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ON THE MEASUREMENT OF THE THERMAL CONDUCTIVITY OF LIQUIDS BY A NON-STATIONARY METHOD *)

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Synopsis

In 1949 in this journal [1]) a paper appeared dealing with a non-stationary method for measuring the thermal conductivity of liquids. This method, indicated first by S t å l h a n e and P y k [2]), was based upon the temperature rise at a certain distance from an electrically heated wire, producing a constant heat flow into the liquid.

Results obtained by using this method were found to be unreliable. The time during which convection does not disturb the measurements appeared to be too short to apply the proposed mathematical approximations. E.g., neglecting the ratio of the specific heats per cm^3 of the liquid and the heating wire ($c\varrho/c_0\varrho_0$) is not allowed. In consequence of a more rigorous mathematical treatment the method has to be changed to yield the correct results as its application to a series of experimental data shows.

As the necessary changes mean a serious drawback of the original method it is suggested to lengthen the time during which measurements are possible by rotating the vessel containing the liquid about the heater to suppress convection.

1. *Nomenclature*

λ	thermal conductivity of the liquid	cal/cm sec°C
c	specific heat of the liquid	cal/g°C
c_0	specific heat of the heater	cal/g°C
ϱ	density of the liquid	g/cm^3
ϱ_0	specific mass of the heater	g/cm^3
a	thermal diffusivity of the liquid	cm^2/sec
r	distance from the heating wire	cm
$2r_0$	diameter of the heater	cm

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q	heat production of the heater per unit time and unit length	W/cm
θ	temperature(rise) at the surface of the heater	°C
t	time	sec
I_i, N_i	Bessel-, respectively Neumann-function of order i	

$kr_0 = 2c\varrho/c_0\varrho_0$.

2. *Introduction.* In 1949 a paper was published by van Drunen and one of us [1]) describing a method for determining the thermal conductivity of liquids. The method was based upon the temperature rise at a certain distance r from an electrically heated, cylindrical wire producing a constant heat flow into the liquid.

The theoretical treatment of this original method is the following: the heater is assumed to be of infinite length and of neglegible thickness. Fourier's equation and the boundary conditions are under these circumstances:

Fourier: $$a(\partial^2\theta/\partial r^2 + \partial\theta/r\partial r) = \partial\theta/\partial t \quad (1)$$

boundary conditions:

$$t = 0 \quad r \neq 0 \quad \theta = 0 \quad (2)$$

$$t > 0 \quad r = \infty \quad \theta = 0 \quad (3)$$

$$t > 0 \quad r \to 0 \quad -2\pi r\lambda\partial\theta/\partial r = q = \text{constant} \quad (4)$$

The solution of (1) is given by

$$\theta = (q/4\pi\lambda)\, K_1\, (r^2/4at) \quad (5)$$

where $K_1(x)$ stands for

$$\int_x^\infty z^{-1}\, e^{-z}\, \mathrm{d}z = -0.5772 + \ln\,(1/x) + (x/1.1!) - (x^2/2.2!) + \ldots.$$

After a period of sufficient length the term $r^2/4at$ and the following terms can be neglected; then sufficient accuracy is obtained by putting

$$\theta = (q/4\pi\lambda)\,(-0.5772 + \ln\,(4at/r^2)) \quad (6)$$

In this case the difference between the temperatures θ_2 and θ_1 at two times t_2 and t_1 is given by the expression

$$\theta_2 - \theta_1 = (q/4\pi\lambda)\ln\,(t_2/t_1) \quad (7)$$

from which it is readily seen that plotting of the measured temperature against the logarithm of time will result in a straight line with the slope $q/4\pi\lambda$ *). As the heat production per second and per cm heaterlength can be measured accurately, from this slope the thermal conductivity of the liquid is inferred.

The experiment is carried out with the heating wire stretched in the axis of a cylindrical vessel containing the liquid to be measured. The heating wire (manganine, 0.3 mm diameter), together with a thermocouple, is stretched in a glass capillary to protect them against being corroded by the liquid. The thermocouple junction is put halfway the tube. At the time zero the current through the heating wire is switched on and the deflection of a galvanometer, connected with the thermocouple, is recorded.

