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THE THERMAL CONDUCTIVITY OF LIQUIDS—IV

TEMPERATURE DEPENDENCE OF THERMAL CONDUCTIVITY

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Abstract—The thermal conductivity of benzene, toluene, m-xylene, carbon tetrachloride, liquid paraffin, and nitrobenzene was measured at several temperatures using a guarded horizontal parallel plate apparatus formerly described. The thickness of the liquid layer was varied within the range in which the measured values are not perceptibly increased by convection according to the results of a former investigation. It was found that the dependence of the thermal conductivity and of its temperature coefficient on the thickness of the liquid layer are in fair agreement with those values which are obtained by calculating the contribution of the radiation to the heat transfer in liquids with small ir-absorption. These values can be calculated by using an absorption diagram of the liquid as has been shown formerly.

The precision of the measured thermal conductivity values is estimated at about ±0·5 per cent. The uncertainty of the calculated temperature coefficients is about $\pm 0{\cdot}1 \times 10^{-6}$ W cm^{-1} degC^{-2}.

The effective thermal conductivity of poorly absorbing liquids like toluene can vary at room temperature by about 5–7 per cent because of a radiative component depending on apparative conditions. The temperature coefficient of thermal conductivity can vary by about 20–30 per cent. A study of measurements published by other authors in the last 20 years shows that nearly all the values of thermal conductivity and more than half of their temperature coefficients are within an interval given by the variability of the radiative component.

The more recently measured values of thermal conductivity seem to be on an average somewhat smaller than the earlier values. We suppose that more efforts are made now to avoid convection.

NOMENCLATURE

a, b, constants defined by [5];
k_{eff}, measured thermal conductivity [W cm^{-1} degC^{-1}];
n, refractive index;
q_r, q'_r, radiative heat flux [W cm^{-2}];
$\bar{q}_r, \bar{q}'_r$, mean values of q_r, q'_r [W cm^{-2}];
s, thickness of the liquid layer [cm];
x, coordinate perpendicular to the plate surfaces [cm];
E_r, Planck function [W cm^{-3}];
T, absolute temperature [degK];
ΔT, temperature difference between the plates [degC];
Y, function calculated in [1]

$$\left[Y = 1 - \frac{3}{\tau}(2 - \varepsilon) \int_0^1 \frac{1 - \exp(-\tau/v)}{1 + (1 - \varepsilon)\exp(-\tau/v)} v^3 \, dv\right].$$

Greek symbols

ε, emissivity of the plate surfaces;
κ, absorption coefficient [cm^{-1}];
λ, wave length [cm];
σ, constant of Stefan–Boltzmann law [W cm^{-2} degK^{-4}];
τ, optical thickness of the liquid layer.

1. INTRODUCTION

By a theoretical investigation formerly reported on [1] we have shown that the effective (measured) thermal conductivity of liquids which have a small ir-absorption contains, already at room temperature, a measurable percentage originating from heat transfer by radiation. This result was verified in a more general form by Kohler [2].

Measurements at 25°C with a guarded horizontal parallel plate apparatus formerly described [3] were in good accordance with the theoretical results [4]. In these experiments, liquids of weak and strong ir-absorption and of different viscosities were compared with regard to the dependence of the measured thermal conductivity on the thickness of the liquid layer between the plates. By this comparison, in which we also varied the temperature difference between the plates, we could determine an upper limit of the plate distance which should not be exceeded if one is to avoid a noticeable increase of the measured values by convection. A relation to the Rayleigh number was not found. It seemed that, above the critical distance, convection arose from small mechanical vibrations caused by the water flowing through the apparatus.

We can deduce from the theoretical and experimental results that not only the measured thermal conductivity but in a larger degree its temperature coefficient, too, must increase with the thickness of the liquid layer for poorly absorbing liquids.

This prediction was checked experimentally by measurements at some temperatures and some layer thicknesses within the region, in which no convection exists.

We also made measurements on two liquids with higher ir-absorption, the thermal conductivities of which have nearly the same values as those of the investigated poorly absorbing liquids. We expected to find a smaller dependence on the thickness of the layer for those two liquids.

2. THEORETICAL CONSIDERATIONS

To obtain knowledge about the contribution of the radiation to the heat transport, many authors consider only the radiation emitted by the surfaces of the plates. This may be quite correct if the medium between the plates is a gas as the optical thickness of the layer is small in this case. Liquids, however, absorb and therefore, following Kirchhoff's theory, also emit much more radiation. For this reason, the inner radiation of the liquid contributes in general more to the heat transfer from plate to plate than the radiation emitted by the plate surfaces. This applies even for the smallest thicknesses of the liquid layer within that range which should not be exceeded for experimental reasons.

At each point of an unlimited space containing a medium emitting and absorbing radiation let there exist a constant total temperature decline in the x-direction $\mathrm{d}T/\mathrm{d}x = a$. We then obtain the following approximation for the heat flux q_r caused by radiation through the unit area of any plane x = constant:

$$q_r = \frac{4}{3}\pi\frac{\mathrm{d}T}{\mathrm{d}x}\int_{\lambda=0}^{\infty}\frac{n^2}{\kappa}\frac{\partial E_r}{\partial T}\,\mathrm{d}\lambda. \tag{1}$$

T is the absolute temperature, λ the wave length of radiation, E_r the Planck function, and n and κ are the refractive index and the absorption coefficient of the medium respectively.

