACY

In order to demonstrate that the instrument described here operates in accordance with the theoretical model of it, we have carried out a number of measurements of the thermal conductivity of toluene at atmospheric pressure as a function of temperature and from atmospheric pressure up to 30 MPa along the 253.15, 273.15, 293.15, 313.15, and 333.15 K isotherms. At atmospheric pressure, toluene has been recommended by IUPAC [10] as a liquid thermal-conductivity standard. Moreover, its thermal conductivity at high pressures has been measured accurately by other investigators.

The measurements of the thermal conductivity of toluene at atmospheric pressure are presented in Table I. In Table II the high-pressure measurements are shown. In Table II values corrected to nominal

**Table I.** Measurements of the Thermal Conductivity of Toluene at Atmospheric Pressure as a Function of Temperature

Temp. $T$ (K)	Density $\rho(T)$ ( $\text{kg} \cdot \text{m}^{-3}$ )	Thermal conductivity $\lambda(T)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )
253.10	904	142.8
259.52	898	141.5
266.59	892	139.7
273.32	885	137.8
282.63	877	135.3
294.32	866	132.4
298.29	862	131.1
302.88	858	129.8
315.18	847	126.2
325.18	837	122.9
333.81	829	120.5
335.28	827	119.9

Table II. Measurements of the Thermal Conductivity of Toluene

Pressure $P$ (MPa)	Temp. $T$ (K)	Thermal conductivity $\lambda(T, P)$ (mW · m <sup>-1</sup> · K <sup>-1</sup> )	Density $\rho(T_{\text{nom}}, P)$ (kg · m <sup>-3</sup> )	Thermal conductivity $\lambda(T_{\text{nom}}, P)$ (mW · m <sup>-1</sup> · K <sup>-1</sup> )
$T_{\text{nom}} = 253.15 \text{ K}$				
0.10	253.10	142.8	904	142.8
4.15	253.08	143.9	906	143.9
8.10	253.04	144.9	908	144.9
11.15	253.02	145.7	910	145.7
14.18	253.04	146.5	912	146.5
17.19	253.03	147.3	914	147.3
20.19	253.03	148.0	915	148.0
$T_{\text{nom}} = 273.15 \text{ K}$				
0.10	273.32	137.8	886	137.8
3.60	273.19	138.8	888	138.8
7.14	273.23	140.0	890	140.0
10.45	273.17	140.9	892	140.9
13.75	273.16	142.0	894	142.0
17.43	273.19	143.1	897	143.1
21.00	273.15	143.9	899	143.9
24.80	273.09	145.1	901	145.1
$T_{\text{nom}} = 293.15 \text{ K}$				
0.10	294.32	132.4	867	132.7
5.20	294.27	134.0	871	134.3
10.15	294.45	135.7	875	136.0
14.95	294.34	137.3	878	137.6
19.60	294.31	138.8	881	139.1
27.60	294.27	141.4	886	141.7
$T_{\text{nom}} = 313.15 \text{ K}$				
0.10	315.18	126.2	848	126.8
5.24	314.92	128.0	853	128.5
10.10	314.87	129.9	857	130.4
14.90	314.84	131.5	860	131.9
20.20	314.80	133.5	864	133.9
24.50	314.82	134.9	867	135.3
27.75	314.75	136.1	870	136.5
$T_{\text{nom}} = 333.15 \text{ K}$				
0.10	333.81	120.5	829	120.7
4.05	333.16	122.4	833	122.4
7.35	333.03	123.7	836	123.7
10.15	333.08	124.8	839	124.8
13.60	333.05	126.0	842	126.1
17.50	333.12	127.5	845	127.5
20.90	333.14	128.8	848	128.8
24.50	333.06	130.0	851	130.0