It appeared that convection in the liquid limits the time during which the temperature measured is determined by the conductivity of the liquid alone. As a consequence, neglecting the term $r^2/4at$ of $K_1(r^2/4at)$ is not allowed. It was shown that the method can be used notwithstanding; adding to the time a correction t_0 makes it possible to write for the difference of the temperatures at two times

$$\theta_2 - \theta_1 = (q/4\pi\lambda) \ln (t_2 + t_0)/(t_1 + t_0) \tag{8}$$

The correction for the finite thickness of the heater, originally assumed to be zero, can also be included in this t_0-correction.

The numerical value of t_0 is determined by plotting the derivative from time with respect to the temperature against time. For

$$\partial t/\partial \theta = 4\pi\lambda \, (t + t_0)/q \tag{9}$$

so the intercept of the resulting straight line with the $\partial t/\partial\theta$-axis gives $-t_0$. Figure 1 shows a recorded temperaturecurve and the accessory straight line, obtained from it by a correction of time, determined according to figure 2 [3]).

However, when we applied this method in the indicated way we did not get reliable results. This is due to the fact that during the period in which convection does not disturb the measurements the original theoretical treatment given above fails in describing the actual temperature rise. It will be shown in the following that the ratio of the specific heats per cm^3 of liquid and heater $c\varrho/c_0\varrho_0$ plays

*) Against custom in the following graphs the indepent variable (t) is plotted along the vertical axis. This is done to facilitate comparison of the curves obtained by the improved method with those previously obtained.

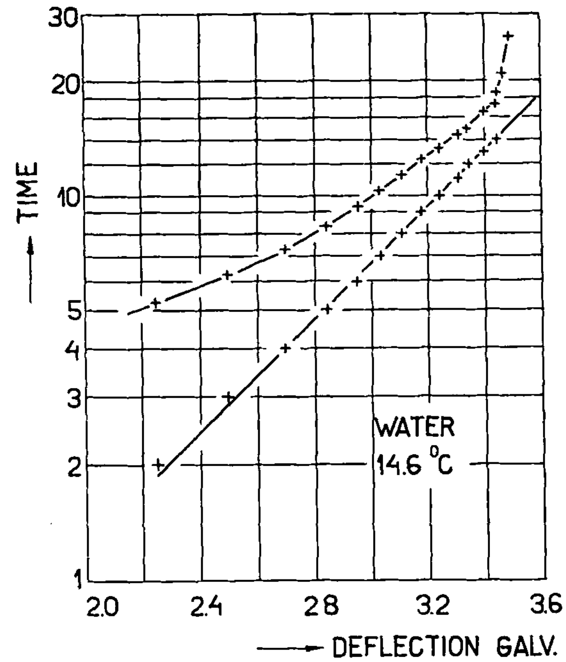

Fig. 1. Plot of log time versus deflection of the galvanometer without and with t_0-correction for water.

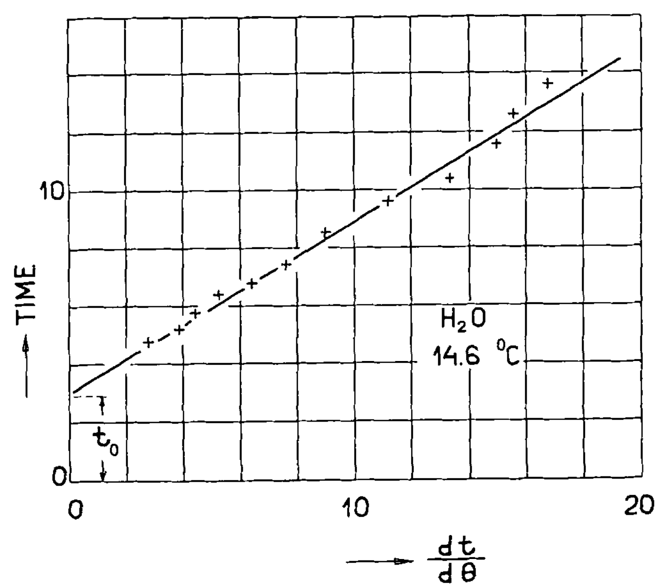

Fig. 2. Determination of the t_0-correction.

an important part in the explanation of the experimental results during this period (section 3*a*) and how it affects the way the thermal conductivity is obtained from the recorded temperature curves (section 3*b*).

