

SECTION C, PHYSICAL SCIENCES

Unsteady State Method for the Determination of Thermal Conductivities of Oils¹

J. E. HURT, E. E. KOHNKE, and A. R. SCHMIDT,
Oklahoma State University, Stillwater

There are a number of applications of liquids in which it is desirable to know the thermal conductivity of the liquids used, preferably under unsteady state conditions. The subject of this paper is the development of a laboratory procedure for measuring the thermal conductivities of liquids at temperatures ranging from room temperature to 500° F., while using an unsteady heat source, and some results obtained by the use of this procedure. The liquids used were five oils from a group specified in a military contract, and some check liquids on which statistics were readily available.

Practically all previous measurements of thermal conductivity have been made using steady state methods. The method used here differs, in that it is based on a measurement of thermal diffusivity, the experimental quantity of interest in an unsteady heat-flow situation. Since the values of density and specific heat of a liquid will show only very slight changes when subjected to a temperature variation on the order of one to two degrees Fahrenheit, it is reasonable to suppose that if the magnitude of its thermal diffusivity is measured using a periodic temperature wave having such an amplitude, accurate values of its thermal conductivity can be obtained, the thermal conductivity being the product of density, specific heat, and thermal diffusivity (α).

Consider the differential equation for one-dimensional heat flow

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (\text{Eq. 1})$$

where T is the temperature at time t and at position x in the conducting medium and α is the thermal diffusivity. If it is assumed that the medium is of semi-infinite dimensions and that the temperature of the plane surface is varied sinusoidally, the solution of Equation 1 is

$$T(x, t) = T_0 e^{-x \sqrt{\frac{w}{2\alpha}}} \sin\left(\omega t - x \sqrt{\frac{\omega}{2\alpha}}\right)$$

where $w/2\pi$ is the frequency of the surface temperature variation. From this we get the relations

$$A_1 - A_2 = \ln \frac{A_1}{A_2} = (x_1 - x_2) \sqrt{\frac{\omega}{2\alpha}}$$

where the ϕ 's are the arguments of the sine function at x , and x , at some instant of time, and A_1 is the ratio of the amplitudes of the attenuated

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temperature wave at x_1 and x_2 . Making a correction to allow for small lateral energy dissipation in the medium, Equation 1 becomes