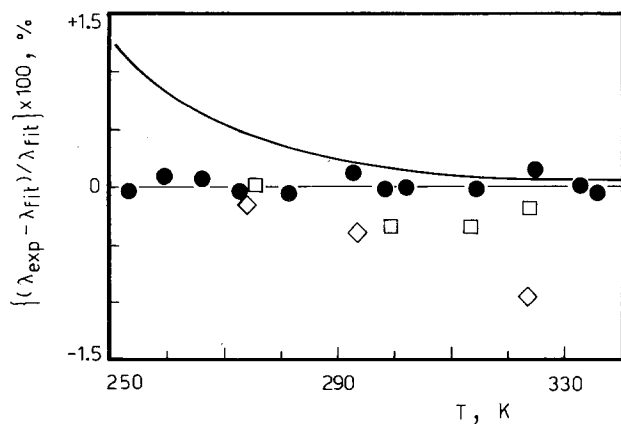
temperatures are also shown. Since this correction amounts to less than  $\pm 0.1\%$ , no additional error is introduced. Density values shown have been obtained from the work of Dymond et al. [11] with a quoted uncertainty of  $\pm 0.1\%$ .

All measurements of toluene have been correlated for interpolation purposes by a least-squares regression analysis to an equation of the form

$$\lambda = \sum_{i=0}^2 \sum_{j=0}^2 C_{ij} \left[ \frac{P}{P_c} \right]^i \left[ \frac{T}{T_c} \right]^j \quad (3)$$

where  $P$  is the absolute pressure in MPa, and  $P_c$  and  $T_c$  are the critical constants. The values of the coefficients  $C_{ij}$  and the constants  $P_c$  and  $T_c$  are given in Table V, together with the standard deviation of the fit, which is  $0.10\%$ .

In Fig. 3 the percentage deviations of the experimental thermal conductivity of toluene at atmospheric pressure from the values obtained by Eq. (3) as a function of temperature are shown. The maximum deviation is  $0.10\%$ . In the same figure, the standard correlation proposed by IUPAC [10] is also shown. For this correlation the proposed uncertainty for this temperature range is  $\pm 1.3\%$ . It can be seen that the present measurements agree fully with the proposed values. The small systematic deviation observed at temperatures below 270 K are probably attributable to the fact



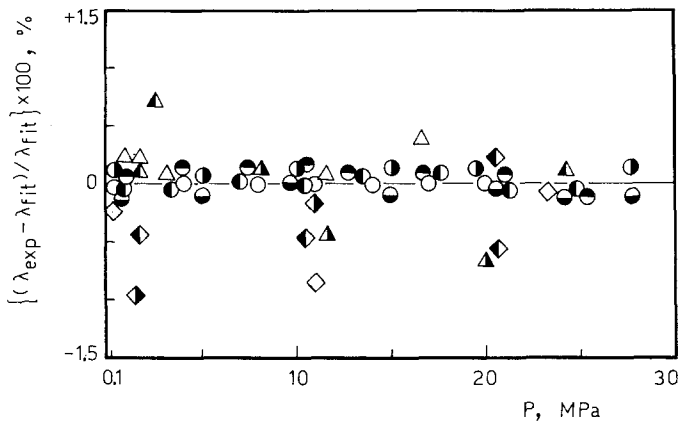
**Fig. 3.** Percentage deviations of the experimental measurements of the thermal conductivity of toluene at atmospheric pressure, from Eq. (1). Present work (●); Ref. 10 (—); Ref. 13 (□); Ref. 14 (◇).



that, below this temperature for the proposed correlation only the values of Pittmann [12] were used. In Fig. 3 measurements of two more investigative groups are also shown. The measurements of Kashiwagi et al. [13] were performed in a transient hot-wire instrument in a relative manner with a quoted uncertainty of  $\pm 1\%$ , while the measurements of Kitazawa and Nagashima [14] were also performed in a similar instrument with a quoted uncertainty of  $\pm 1.6\%$ . Both sets of measurements show only small deviations from Eq. (3), well within the mutual uncertainties.

In Fig. 4 the percentage deviations of the experimental thermal conductivity of toluene at high pressures from the values obtained by Eq. (3), as a function of pressure, are shown. The maximum deviation of the present measurements is 0.20%. In the same figure high-pressure measurements of two other investigative groups are also shown. In addition to the measurements of Kitazawa and Nagashima [14] already discussed above, the measurements of Nieto de Castro et al. [15] were performed in a transient hot-wire instrument in an absolute manner with a quoted uncertainty of  $\pm 0.3\%$ . Both sets of measurements show deviations from the present measurements, well within the mutual uncertainties of the instruments.