The expression (1) can be easily derived from formula (5) in [1] or formula (18) in [2]. If we replace n and κ by mean values $\bar{n}$ and $\bar{\kappa}$ independent of the wave length we obtain from (1) an equation for the radiative heat flux known for some time (see Genzel [5]):

$$q_r' = \frac{16}{3}\frac{\bar{n}^2}{\kappa}\sigma T^3\frac{\mathrm{d}T}{\mathrm{d}x} \tag{2}$$

where σ is the Stefan–Boltzmann constant.

Equation (1) may easily be evaluated for any liquid of which a spectrum of the ir-absorption is available. Such spectrums exist for a very great number of liquids [6]. The function $\partial E_r/\partial T$ is tabulated by Czerny and Walther [7]. The refractive index n shows no large dependence on wave length for poorly absorbing liquids within the region of interest. Therefore, we can use a mean value $\bar{n}$ for n. A numerical evaluation done in this way for such a liquid, e.g. toluene, leads to a value q_r which is, at room temperature, about 5 per cent of the heat flux q_c due to conduction. In our case we have $q_c = k\ \mathrm{d}T/\mathrm{d}x$, k being the "true" thermal conductivity.

These conditions of simultaneous heat flow by conduction and radiation in liquid layers of great thickness are well known. But there were, as far as we know, no efforts made to calculate the amount of the radiative heat flux using spectroscopic data. In the case of poorly absorbing liquids, the results of such calculations are surprising as such large values of this flux at moderate temperatures had not been expected.

At smaller thicknesses, the contribution of the radiation to the heat transfer decreases by the influence of the surfaces touching the layer. In the case of parallel plates and of a small temperature difference $\Delta T = T_1 - T_2 \ll T_2$ between them and for predominate heat flow by conduction we obtain instead of (1) the more general expression

$$\bar{q}_r = \frac{4}{3}\pi\frac{\Delta T}{s}\int_{\lambda=0}^{\infty}\frac{n^2}{\kappa}\frac{\partial E_r}{\partial T}Y(\varepsilon,\tau)\,\mathrm{d}\lambda, \qquad (3)$$

$\bar{q}_r$ is the mean heat flux due to radiation between the plates and s their distance. Y is a function of the emissivity ε of the plate surfaces and the optical thickness τ of the liquid layer. τ is the product $\kappa \times s$ and depends upon the wave length. Equation (3) is identical with Kohler's formula (18) [2]. Y was calculated as a function of τ *f*or some parameters ε [1]. Therefore, it is possible to calculate the heat flux $\bar{q}_r$ by using (3) in the general case of any given distance of the plates if the optical data of the investigated liquid are available.

After replacing n and κ by wave independent mean values $\bar{n}$ and $\bar{\kappa}$ we can transform (3) into the following expression corresponding to (2)

$$\bar{q}'_r = \frac{16}{3}\frac{\bar{n}^2}{\bar{\kappa}}\sigma T^3 Y\frac{\Delta T}{s}. \qquad (4)$$

If s or τ increases from 0 to ∞, the function Y increases from 0 to 1. Y represents a factor indicating how much the heat flux due to radiation is reduced by the influence of the plate surfaces touching the liquid layer.

Figure 1 shows Y as a function of the optical thickness τ for a few values of the emissivity ε. The vertical broken lines b and c define the range of values of τ, within which our measurements on poorly absorbing liquids were performed. As there are authors having used still smaller thicknesses of the liquid layer (down to about 0·25 mm) the range between the broken line a and $\tau = \infty$ includes the optical thicknesses as chosen for all measurements realized till now.

The lowest curve of Fig. 1 represents the function Y for $\varepsilon = 0$, that is for the hypothetical case of the plate surfaces emitting not the least radiation and the radiative heat transfer between the plates being performed only by inner radiation of the liquid. The reduction of the heat flow compared with that in the case of large distances of the plates, then, is caused by the reflections of the radiation on the plate surfaces.

The distance between the curve for $\varepsilon = 0$ and one of the upper curves represents the contribution of the radiation emitted by the plate surfaces compared to the total radiative heat flow from plate to plate. As metallic surfaces have in general an emissivity below 0·2, it is to be seen that this contribution is very small even at the smallest distances between the plates which, for experimental reasons, are possible.

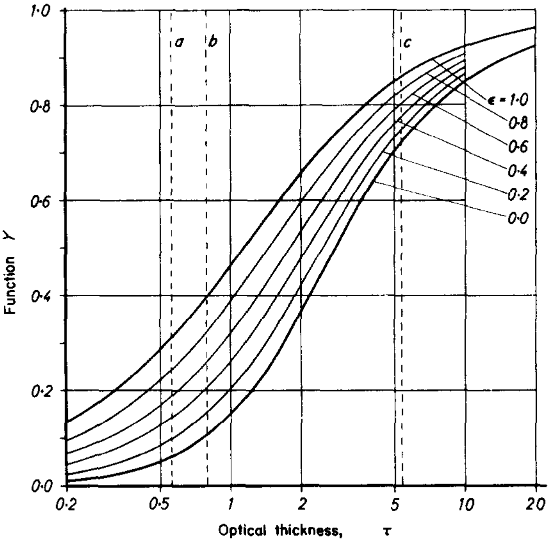

FIG. 1. Y as a function of the optical thickness τ.

The distance between any point of a curve and the maximum value $Y = 1$ gives the reduction of the radiative heat flux caused by the presence of the plates.