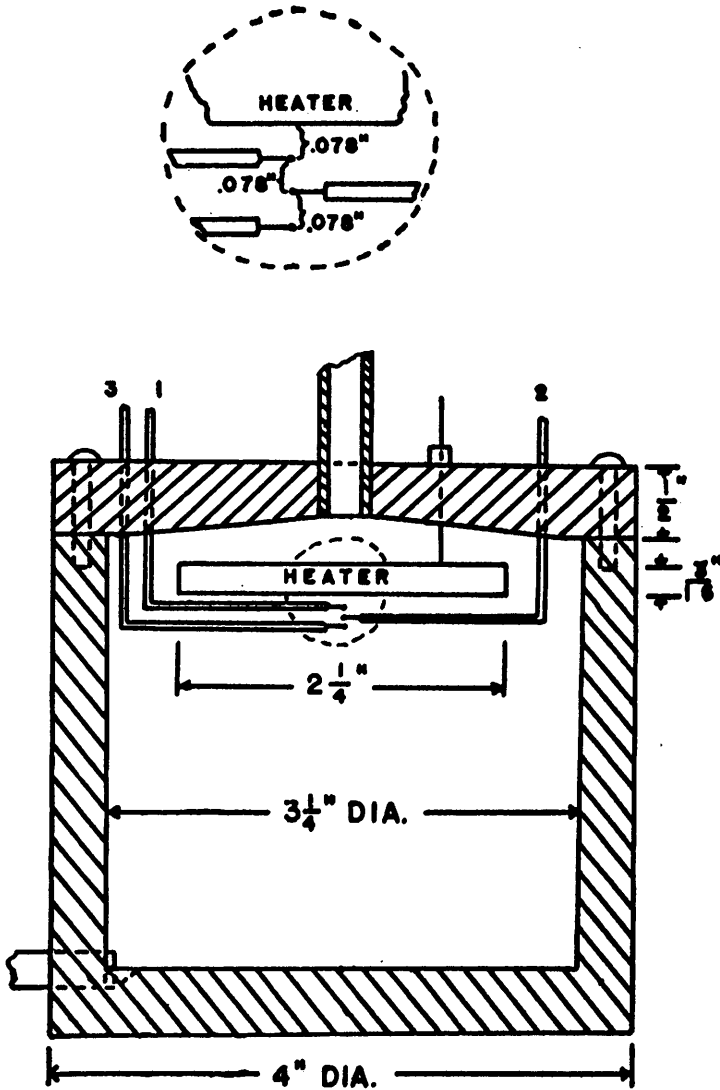


Fig. 1
Diagram of Sample Holder

$$\frac{\partial T}{\partial x} = \alpha \frac{\partial^2 T}{\partial x^2} - \mu T \quad (\text{Eqn. 2})$$

It is assumed that energy storage in the medium is negligible. From the solution of Equation 2 can be derived the expression which was finally used for all computations of thermal diffusivity,

$$\alpha = \frac{\omega(x_2 - x_1)^2}{2(\theta_1 - \theta_2) \ln A_1/A_2} \quad (\text{Eqn. 3})$$

From this expression it can be seen that if two measuring stations are placed a known distance apart along a line perpendicular to the plane surface from which the temperature wave is generated, continuous recordings of temperatures at these two points will supply the information necessary to compute the thermal diffusivity of the medium. Solutions were also obtained for three-dimensional heat flow, but these solutions proved to be of too complex a form to be practical.

The apparatus, a diagram of which is shown in Figure 1, was designed so as to satisfy the conditions for which the solution to be used was obtained. The heating coil was made in the shape of a pancake in order to produce as nearly a plane wave as possible, and was made with a diameter large in comparison with the dimensions of thermocouple junctions which were used as the temperature measuring devices. The electrical input to the heating coil was varied sinusoidally so that the heat output would be of a sinusoidal form, which would give a mathematical function simple to handle in the calculations.

These factors and others were important in the construction of a sample holder. Probably of greatest importance was the behavior of the liquids at temperatures up to 500°F. Allowances had to be made for thermal expansion and for gases that might be produced in boiling or chemical breakdown. For this purpose, and to allow for draining, cleaning, and filling the apparatus without disassembly, the container was constructed with two openings. Also of great importance was the elimination of radiative and convective heat transfer between the heating coil surface and the thermocouples. Radiation was negligible and convection was reduced by placing the heating coil near the top of the sample holder and the thermocouples below the coil. With an arrangement such as this, it was supposed that the majority of the turbulence caused by convection would be contained in the small space above the coil, and that conduction would carry a temperature wave downward past the thermocouples with relative freedom from turbulence. If there were very little or no turbulence in the vicinity of the thermocouples, the result would be an electrical output from the thermocouples similar to the sinusoidal input to the heating coil. An agreement of this sort would be necessary in order to obtain any data that would be meaningful in calculating the thermal conductivity. Before the final sample holder was constructed, some visual observations were made of a heating coil submerged in a liquid to get some idea of what the pattern of convection around the coil and in the vicinity of the thermocouples would be. It was found that for power dissipation at the coil surface of less than $\frac{1}{2}$ watt per square centimeter, there was no noticeable turbulence due to convection.

The sample holder was of a cylindrical shape and was machined from solid brass. The dimensions of the container and heating coil were chosen large in order to produce a temperature wave as nearly a plane wave as possible in the region of the thermocouples to justify a semi-infinite approximation in the mathematical treatment. The comparatively large thermal inertia of the container and liquid sample also acted to slow any changes in the ambient temperature.

The close spacing of the thermocouples beneath the coil was necessary because of the rapid attenuation of the temperature wave. The amplitude of this wave decreased as an exponential function of the distance from the coil surface.