The aforementioned discussion of the measurements of toluene confirms the correct operation of the present instrument and its estimated



**Fig. 4.** Percentage deviations of the experimental measurements of the thermal conductivity of toluene at high pressures, from Eq. (1). Present work: (○) 253.15 K; (●) 273.15 K; (◐) 293.15 K; (◑) 313.15 K; (◒) 333.15 K. Ref. 15: (△) 308.15 K; (▲) 320.15 K; (▲) 330.15 K. Ref. 14: (◇) 273 K; (◆) 292 K; (◆) 322 K.

absolute uncertainty being better than  $\pm 0.5\%$ . It should also be pointed out that the precision and reproducibility of the present measurements are better than  $\pm 0.3\%$ .

## 5. THE THERMAL CONDUCTIVITY OF R11 AND R12

The measurements of the thermal conductivity of R11 and R12, listed in Tables III and IV, were performed along the isotherms of 253.15, 273.15, 283.15, 313.15, and 333.15 K from just above the saturation pressure up to about 30 MPa. As in the case of toluene, in these tables, values corrected to nominal temperatures are also shown. Density values were obtained from Platzter et al. [16] with a quoted uncertainty of  $\pm 0.10\%$ . The measurements of R11 and R12 were also correlated by a least-squares regression analysis as Eq. (3). The values of the coefficients  $C_{ij}$  and the constants  $P_c$  and  $T_c$ , respectively, are shown in Table V, together with the standard deviation of the fits, which are equal to 0.12% for R11 and 0.08% for R12. In Table VI values along the saturation line are presented. These values were obtained by the extrapolation of Eq. (3), while their validity can easily be confirmed by comparison with the measurements performed just above the saturation line.

In Figs. 5 and 6, the percentage deviations of the experimental thermal conductivity of R11 at saturation pressure and at high pressures, from the values obtained by Eq. (3), are shown. The maximum deviation is 0.20%. In both figures measurements of other investigators are also shown. The measurements of Kitazawa and Nagashima [14] performed in a relative manner up to high pressures in a transient hot-wire instrument with a quoted uncertainty of  $\pm 1.6\%$ , show a maximum deviation of 1.2% over the whole range, which is well within the mutual uncertainty of the two instruments. The measurements of Tauscher [17] and Sadykov et al. [18] were both performed in a relative manner in transient hot wire-type instruments with quoted uncertainties of 2.5%. Both sets of measurements show deviations from the values of Eq. (3) which are well within the mutual uncertainty of the instruments. Finally, the measurements of Yata et al. [19] were performed along the saturation line in a relative manner also in a transient hot-wire instrument with a quoted uncertainty of  $\pm 1.5\%$ . However, these measurements show deviations which rise up to 3.5% at low temperatures. The reason for this deviation, we believe, lies in the fact that their instrument was calibrated against measurements of toluene performed only in the limited temperature range of 290–360 K. Furthermore they employed high measurement times, up to 3 s, so their measurements may have been influenced by convection [2].

Table III. Measurements of the Thermal Conductivity of R11

Pressure $P$ (MPa)	Temp. $T$ (K)	Thermal conductivity $\lambda(T, P)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	Density $\rho(T_{\text{nom}}, P)$ ( $\text{kg} \cdot \text{m}^{-3}$ )	Thermal conductivity $\lambda(T_{\text{nom}}, P)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )
$T_{\text{nom}} = 253.15 \text{ K}$				
0.10	253.46	97.3	1579	97.4
2.55	253.30	98.1	1584	98.1
5.50	253.33	99.0	1589	99.0
8.40	253.33	100.0	1594	100.0
10.85	253.27	100.8	1597	100.8
13.70	253.22	101.7	1602	101.7
16.00	253.34	102.4	1606	102.4
$T_{\text{nom}} = 273.15 \text{ K}$				
0.10	273.29	92.2	1534	92.2
3.00	273.27	93.2	1540	93.2
5.95	273.19	94.3	1546	94.3
9.03	273.19	95.4	1552	95.4
12.20	273.10	96.5	1558	96.5
15.23	273.01	97.6	1563	97.6
18.80	273.08	98.6	1570	98.6
21.00	273.11	99.5	1573	99.5
$T_{\text{nom}} = 293.15 \text{ K}$				
3.06	293.55	88.2	1495	88.3
6.10	293.49	89.4	1502	89.5
9.05	293.44	90.4	1509	90.5
12.17	293.33	91.8	1516	91.8
15.08	293.23	92.8	1522	92.8
18.20	293.23	94.1	1528	94.1
21.05	293.37	95.2	1533	95.3
$T_{\text{nom}} = 313.15 \text{ K}$				
4.20	313.33	83.3	1452	83.4
6.40	313.29	84.1	1458	84.1
8.80	313.19	85.2	1464	85.2
11.10	313.21	86.3	1470	86.3
13.60	313.23	87.2	1476	87.2
15.96	313.12	88.3	1482	88.3
18.60	313.09	89.4	1488	89.4
$T_{\text{nom}} = 333.15 \text{ K}$				
1.05	333.60	76.2	1392	76.3
3.10	333.55	77.3	1399	77.4
6.10	333.54	78.9	1410	79.0
9.00	333.50	80.4	1419	80.5
14.95	333.38	83.4	1436	83.5
17.80	333.40	84.8	1444	84.9