Experimental results show that the thermal conductivity can be represented by a linear function of temperature if the temperature range is not too wide. We then obtain using (4) the effective thermal conductivity

$$k_{\mathrm{eff}} = a - bT + \frac{16}{3}\frac{\bar{n}^2}{\bar{\kappa}}\sigma T^3 Y \qquad (5)$$

where the first two terms give the "conductive" thermal conductivity k, and the factor of Y gives the "radiative" thermal conductivity k_r. As Y is dependent on the layer thickness of the liquid sample and the emissivity of the plate surfaces, k_{eff} is not a constant of the material excepted for the distances $s = 0$ and $s = \infty$.

Differentiating (5) gives

$$\frac{\mathrm{d}k_{\mathrm{eff}}}{\mathrm{d}T} = -b + 16\frac{\bar{n}^2}{\bar{\kappa}}\sigma T^2 Y. \qquad (6)$$

The temperature coefficient $\mathrm{d}k_{\mathrm{eff}}/\mathrm{d}T$ is usually negative. Because of the second term of (6) it increases with increasing temperature and, on account of Y, also with increasing thickness of the liquid layer. If $|b|$ is small, the coefficient may become positive for great thicknesses.

Formerly [1], we had found by evaluating optical data of toluene that the temperature coefficient of thermal conductivity should vary by about 20–30 per cent at room temperature, due to the influence of the layer thickness, for samples with values of material constants similar to toluene.

3. EXPERIMENTAL DETAILS

The apparatus, the mode of measurement, and its evaluation have formerly been described [3, 4]. The plane shape of the surfaces of the copper plates should not have an error of more than ±0·3 μm. This was often controlled by comparison with a plane-parallel glass plate and was, if necessary, corrected by grinding and polishing. From time to time the surfaces of the copper plates must be desoxidized as a little diminishing of the metallic brilliance caused a noticeable rise of the measured values of k_{eff}.

After degassing, the liquid sample was filled into the apparatus which had been evacuated by a gas ballast pump. After filling air or nitrogen was let into the apparatus in order to avoid any deformations of the plates caused by stresses. Thoroughly dried air or nitrogen was used to prevent the sample to become contaminated by water. In cases of doubt the percentage of water contained in the sample was controlled spectroscopically after the measurements. It was always below 0·1 per cent.

The temperature measurements were performed by using thermocouples of the alloy manganin and Isotan (constantan). The wire material was manufactured by the Isabellen-Hütte at Dillenburg (West Germany). The relative temporal variations of the thermo-electric forces of each couple were continuously controlled. The measured voltages were corrected accordingly.

Table 1 shows the alterations in the relative deviations from the mean value in the temperature records of the single thermocouples within half a year. To give an idea of the errors of the temperature measurements Table 2 presents, for one temperature, the deviations for two consecutive days.

Liquids of the highest degree of purity obtainable in trade were used for the measurements. The percentage of impurities was in general specified on the package. In single cases more details were communicated by the manufacturers. The sum of the impurities was always too low to be able to influence perceptibly the measured values.

4. RESULTS AND TESTING OF THE THEORY

The measured thermal conductivities of five poorly absorbing liquids are represented in the Tables 3–5 together with the values resulting by calculating the thermal conductivities by use of equation (5). This calculation was performed in the following way:

The optical value of the refractive index

Table 1. Deviations of the indications of the thermocouples from the mean value on 3 March 1966 (upper numbers) and on 19 September 1966 (lower numbers). The numbers are obtained by linear smoothing over the temperature

Temp. °C	Deviations in millidegrees for the indicator point No.									
	1	2	3	4	5	6	7	8	9	10
0	− 5	− 2	−1	− 6	− 5	− 4	+5	+ 8	+ 9	+12
	− 4	+ 1	−6	− 9	− 4	− 6	+9	+ 1	+ 5	+18
10	− 9	− 5	−1	0	− 6	− 5	+3	+ 5	+11	+14
	− 9	− 2	−5	− 1	− 5	− 9	+9	0	+ 8	+19
20	−14	− 7	−1	+ 6	− 6	− 5	+2	+ 3	+14	+15
	−14	− 6	−5	+ 6	− 7	−11	+9	− 1	+11	+19
30	−18	− 9	−2	+11	− 7	− 5	0	+ 1	+17	+16
	−19	−10	−5	+14	− 8	−13	+9	− 2	+15	+19
40	−22	−12	−2	+17	− 7	− 6	−2	− 2	+19	+17
	−24	−13	−4	+21	− 9	−15	+8	− 3	+18	+19
50	−26	−16	−2	+23	− 8	− 6	−3	− 4	+21	+19
	−29	−17	−4	+28	−10	−17	+8	− 5	+21	+19
60	−30	−18	−2	+28	− 8	− 6	−5	− 6	+24	+20
	−34	−20	−4	+34	−11	−19	+8	− 6	+24	+19
70	−34	−21	−2	+35	− 8	− 7	−6	− 9	+26	+21
	−39	−24	−3	+41	−12	−21	+8	− 7	+28	+20
80	−37	−24	−3	+41	− 9	− 7	−8	−11	+27	+22
	−43	−27	−3	+48	−13	−23	+7	− 8	+31	+20

Table 2. Error of the temperature measurements at 50°C

Date of the measurement	Deviation of the measured value from the mean value at indicator point No. in millidegrees									
	1	2	3	4	5	6	7	8	9	10
19.9.66	−30	−18	−3	+28	−10	−18	+10	−5	+20	+20
20.9.66	−28	−15	−5	+30	−10	−18	+ 5	−5	+23	+18

n (n_D) was used as mean value $\bar{n}$. This may be allowed for these liquids because n does not considerably depend on the wave length. As the Maxwell formula is valid for these substances, we could have used as well the dielectric constant instead of n^2. The emissivity ε of the plate surfaces was 0·04. Values of the function Y were drawn from Table 1 in [1]. The constants a, b, and $\bar{\kappa}$ in formula (5) were calculated by a least squares approximation using the measured values k_{eff}. Therefore, the calculated values can merely serve to control whether the measurements can be interpreted correct by formula (5). However, it should be noted that the values of the mean absorption coefficients, $\bar{\kappa}$, obtained in this way from the measured thermal conductivities, k_{eff}, are in satisfactory agreement with the values obtained from optical data, as has been shown previously [1].