3. *The improved method. a.* Theoretical treatment. It is possible to solve Fourier's equation (1) exactly assuming that the cylindrical heater has a diameter $2r_0$ cm and a constant heat production per unit length. Moreover, the temperature of the heater and its warming up are assumed to be homogeneous and the contact between the heater and the surrounding liquid to be a perfect one. Fourier's equation and the boundary conditions in that case are:

Fourier: $$a(\partial^2\theta/\partial r^2 + \partial\theta/r\partial r) = \partial\theta/\partial t \qquad (1)$$

boundary conditions:

$$t = 0 \quad r \neq 0 \quad \theta = 0 \qquad (10)$$

$$t > 0 \quad r = \infty \quad \theta = 0 \qquad (11)$$

$$t > 0 \quad r = r_0 \quad -2\pi r_0 \lambda \partial\theta/\partial r + \pi r_0^2 c_0 \varrho_0 \, \partial\theta/\partial t = q \qquad (12)$$

Using a Laplace-transformation of time, the solution of (1) under the conditions(10), (11) and (12) is proved to be [4]:

$$\frac{4\pi\lambda\theta}{q} = \frac{8(kr_0)^2}{\pi^2}\int_0^\infty (1 - e^{-atx^2/r_0^2}) \cdot \frac{\mathrm{d}x}{x^3[\{xI_0(x) - kr_0\,I_1(x)\}^2 + \{x\,N_0(x) - kr_0\,N_1(x)\}^2]} . \qquad (13)$$

From the behaviour of the transformed solution for small values of the new variable the behaviour of (13) for large values of time is deduced by using a Tauber-theorem [5]). It is found to be:

$$4\pi\lambda\theta/q = -0.5772 + \ln(4at/r_0^2) \qquad (14)$$

showing that for very large values of time the original method may be used, as the finite thickness of the heater does not alter the results. However, this does not apply to the values of time during the period before convection starts disturbing the measurements. Numerical integration of (13) for several values of $c\varrho/c_0\varrho_0$ gives temperature curves considerably deviating from the original expression (5), as is shown in figure 3. In this figure both temperature and time are inserted in a dimensionless number; to compare the results with those previously obtained the expressions (5) and (6) in the case $r = r_0$ are also drawn.

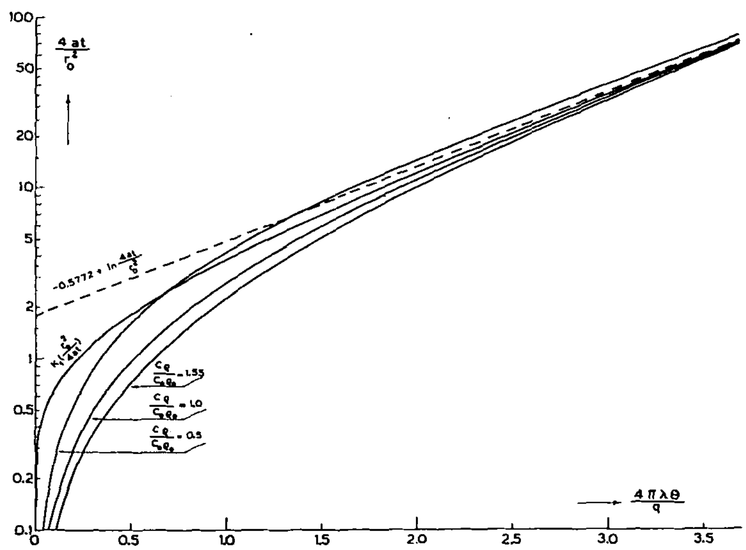

Fig. 3. Expression (13) for different values of $kr_0 = 2c\varrho/c_0\varrho_0$. To facilitate comparison the curves

$$4\pi\lambda\theta/q = K_1(4at/r_0^2) \text{ and } 4\pi\lambda\theta/q = -0.5772 + \ln(4at/r_0^2)$$

are also drawn.