Table IV. Measurements of the Thermal Conductivity of R12

Pressure $P$ (MPa)	Temp. $T$ (K)	Thermal conductivity $\lambda(T, P)$ (mW · m <sup>-1</sup> · K <sup>-1</sup> )	Density $\rho(T_{\text{nom}}, P)$ (kg · m <sup>-3</sup> )	Thermal conductivity $\lambda(T_{\text{nom}}, P)$ (mW · m <sup>-1</sup> · K <sup>-1</sup> )
$T_{\text{nom}} = 253.15 \text{ K}$				
0.46	253.00	80.8	1459	80.8
1.17	253.45	81.0	1461	81.0
3.55	253.49	82.0	1469	82.1
7.08	253.33	83.5	1482	83.6
10.08	253.30	84.9	1491	84.9
13.00	253.32	86.1	1497	86.2
16.00	253.25	87.7	1504	87.7
19.05	253.23	89.1	1512	89.1
22.05	253.13	90.5	1519	90.5
$T_{\text{nom}} = 273.15 \text{ K}$				
0.59	273.67	74.3	1397	74.5
1.92	273.09	75.0	1403	75.0
4.80	273.07	76.4	1415	76.4
7.93	273.10	78.0	1427	78.0
10.84	272.97	79.5	1437	79.5
13.80	272.81	80.9	1446	80.8
16.60	272.88	82.3	1455	82.2
19.25	272.74	83.5	1462	83.4
$T_{\text{nom}} = 293.15 \text{ K}$				
0.83	293.47	68.0	1330	68.1
2.31	293.40	68.9	1339	69.0
6.21	293.26	71.0	1359	71.0
9.00	293.12	72.6	1372	72.6
11.91	293.22	74.2	1384	74.2
15.10	293.08	75.9	1397	75.9
17.90	293.06	77.4	1407	77.4
21.24	293.10	79.1	1418	79.1
$T_{\text{nom}} = 313.15 \text{ K}$				
1.22	313.41	61.7	1256	61.8
4.60	313.34	64.1	1283	64.2
7.60	313.19	66.2	1302	66.2
11.11	313.12	68.4	1321	68.4
14.62	313.05	70.4	1338	70.4
17.85	312.95	72.4	1352	72.4
21.65	313.01	74.4	1367	74.4
$T_{\text{nom}} = 333.15 \text{ K}$				
1.52	333.68	55.3	1168	55.5
3.17	333.46	56.8	1189	56.9
5.53	333.27	58.8	1214	58.8
9.18	333.12	61.5	1244	61.5
12.35	333.05	63.8	1265	63.8
15.65	332.94	66.0	1284	66.0
19.20	332.83	68.4	1302	68.3
22.83	332.81	70.5	1319	70.4