The temperature dependence of the thermal conductivity of the five liquids, as calculated with help of (5), is represented in Figs. 2–6. The thickness of the liquid layer is used as a parameter. The dashed lines give the calculated curves for the limits $s = 0$ and $s = \infty$. The measured values of thermal conductivity are figured as small circles.

Tables 3–5 and the Figs. 2–6 show that the

Table 3. *Thermal conductivity of benzene and benzene homologues*

Thickness of the liquid layer s	Thermal conductivity $k_{eff} \times 10^3$ (W × cm^{-1} × degC^{-1}) 10°C		25°C		40°C		55°C		$(dk_{eff})/(dT) \times 10^6$ at 25°C
mm	meas.	calc.	meas.	calc.	meas.	calc.	meas.	calc.	W/cm degC^2
					Benzene				
0		1·444		1·390		1·337			−3·56
0·4581	1·457	1·456	1·404	1·404	1·352	1·353			−3·42
0·9578	1·471	1·471	1·422	1·422	1·376	1·374			−3·24
1·4559	1·479	1·480	1·431	1·432	1·384	1·386			−3·14
1·9293	1·487	1·485	1·436	1·438	1·394	1·392			−3·08
∞		1·501		1·457		1·414			−2·89
					Toluene				
0				1·292		1·249		1·205	−2·88
0·4581			1·306	1·306	1·264	1·265	1·224	1·224	−2·74
0·9578			1·323	1·324	1·286	1·286	1·247	1·248	−2·55
1·4559			1·335	1·336	1·297	1·299	1·266	1·264	−2·44
1·9293			1·344	1·342	1·309	1·307	1·273	1·273	−2·37
∞				1·364		1·333		1·302	−2·15
					m-Xylene				
0				1·277		1·235		1·194	−2·75
0·4581			1·290	1·291	1·251	1·251	1·213	1·213	−2·61
0·9578			1·308	1·309	1·271	1·273	1·237	1·237	−2·43
1·4559			1·322	1·320	1·288	1·286	1·253	1·252	−2·31
1·9293			1·327	1·327	1·292	1·293	1·261	1·261	−2·25
∞				1·348		1·318		1·290	−2·03

Table 4. *Thermal conductivity of carbon tetrachloride*

Thickness of the liquid layer s	Thermal conductivity $k_{eff} \times 10^3$ (W × cm^{-1} × degC^{-1}) 10°C		25°C		40°C		$(dk_{eff})/(dT) \times 10^6$ at 25°C
mm	meas.	calc.	meas.	calc.	meas.	calc.	W/cm degC^2
0		0·978		0·962		0·926	−2·39
0·4581	1·011	1·010	0·978	0·976	0·943	0·942	−2·25
0·9578	1·023	1·024	0·988	0·992	0·960	0·961	−2·09
1·4559	1·029	1·032	1·001	1·001	0·972	0·972	−1·99
1·9293	1·038	1·036	1·009	1·007	—	—	−1·94
∞		1·050		1·023		0·997	−1·77

measured values of k_{eff} can be well presented by formula (5). The increase of the slope of the curves gives the increase of the temperature coefficient of thermal conductivity with the thickness of the layer. Figure 6 shows that this coefficient becomes positive at large thicknesses for liquid paraffin.

The temperature coefficients at 25°C were calculated with help of formula (6) for the single plate distances used in the measurements and also for the distances $s = 0$ and $s = \infty$. The results are represented in the last columns of the tables and in Figs. 7 and 8 where the dependence of the temperature coefficients on the layer thickness is shown.

Table 6 gives the measured values of k_{eff}

Table 5. Thermal conductivity of liquid paraffin

Thickness of the liquid layer s mm	Thermal conductivity $k_{\mathrm{eff}} \times 10^3$ (W × cm^{-1} × degC^{-1})										$(\mathrm{d}k_{\mathrm{eff}})/(\mathrm{d}T) \times 10^6$
	25°C		40°C		55°C		70°C		80°C		at 25°C
	meas.	calc.	meas.	calc.	meas.	calc.	meas.	calc.	meas.	calc.	W/cm degC^2
0		1·193		1·182		1·171		1·160		1·153	−0·74
0·4581	1·203	1·204	1·194	1·195	1·185	1·185	1·177	1·176			−0·63
0·9578	1·224	1·221	1·216	1·215	1·209	1·209	1·207	1·203			−0·45
1·4559	1·235	1·235	1·229	1·231	1·223	1·227	1·223	1·224	1·219	1·222	−0·32
1·9293	1·245	1·244	1·241	1·241	1·239	1·239	1·241	1·238	1·237	1·237	−0·22
∞		1·278		1·280		1·284		1·289		1·294	+0·12

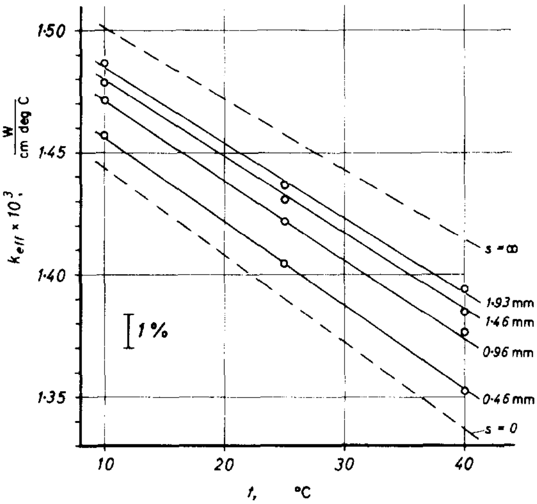

FIG. 2. Thermal conductivity of benzene.