The coil itself consisted of a circular ceramic disk wound with resistance wire and cemented into a machined aluminum cup presenting a plane surface to the liquid, which improved the distribution of temperature by evening out lateral differences across the wave. The electrical input to the coil was a sinusoidally varied voltage having a period of 20 minutes. The resulting temperature waves had maxima corresponding to both the maxima and minima of the coil input, being independent of the direction of current flow in the coil, and, therefore, had a period of 10 minutes. The long period and small distance values finally chosen were expected to provide optimum experimental accuracy when all factors were considered.

The thermocouples were of iron and constantan, junctions of which produced a thermal electromotive force of about 30 microvolts per degree Fahrenheit. Melting ice was used as the constant temperature bath, and conversion of electrical outputs of the thermocouple to temperature was accomplished by means of tables. The thermocouple duplexes were attached permanently to the top of the sample holder, as was the heating coil.

The sample holder was vacuum filled, after which measurements were made at atmospheric pressure. Attached to the pipe leading from the upper opening was a length of transparent plastic tubing, in which the level of the liquid during filling, or its behavior during heating, could be observed. When it was reasonably certain that no air bubbles were trapped in the sample holder after filling, the vacuum pump was disconnected and the tube left open so that measurements could be made at atmospheric pressure. This arrangement reduced the area of liquid directly exposed to air to a very small amount, and also permitted free expansion of the liquid during heating. The small surface of the liquid exposed to air was some distance from the sample holder, and even at high sample temperatures, remained relatively cool.

Before being fed into the sample holder, each liquid to be tested was mechanically degassed to reduce the amount of gases that might come out of solution and cause turbulence during heating.

The sample holder was housed in a thermostatically regulated commercial oven capable of maintaining a constant temperature within a range of two degrees Fahrenheit. This small oven variation, along with the thermal inertia of the sample holder and the liquid, served to keep the ambient temperature of the sample very nearly constant during periods of taking data.

Figure 2 is a photograph of the sample holder. On the left is the top of the holder, showing the arrangement of the attached heating coil and thermocouple duplexes. The object at the right is the liquid chamber.

On all liquids for which the thermal diffusivity was measured, measurements began at room temperature, which was usually in the neighborhood of 80°F to 85°F. When the heating coil was turned on at room temperature, a period of a few cycles was required for the ambient temperature to regain equilibrium. Only with a stable ambient temperature could usable data be obtained. When suitable data had been taken at a particular temperature level, the oven temperature was raised a number of degrees, usually about 20°F. to 30°F. With a temperature increase of this magnitude, a settling-down period of several hours was usually necessary. Later measurements were made at successively higher temperature levels