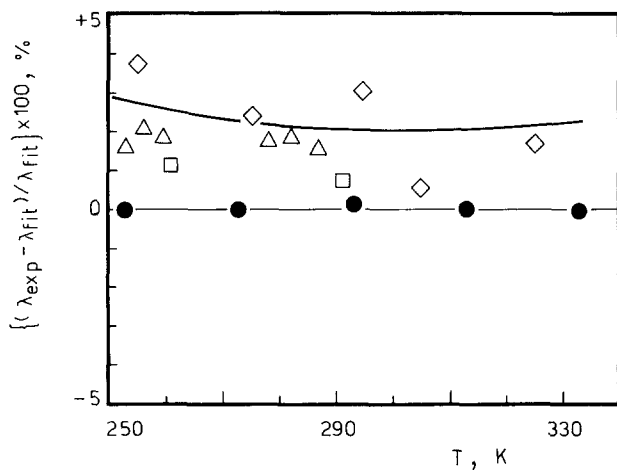
Table V. Coefficients and Constants of Eq. (3)

Coefficients $C_{ij}$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )	Toluene	R11	R12
$C_{00}$	+170.53	+145.29	+155.81
$C_{01}$	+10.578	-61.110	-105.06
$C_{02}$	-177.34	-52.438	-14.177
$C_{10}$	-1.612	+5.192	+5.3081
$C_{11}$	+8.1207	-15.875	-16.283
$C_{12}$	-4.2028	+16.479	+16.391
$C_{20}$	0	0	+0.46064
$C_{21}$	0	0	-0.65065
$C_{22}$	0	0	0
$P_c$ (MPa)	4.2151	4.4026	4.1290
$T_c$ (K)	593.95	471.15	384.95
$\sigma$ (%)	$\pm 0.10$	$\pm 0.12$	$\pm 0.08$

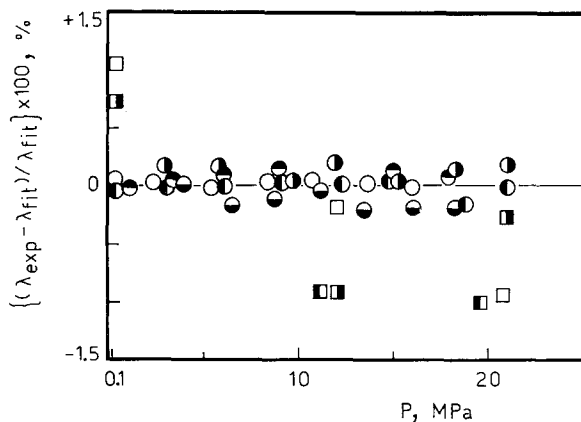
In Figs. 7 and 8, the percentage deviations of the experimental thermal conductivity of R12 at saturation pressure and at high pressures, from the values obtained by Eq. (3), are shown. The maximum deviation is 0.14%. In both figures measurements of other investigators are also shown. The only other set of measurements performed in an absolute manner over the whole range is the set of Venart and Mani [20]. These measurements were performed in a transient hot-wire instrument with many different types of wires and a quoted absolute uncertainty of  $\pm 2\%$ . The deviations of these

Table VI. The Thermal Conductivity of R11 and R12 at Saturation

	Temperature $T_s$ (K)	Pressure $P_s$ (MPa)	Density $\rho_s$ ( $\text{kg} \cdot \text{m}^{-3}$ )	Thermal conductivity $\lambda(T_s, P_s)$ ( $\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )
R11	253.15	0.0157	1579	97.3
	273.15	0.0403	1534	92.3
	293.15	0.0890	1487	87.0
	313.15	0.1750	1439	81.6
	333.15	0.3141	1389	76.0
R12	253.15	0.1519	1457	80.7
	273.15	0.3105	1395	72.3
	293.15	0.5700	1328	67.9
	313.15	0.9630	1254	61.6
	333.15	1.5258	1168	55.5



**Fig. 5.** Percentage deviations of the experimental measurements of the thermal conductivity of R11 at the saturation pressure, from Eq. (1). Present work (●); Ref. 17 (—); Ref. 14 (□); Ref. 19 (◇); Ref. 18 (△).



**Fig. 6.** Percentage deviations of the experimental measurements of the thermal conductivity of R11 at high pressures, from Eq. (1). Present work: (○) 253.15 K; (●) 273.15 K; (●) 293.15 K; (●) 313.15 K; (●) 333.15 K. Ref. 14: (□) 262 K; (■) 282.8 K; (■) 321 K.