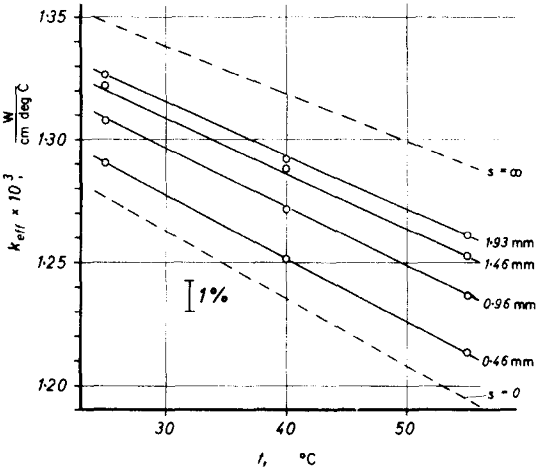

FIG. 4. Thermal conductivity of m-xylene.

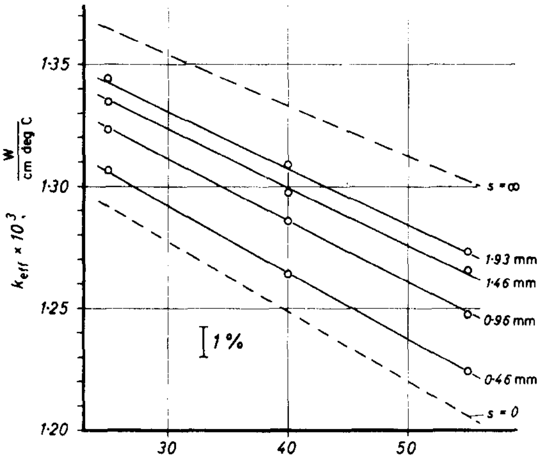

FIG. 3. Thermal conductivity of toluene.

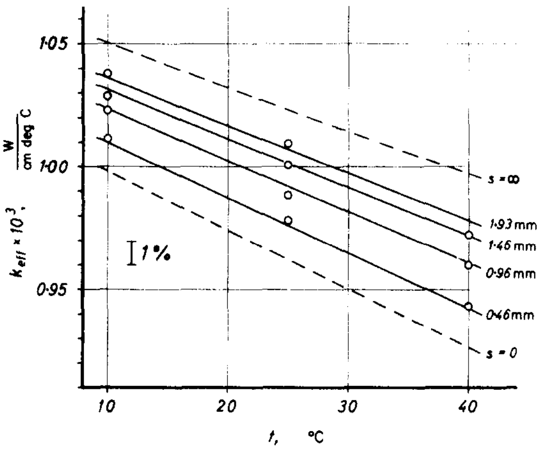

FIG. 5. Thermal conductivity of carbon tetrachloride.

of nitrobenzene. This liquid has a stronger ir-absorption than the other five substances. We find, in consequence, its thermal conductivity being less dependent on the plate distance.

A quantitative representation of the measured thermal conductivity of such liquids absorbing more strongly than, e.g. toluene by formula (5) seems, however, to be problematic. The validity of this formula is doubtful for substances showing absorption coefficients the reciprocal of which is of the same magnitude as the wave length in some regions of the absorption spectrum. In this case, Kirchhoff's theory is no longer valid. Moreover, there is a greater error in determining a mean value of the refractive index.

For these reasons we have not interpreted the measured values of the thermal conductivity k_{eff} of nitrobenzene by formula (5). We have only smoothed these values by a least square method, supposing that k_{eff} is, as a first-order approximation, linearly dependent on the reciprocal value of the layer thickness s and that it is

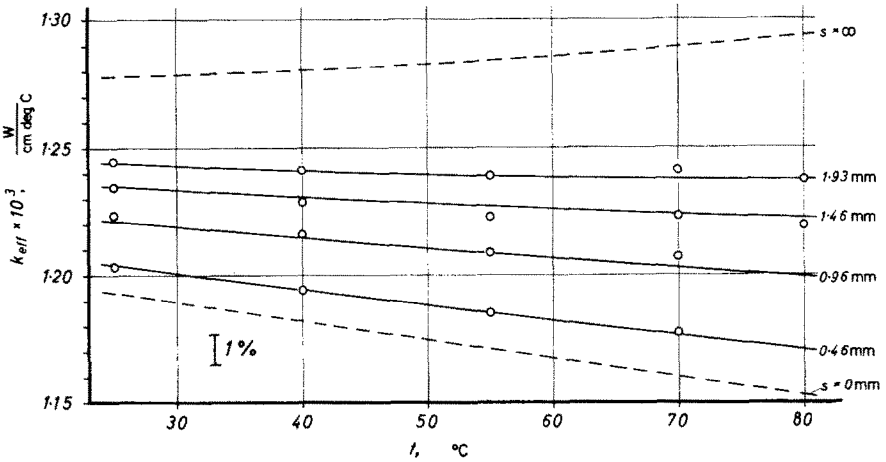

FIG. 6. Thermal conductivity of liquid paraffin.