Moreover, comparison of the figures 3 and 1 shows that the measured curve turns its convex side to the horizontal axis as the theoretical curves turn their concave side to it. Consequently the correction of time of figure 1 has the opposite sign of the correction expected for theoretical reasons.

Finally it may be noticed that by supposing the warming up of the heater to be homogeneous and the contact between heater and liquid to be a perfect one a constant temperature difference between the actual and the theoretical temperature is introduced. This does not affect the results as these are obtained from the slope of the recorded and corrected curves.

b. Measurements and results. The apparatus used is the same as the one described previously [1]), except for one modification. The glass capillary containing the heating wire and the thermocouple was suspected to stimulate convection of the air by being hollow. Consequently heating wire and thermocouple were melted in pyrexglass; the in this way shaped cylindrical solid heater was framed as the axis of the vessel containing the liquid. As the melting requires a high temperature the thermocouple consists of chromel-alumel wire (diameter 0.35 mm), its electromotive force being 0.417 mV per 10°C rise of temperature. The heating wire is a constantan wire (diameter 0.3 mm), its resistance being 0.0529 Ω/cm. The diameter of the heater averages 2.2 mm; its specific heat per cm^3 $c_0\varrho_0$ being 0.658 cal/cm^3 °C.

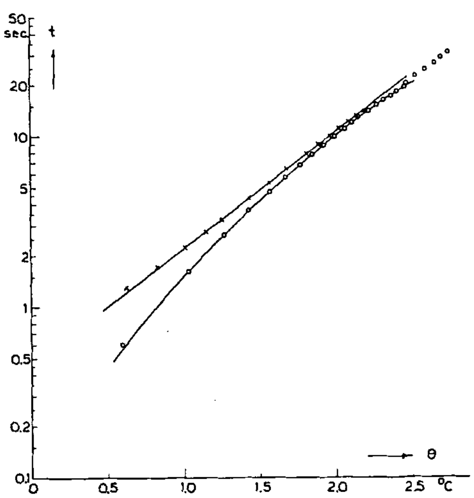

Fig. 4. Recorded temperature in the case water ($c\varrho/c_0\varrho_0 = 1.52$) is measured. Heat production: $6.29 \cdot 10^{-2}$ W/cm; time correction: 0.7 sec; heat conductivity: $1.53 \cdot 10^{-3}$ cal/cm sec °C.

Figure 4 gives the temperature rise of the hot thermocouple junction in the case water ($c\varrho/c_0\varrho_0 = 1.52$) is measured. It is shown that the experimental curve turns its concave side to the horizontal axis as is expected for theoretical reasons. The time-correction needed and the accessory straight line obtained by applying this correction are adapted by the trial and error method to those found theoretically.

Figure 5 shows the curve obtained by numerical integration of (13) in the case $c\varrho/c_0\varrho_0 = 1.55$. A correction of time $4at_0/r_0^2 = 1.0$

gives a straight line in the region

$$2 \leqslant 4at/r_0^2 \leqslant 15 \qquad (15)$$

whereas the experimental curve (figure 4) is straightened by a correction $t_0 = 0.7$ sec in the region

$$1.3 \leqslant t \leqslant 10 \qquad (16)$$

From both conditions $4at_0/r_0^2 = 1.0$ and $t_0 = 0.7$ sec it follows that $4a/r_0^2 = 1.4\ \text{sec}^{-1}$; this value combined with (15) makes it necessary that

$$1.4 \leqslant t \leqslant 10.8 \qquad (17)$$

which is in good agreement with (16).