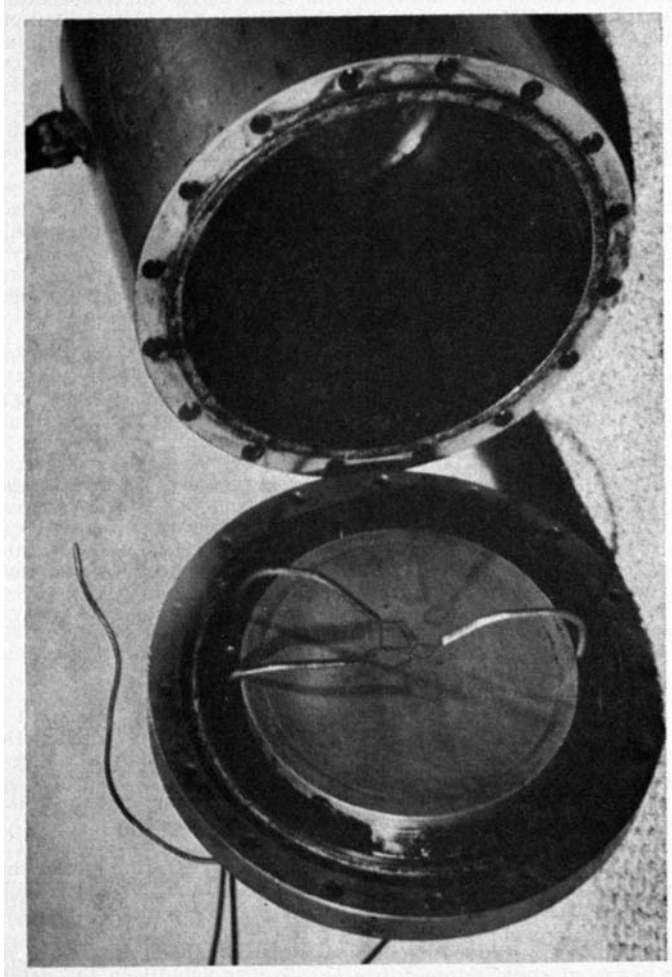


Fig. 2
Photograph of Sample Holder

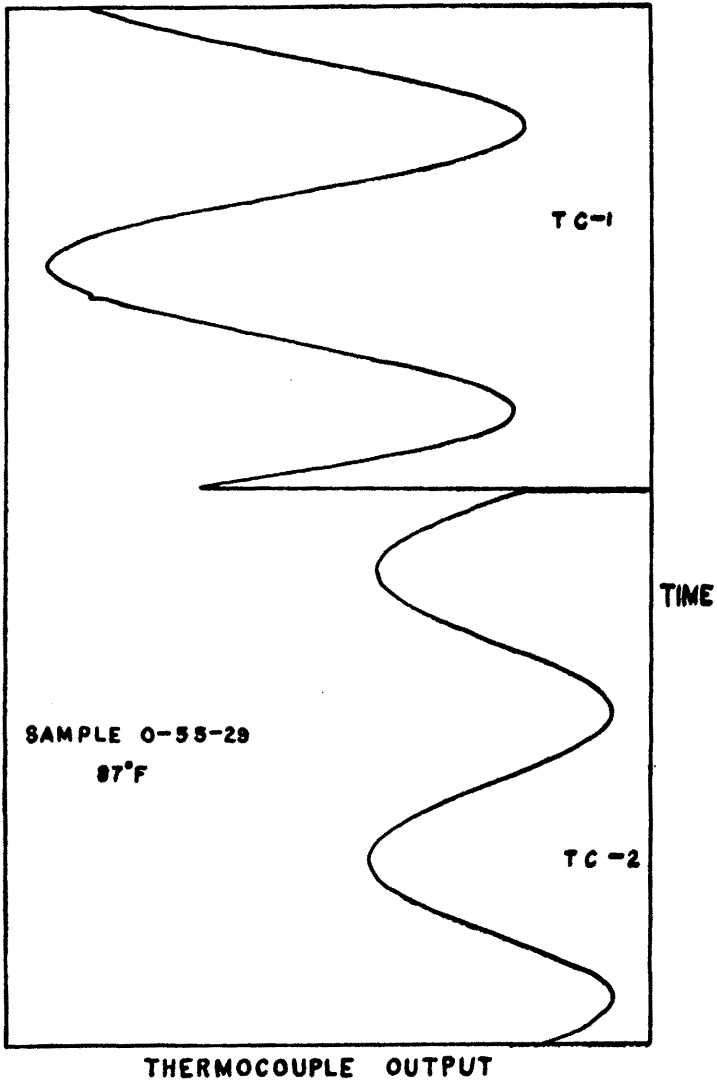


Fig. 3

Smooth Temperature Curve

until turbulence due to chemical breakdown in the liquid caused the data obtained to be so erratic as to be of no value.

The method of taking data was to record the output of two thermocouples on the rectilinear chart of a single-trace, voltage-sensitive recorder. Certain adaptations were necessary in order to get a suitable recording of the desired part of the thermocouple output by this recorder. The outputs of the thermocouples had the form of the sum of a large DC component and a small low frequency AC component. The DC component was caused by the ambient temperature, and the AC component by the temperature wave variation at the measurement point. In order to amplify the sinusoidal component and remove enough of the DC component to get the wave on the chart, an electrical network and switching device was constructed. Because of the very low frequency of the sinusoidal component, a DC amplifier was necessary. Excess non-oscillatory DC component was reduced by applying an opposed voltage to the circuit, this bucking voltage being adjustable to any value within the range of the thermocouple output. The component left after removal of excess DC was passed on to the amplifier and then to the recorder. Switches were included to provide for selection of the thermocouple output to be recorded, and for diverting the thermocouple output past the bucking voltage and amplifier to a sensitive potentiometer in case a direct temperature reading was needed. The lowest of the three thermocouples was usually used in making ambient temperature readings.