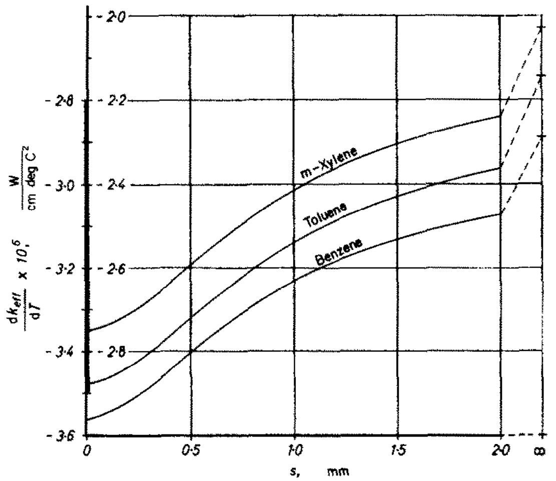

FIG. 7. Temperature coefficient of the thermal conductivity of benzene and homologues.

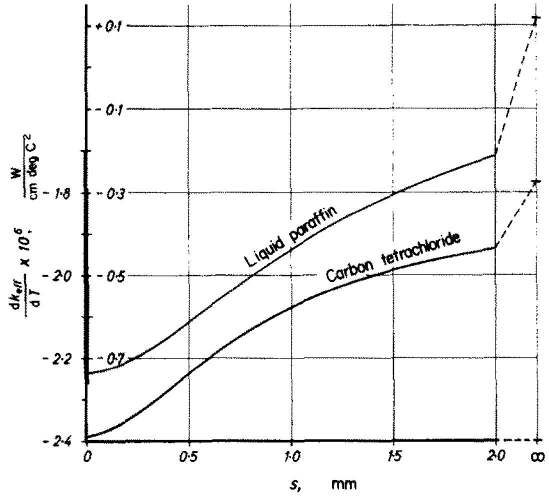

FIG. 8. Temperature coefficient of the thermal conductivity of carbon tetrachloride and liquid paraffin.

a linear function of the temperature T. The result is represented in Fig. 9. The last column in Table 6 gives the mean value of the temperature coefficient of nitrobenzene.

We intend to investigate in greater detail the decreasing of the dependence of k_{eff} on the plate distance for increasing ir-absorption. As a preliminary result, some data on iso-propanol at 25°C is given. Iso-propanol has an absorption somewhat stronger than nitrobenzene.

thickness of the layer s (mm)	0·458	0·958	1·929
thermal conductivity $k_{eff} \times 10^3$ (W cm^{-1} degC^{-1})	1·340	1·346	1·349

Figure 10 shows the increase of the measured thermal conductivity with increasing layer thickness s between the limits $s_1 = 0{\cdot}458$ and $s_2 = 1{\cdot}929$ mm at 25°C for the liquids toluene, nitrobenzene, and iso-propanol. The diminution

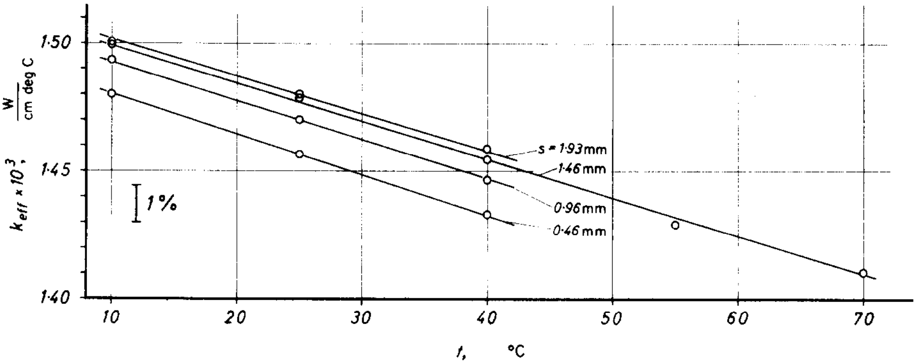

FIG. 9. Thermal conductivity of nitrobenzene.

Table 6. Thermal conductivity of nitrobenzene

Thickness of the liquid layer s mm	Thermal conductivity $k_{eff} \times 10^3$ (W $\times$ cm^{-1} $\times$ degC^{-1})					$(dk_{eff})/(dT) \times 10^6$ (mean value) W/cm degC^2
	10°C	25°C	40°C	55°C	70°C	
0·4581	1·480	1·456	1·433			
0·9578	1·493	1·470	1·446			−1·51
1·4559	1·499	1·478	1·454	1·429	1·410	
1·9293	1·500	1·480	1·459			

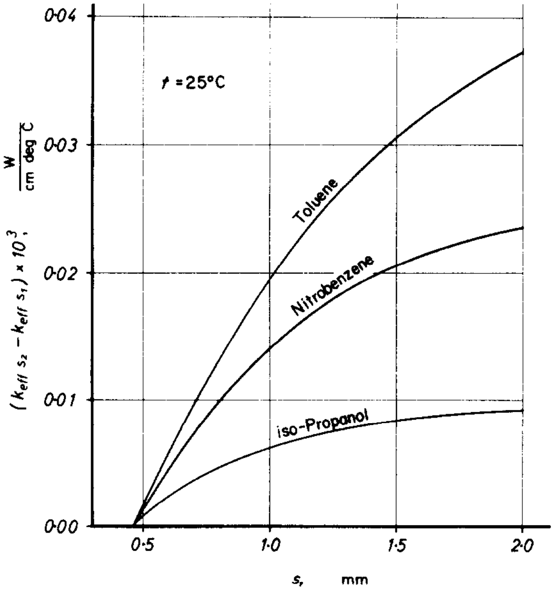

FIG. 10. Increase of the measured thermal conductivity with increasing thickness of the liquid layer.

of this increase with increasing absorption is considerable.