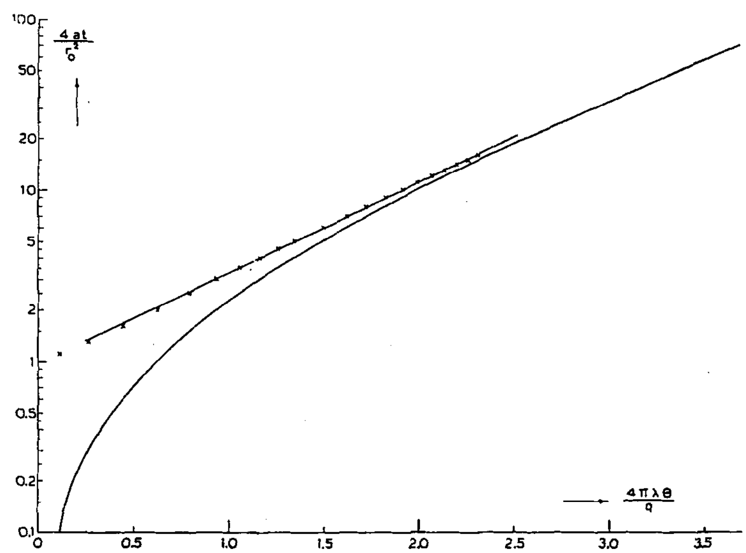

Fig. 5. Expression (13) for $c\varrho/c_0\varrho_0 = 1.55$. The accessory straight line is obtained by a time correction $4\ at_0/r_0^2 = 1.0$.

However, comparison of the slope of the straight line drawn in figure 5 to the slope of (14) shows, that the former is a factor 1.21 too small, so determining the thermal conductivity as indicated by the original method (section 2) would have resulted in a value 1.21 times too large.

Applying the correction factor found in this way to the slopes of the straight lines obtained from eleven experimental curves, giving the temperature rise at heat productions varying from $1.38 \cdot 10^{-2}$ to $10.35 \cdot 10^{-2}\ W/\text{cm}$, yields a value of the thermal conductivity of water at 20°C of 149($\pm$ 4) $\cdot$ 10^{-5} cal/cm sec °C. Comparison of this value to those given in literature [6] [7]) indicates a systematical error of about 5% probably caused by the unaccurate estimation of the specific heat per cm^3 $c_0\varrho_0$ of the heater and the unequality of the values $c\varrho/c_0\varrho_0$ in theory and experiment.

Similarly the thermal conductivity has been measured for other values of $c\varrho/c_0\varrho_0$ as given in figure 3. All results are comprised in the following table:

liquid measured	$c\varrho/c_0\varrho_0$	correction $4\,at/r_0^2$ of theor. curve	correction of slope	$\lambda \cdot 10^5$
Water	1.52	1.0	1.21	149 $\pm$ 4
Ethylene glycol	0.96	2.0	1.00	66.0 $\pm$ 0.1
Carbon tetrachloride	0.49	3.0	0.89	34 $\pm$ 1

4. *Conclusion.* The necessary modifications of the original method as described in the above make the method unsuitable for the quick and accurate determination of the thermal conductivity of liquids. Specific heat and density of the liquid to be measured must be known to perform the numerical integration, without which the correction-factor for the slope of the measured straight lines cannot be calculated. This numerical integration as well as the adaptation of the experimental temperature curves to the theoretical ones takes much time, thus causing an important diminution of the advantages gained by using non-stationary methods to determine thermal conductivities. To prevent this drawback it is necessary to lengthen the period in which convection currents do not disturb the measurements. This can be achieved by rotating the vessel containing the liquid about the heater. The results obtained in this way will be reported in a second paper.

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REFERENCES

1) Van der Held and Van Drunen, Physica **15** (1949) 865. Figures 1 and 2 are reprinted from this paper.
2) Stålhane and Pyk, Teknisk Tidskrift **61** (1931) 389.
3) For full details, s. Van Drunen, Thesis Utrecht, 1949.
4) Carslaw and Jaeger, Conduction of heat in solids. Oxford University Press (1950) 284.
5) Doetsch, Theorie und Anwendung der Laplace-Transformation, Dover Publications (1943) 222.
6) Koch, Grundlagen des Wärmeaustausches, Beucke u. Söhne (1950).
7) Palmer, Ind. Eng. Chem., **40** (1948) 89.