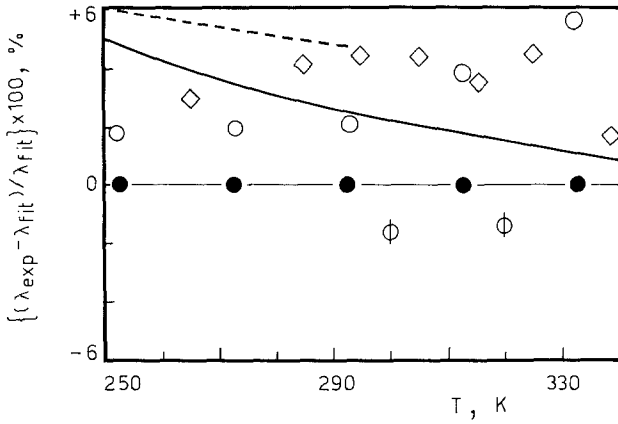


Fig. 7. Percentage deviations of the experimental measurements of the thermal conductivity of R12 at the saturation pressure, from Eq. (1). Present work (●); Ref. 1 (—); Ref. 17 (- -); Ref. 19 (◇).

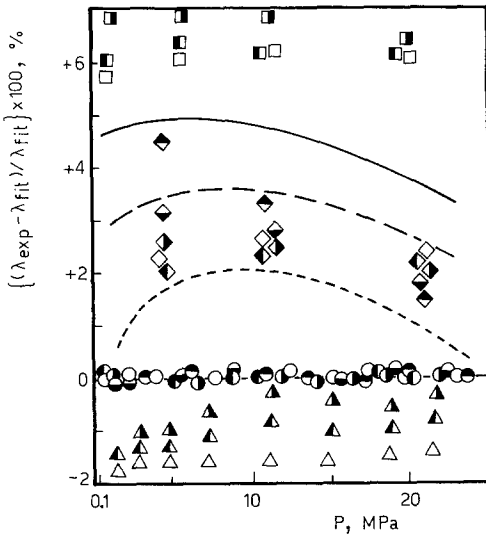


Fig. 8. Percentage deviations of the experimental measurements of the thermal conductivity of R12 at high pressures, from Eq. (1). Present work: (○) 253.15 K; (●) 273.15 K; (◐) 293.15 K; (◑) 313.15 K; (◒) 333.15 K. Ref. 1: (—) 253 K; (- -) 283 K; (- - -) 333 K. Ref. 20: (△) 300 K; (▲) 320 K; (▲) 340 K. Ref. 22: (□) 259 K; (◻) 275 K; (◼) 295 K. Ref. 21: (◇) 253.15 K; (◈) 273.15 K; (◈) 293.15 K; (◈) 313.15 K; (◈) 323.15 K.

measurements from the values of Eq. (3) are well within the mutual uncertainty of the two instruments. The high-pressure measurements of Geller et al. [21], performed in a relative manner in a transient hot-wire instrument with a quoted uncertainty of  $\pm 3\%$ , show deviations just within the mutual uncertainty of the instruments. The high-pressure measurements of Tsvetkov and Chilipenok [22], performed in a non-steady-state concentric cylinder-type instrument with a quoted uncertainty of  $\pm 3\%$ , show much higher deviations, however. Along the saturation line the measurements of Yata et al. [19] show a similar pattern discussed previously in the case of R11, while the correlation proposed by Tauscher [17] is much higher than all other measurements. Finally, in the case of the thermal conductivity of R12, Krauss and Stephan [1] very recently published a thorough investigation of many experimental measurements covering a wide range of conditions. Based on these measurements they proposed a correlation with an uncertainty of  $\pm 6\%$ . The deviations between the values obtained from their correlation and the values obtained by Eq. (3) are well within the uncertainty of their correlation. The systematic relatively high deviation at low temperatures is attributed to their use of the measurements of Taucher [17]. The present experimental data are to be preferred in their limited range of conditions.

## 6. CONCLUSION

A new transient hot-wire instrument employing two anodized tantalum wires is described. The measurements, performed in an absolute manner, have an estimated overall uncertainty of  $\pm 0.5\%$ , confirmed by the measurements of the thermal conductivity of toluene.

Measurements of the thermal conductivity of R11 and R12 are presented from just above the saturation pressure up to 30 MPa along the 253.15, 273.15, 293.15, 313.15, and 333.15 isotherms.

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