The precision of the measured thermal conductivities is valued at about ±0·5 per cent and that of the temperature coefficients at about $\pm 0{\cdot}1 \times 10^{-6}$ W cm^{-1} degC^{-2}.

5. DISCUSSION OF THE RESULTS

Table 7 shows a list of measured thermal conductivities k_{eff} and temperature coefficients at 25°C published by other authors in the last twenty years. At the end of the list our own values are given for a plate distance of 1 mm and also the minimum and maximum values possible according to our measurements. It can be seen that nearly all values of the thermal conductivity and most of the temperature coefficients are within the intervals which arise from various radiative components due to different apparative conditions. The extent of

*Table 7. Comparison of values of thermal conductivities and temperature coefficients measured by several authors at 25°C**

No.	Author	Benzene		Toluene		m-Xylene		CCl_4		Nitrobenzene		Liquid paraffin	
		a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
1	Riedel 1940–51 [8]	1·460	−3·48	1·336	−2·55			1·023	−2·43				
2	McNall 1951 [9]	1·451	−3·77										
3	Filippov 1954 [10]	1·449	−2·59					1·009	−1·68	1·492	−1·50		
4	Schmidt 1954 [11]	1·442	−2·30	1·348	−2·60			1·025	−1·02				
5	Mason 1954 [12]							1·019	−1·40				
6	Challoner 1956 [13]			1·365	−3·14			1·063	−1·34			1·264	−0·13
7	Briggs 1957 [14]	1·450	−0·59	1·361	−0·71	1·306	−0·75						
8	Vargaftik 1958 [15]			1·348	−2·38					1·492	−1·67		
9	Eldarov 1958 [16]	1·419	−2·51										
10	Spencer 1960 [17]											1·243	0·00
11	Ziebland 1961 [18]			1·330	−2·85								
12	Turnbull 1962 [19]											1·220	−0·29
13	Jamieson 1963 [20]	1·457	—							1·499	−2·68		
14	Horrocks 1963 [21]	1·421	−3·20										
15	Horrocks 1963 [22]	1·420	−3·21	1·330	−2·92								
16	Venart 1964 [23]			1·338	−3·04			1·020	−1·92				
17	Venart 1965 [24]	1·454	−3·28	1·321	−2·67								
18	Poltz 1965 [4]	1·424	—	1·323	—			0·998	—			1·217	
19	Tufeu 1966 [25]	1·430	−3·6	1·340	−3·2	1·303	−3·1	0·995	−2·6				
20	This work ($s = 1$ mm)	1·424	−3·23	1·326	−2·54	1·311	−2·42	0·993	−2·08	1·470	−1·51	1·222	−0·44
limits	$k(s = 0)$	1·39	−3·6	1·29	−2·9	1·28	−2·8	0·96	−2·4			1·19	−0·74
		to	to	to	to	to	to	to	to			to	to
	$k + k_r(s = \infty)$	1·46	−2·9	1·36	−2·1	1·35	−2·0	1·02	−1·8			1·28	+0·12

$a = k_{eff} \times 10^3$ (W × cm^{-1} × degC^{-1}) $b = (dk_{eff})/(dT) \times 10^6$ (W × cm^{-1} × degC^{-2})

* See also Jamieson [26].

the intervals is about 5–7 per cent of the thermal conductivity. The first four liquids, which have temperature coefficients not very different from each other, show an increase of the coefficients of about 20–30 per cent. These are, for both physical quantities, just the amounts which have been calculated from the optical data, as we have shown for toluene [1].

The equations (3–6) are only correct for the parallel plate arrangement. For the limits $s = 0$ $(Y = 0)$ and $s = \infty\,(Y = 1)$, however, these equations contain no quantities dependent on geometric conditions. Therefore, we suppose that the range within which the measured values can vary due to various radiative heat flows is the same for all geometric arrangements. In consequence, we have considered in Table 7 measurements performed by all methods.

The values in Table 7 are listed chronologically. There seems to exist a tendency in the measured thermal conductivities k_{eff} to decrease a little in the course of the years. We suppose that there is spent more care to avoid convection in the last time. When this was secured by reducing the layer thicknesses, an additional decrease of k_{eff} results from a smaller radiative heat flux.

Convection can be caused thermally or mechanically. The latter may occur if the apparatus is exposed to small vibrations, e.g. by water flowing through it. From the value of the Rayleigh number one cannot, according to our opinion, decide upon the question whether thermally caused convection has noticably influenced the measured values. Without regard to the fact that this depends on the accuracy of the measurements it will, of course, depend very considerably upon the direction and the magnitude of the density gradient in the liquid.

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Résumé—Les conductivités thermiques du benzène, du toluène, du m-oxylene, du tétrachlorure de carbone, de l'huile de paraffine et du nitrobenzène ont été mesurées à plusieurs températures en employant un appareil à plaques parallèles horizontales avec anneau de garde décrit auparavant. On a fait varier l'épaisseur de la couche liquide dans la gamme où les valeurs mesurées ne sont pas augmentées par la convection d'une façon perceptible en accord avec les résultats d'une étude précédente. On a trouvé que la dépendence de la conductivité thermique et de son coefficient de variation thermique en fonction de l'épaisseur de la couche liquide sont en bon accord avec les valeurs obtenues en calculant la contribution du rayonnement au transport de chaleur dans les liquides absorbant peu les infra-rouges. Ces valeurs peuvent être calculées à l'aide du diagramme d'absorption du liquide comme on l'a montré auparavant.