The graph shown in Figure 3 is that of the outputs, on an arbitrary voltage scale, of the top two thermocouples for one of the military oils at room temperature. The thermocouples are numbered in order of increasing distance from the heating coil surface, and the left side of the graph is that of higher temperature. The reduced amplitude of the wave from the lower thermocouple gives some idea of the rapidity with which the temperature wave is attenuated. Smooth recordings such as this were used to determine phase differences and amplitude ratios, a mechanical harmonic analyzer being employed for the actual measurements. Waves such as are shown here are very nearly sinusoidal, with little distortion due to drift in ambient temperature or radiation from the heating coil, so phase differences and amplitude ratios obtained from them are, within a small range of error, the same as would be obtained from a perfect sine wave. Simple calculations based on Equation 3 gave values for the thermal diffusivities of the samples. It was found that for a given thermocouple and a given sample, there was a decrease in wave amplitude with increasing ambient temperature.

For each sample tested, there was some temperature above which the thermocouple output would become irregular, as shown in Figure 4. With such roughness as this, accurate analysis became impossible. Usually this roughness was accompanied by appearance of bubbles in the plastic tube, and, in some of the oils, discoloration of the sample. Because of this, the spikes on the graph were attributed to chemical breakdown of the oil or additives. The breakdown temperature of the oils ranged from 262° F. for sample 0-55-29 to 443° F. for sample DC-550, and in some cases, notably the two just mentioned, were rather sharply defined. For sample 0-55-29, a variation in ambient temperature of only $\pm 2^\circ$ F. was sufficient to make the difference between smooth curves and rough ones.

As was to be expected, the trend was for the measured thermal diffusivity to decrease with increasing temperature. The thermal conductivity was calculated, using the experimental thermal diffusivities with densities obtained by conventional methods, and specific heats calculated using formulas expressing specific heats of various types of liquids as functions of the temperature (anon., 1927).