On estime la précision des valeurs mesurées de la conductivité thermique à environ ± 0,5 pour cent. L'incertitude sur les coefficients de variation thermique, calculés est d'environ $\pm\ 0{,}1 \times 10^6$ W cm^{-1} $(\mathrm{degC})^{-2}$.

La conductivité thermique effective des liquides peu absorbants comme le toluène peut varier à la température ambiante d'environ 5 à 7 pour cent à cause d'une composante de rayonnement dépendant des conditions de l'appareillage. Le coefficient de variation thermique de la conductivité thermique peut varier d'environ 20 à 30 pour cent. Une étude des mesures publiées par d'autres auteurs dans les 20 dernières années montre que presque toute les valeurs de la conductivité thermique et plus de la moitié de leurs coefficients de variation thermique sont à l'intérieur d'un intervalle donné par la variation de la composante de rayonnement.

Les valeurs les plus récemment mesurées de la conductivité thermique semblent être en moyenne quelque peu plus faibles que les valeurs les plus anciennes. Nous pensons qu'actuellement on fait plus d'efforts pour éviter la convection.

Zusammenfassung—Die Wärmeleitfähigkeit von Benzol, Toluol, m-Xylol, Tetrachlorkohlenstoff, Paraffinöl und Nitrobenzol wurde bei mehreren Temperaturen mit einer früher beschriebenen Parallelplatten-Apparatur mit Schutzring gemessen. Dabei wurde die Dicke der Flüssigkeitsschicht innerhalb des Bereichs variiert, in dem nach den Ergebnissen einer früheren Untersuchung die Messwerte nicht merklich infolge von Konvektion anwachsen. Es ergab sich, dass die Abhängigkeit der Wärmeleitfähigkeit und ihres Temperaturkoeffizienten von der Dicke der Flüssigkeittsschicht in guter Übereinstimmung mit den Werten ist, die durch Berechnung des Beitrages der Strahlung zum Wärmetransport in Flüssigkeiten mit geringer IR-Absorption erhalten werden. Diese Werte lassen sich mit Hilfe eines Absorptions-Diagramms der Flüssigkeit berechnen, wie früher gezeigt wurde.

Die Genauigkeit der gemessenen Werte der Wärmeleitfähigkeit wird auf etwa ±0,5 Prozent geschätzt. Die Unsicherheit der berechneten Temperatur-Koeffizienten beträgt etwa $\pm 0{,}1 \,.\, 10^{-6}$ Wcm^{-1} $\mathrm{gvd.}^{-2}$

Die effektive Wärmeleitfähigkeit von schwach absorbierenden Flüssigkeiten, wie Toluol, kann wegen des von den apparativen Bedingungen abhängenden Strahlungsanteils bei Raumtemperatur um etwa 5 bis 7 Prozent variieren und der Temperaturkoeffizient der Wärmeleitfähigkeit um etwa 20 bis 30 Prozent. Ein Studium von Werten, die von anderen Autoren in den letzten 20 Jahren veröffentlicht worden sind, zeigt, dass fast alle Werte der Wärmeleitfähigkeit und die meisten Temperatur-Koeffizienten innerhalb eines Intervalls liegen, das durch die mögliche Variation der von den apparativen Bedingungen abhängenden Strahlungs-Komponente gegeben ist.

Die in letzter Zeit gemessenen Werte der Wärmeleitfähigkeit scheinen im Mittel etwas kleiner zu sein als die früheren. Wir vermuten, dass jetzt mehr Mühe auf die Vermeidung von Konvektion aufgewendet wird.

Аннотация—Измерялись коэффициенты теплопроводности бензина, толуола, ксилола, четыреххлористого углерода, жидкого парафина и нитробензола при различных температурах с помощью ранее описанного прибора с горизонтальными параллельными пластинками. Выбранная толщина жидкого слоя в соответствии с результатами предыдущего исследования находилась в пределах, для которых на измеренные величины мало влияла конвекция в зазоре. Было обнаружено, что зависимость теплопроводности и её температурного коэффициента от толщины жидкого слоя хорошо согласуется с расчетными величинами, полученными при учете теплового излучения в жидкостях с малым коэффициентом поглощения. Эти величины, как было показано прежде, можно вычислить с помощью диаграммы поглощения жидкости. Точность экспериментального определения коэффициента теплопроводности находится в пределах ± 0,5%. Погрешность рассчитанных температурных коэффициентов составляет примерн $\pm 0{,}1 \times 10^{-6}$.

Эффективная теплопроводность плохо поглощающих жидкостей, например, толуола, может изменяться при комнатной температуре от 5 до 7% из-за лучистой составляющей, зависящей от условий опытов. Температурный коэффициент теплопроводности может изменяться в пределах от 20 до 30%. Анализ измерений, опубликованных другими авторами за последние 20 лет, показывает, что почти все величины теплопроводности и больше половины их температурных коэффициентов оказываются в диапазоне величин изменения лучистой составляющей.

Вновь измеренные величины коэффициента теплопроводности оказываются в среднем несколько меньшими, нежели прежде известные. Мы полагаем, что нам удалось принять все меры для устаранения конвекции.