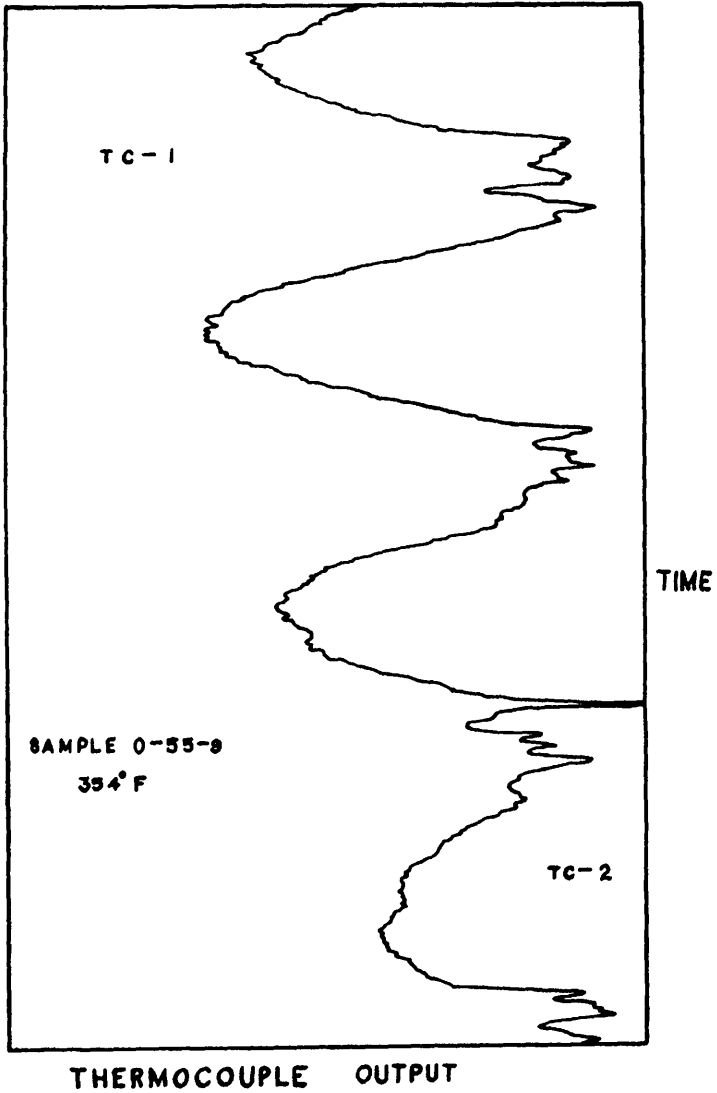


Fig. 4

Rough High Temperature Curve

In addition to the oils specified in the contract, several other liquids, mostly organic, were tested for purposes of checking the accuracy of data obtained by this method. Also, measurements of viscosity of all liquids tested, both oils and check liquids, were made, using a viscosimeter.

TABLE I.

SAMPLE	VISCOSITY	LOGARITHMIC	$\phi_1 - \phi_2$	α	$\frac{\alpha \text{ unsteady}}{\alpha \text{ static}}$
	at 100°F. (Centistokes)	DECREMENT In A_1/A_2	PHASE DIFFERENCE (Radians)	at 85°F. (ft. ² /hr.)	
0-55-13	196.3	0.571	0.399	0.0043	
Glycerol	130.3	0.531	0.474	0.0039	0.98
0-55-9	78.8	0.751	0.369	0.0024	
DC-550	71.8	0.507	0.431	0.0031	0.80
0-55-29	52.4	0.698	0.326	0.0029	0.75
0-55-22	15.4	0.948	0.531	0.0013	
2-Hexyl Ethyl Azelaate	8.9	0.833	0.597	0.0015	0.51
Ethanol	1.1	1.068	1.181	0.0008	0.22
Water	0.7	0.824	0.629	0.0019	0.34
Benzene	0.6	0.488	0.901	0.0022	0.54

Table 1 shows a tabulation of experimental values for the liquids tested. The liquids are listed in order of decreasing kinematic viscosity, which is given in the first column in centistokes, all of these values taken at 100° F. The other columns, from left to right, give the ratio of the natural logarithms of the amplitudes of the temperature waves at Thermocouple No. 1 to those at Thermocouple No. 2, the phase differences between the same two thermocouples, the thermal diffusivity α in the room temperature range, and the ratios of the α 's measured by the unsteady state method to those measured by steady state methods, where these values were available. Values of α for the check liquids were obtained from handbook tables and current literature, and values for two of the military oils were furnished by the Dow Corning Corporation (Cecil and Munch, 1956; Sakiadis and Coates, 1955). It should be noted that the agreement between the α measured by the unsteady state method and that measured by steady state techniques shows an improvement with increasing viscosity.

From the mathematics for the case of a semi-infinite plane wave, it is to be expected that the logarithmic decrement and the phase difference should be numerically equal. However, examination of the middle two columns shows that there is very little agreement. Because of this lack of agreement, the temperature wave solution for a pure semi-infinite medium was abandoned and Equation 3 was used for purposes of computation.

As a result of this study, it has been shown that certain experimental simplifications in the determination of thermal diffusivities of liquids can be introduced by this method, but measurements are still time-consuming and in most cases there is considerable disagreement between unsteady state values and steady state values. The cause for this disagreement has yet to be determined.

With this question and others to be answered, and the fact that most applications involving liquids subject them to unsteady state conditions, it

would seem to be of both theoretical and practical importance to make further investigations into the unsteady state measurement of physical properties of liquids.

LITERATURE CITED

- Anon. 1927. International Critical Tables. 2: 145. New York and London: McGraw- Hill Inc.
- Cecil, O. B. and Munch, R. H. 1956. Thermal conductivity of some organic liquids. Ind. Eng. Chem. 48: 437.
- Sakiadis, B. C. and Coates, J. 1955. Studies of thermal conductivities of liquids. A. I. Ch. E. Journ. 1: 275.
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