Thermal Conductivities of Liquids at High Temperatures

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THERMAL CONDUCTIVITIES of most pure organic liquids vary with temperature in the manner shown in Figure 1, where the abscissa indicates the fractional distance of the saturated liquid from melting point to critical point. On the scale the normal boiling point is usually around $\theta = \frac{1}{2}$. During the past 40 years the number of measurements of liquid conductivities has greatly increased, but all except a few fall in the region below the boiling point, where the variation with temperature is practically linear. The part of Figure 1 above $\theta = \frac{1}{2}$ is based on data for eleven liquids obtained by five observers (*1-3, 16, 23*). Conductivity in the absence of measured values can at present be calculated by one or another of varyingly successful methods (*11, 20*) as long as one does not go beyond the linear region (θ less than approximately 0.7). Because of the scarcity of data on any liquid properties at higher temperatures, none of the methods of prediction has been tested properly for $\theta > 0.7$. The purpose of the present work was to measure the conductivities of some representative compounds at these higher temperatures, to establish more firmly the general behavior in this region and to aid in the development of methods of prediction in the absence of direct data.

APPARATUS

For the conductivity measurements a steady-state, thin-film apparatus was used. The conducting liquids were contained in three concentric annular spaces (Figure 2). The cylindrical shape was chosen for convenient control of heat losses as well as adaptability to a high-pressure system. The principle of the thin film to control convection is well known, having been applied by most previous workers, regardless of the shape of the apparatus. Three films in series were used in this work, to increase the magnitude of the basic temperature drop and its accuracy of measurement while meeting Kraussold's criterion for absence of convection.

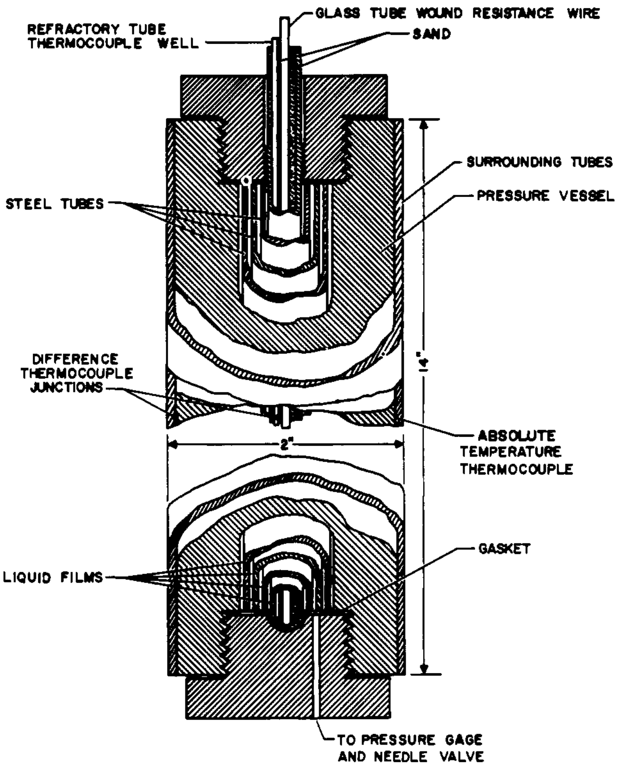

Figure 2. Schematic section of high-temperature thermal conductivity apparatus (not to scale)

The apparatus was made entirely of stainless steel to prevent corrosion with a wide variety of liquids. The low thermal conductivity of Types 304 and 316 steel helped to minimize extraneous conduction. The three annuli for the liquids were formed by two removable tubes positioned by steel spacers soldered to the ends. Each of the annular

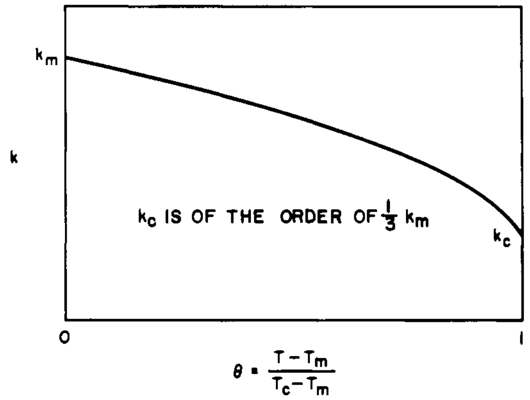

Figure 1. Typical variation of thermal conductivity of a liquid with temperature

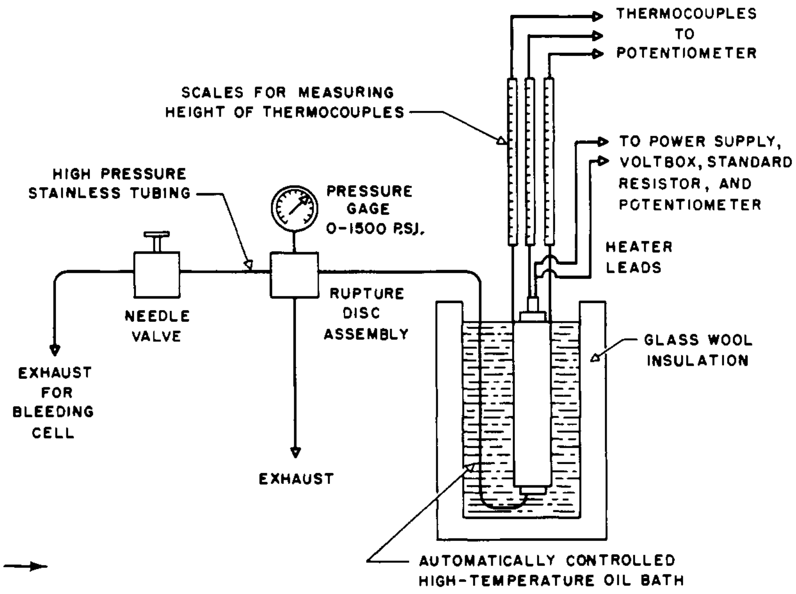

Figure 3. High-temperature experimental arrangement →

films was 0.0275 inch thick, a figure which represented a compromise between the possibility of convection at the extreme conditions for some liquids and the ease of measurement and centering of the films. The outer part of the vessel, built by the American Instrument Co., was a cylindrical shell (1.875 inches o.d., 0.805 inch i.d., fitted with a plug at each end. It could withstand pressures much higher than the critical pressures of most substances. The upper plug assembly contained a standard steel well which extended along the central axis of the vessel and fitted in a depression in the lower plug. Centered in this well was the heat source, nickel-chrome wire wound on a 3-mm. borosilicate glass tube and surrounded by a 5-mm. borosilicate glass tube which was kept in place in the well by silicone rubber spacers. The wire heating coil extended the entire length of the well, so that the heated section was longer than the liquid test section. This arrangement provided a degree of guard heating at each end. Figure 2 shows that the ends of the test section were further guarded against heat loss by horizontal liquid films, which have a considerable thermal resistance. These horizontal films and the fluid connections they provided among the vertical films may have been responsible for the apparent convection observed in some of the higher-temperature experiments.

A thermocouple well was provided next to the heater by a thin refractory tube. The remaining space in the heater well was filled uniformly with fine sand to obtain the best possible radial symmetry. Three uniformly spaced thermocouple wells were made on the outside of the vessel by milling vertical slots and fitting a steel tube (0.065-inch wall thickness) over the vessel body. All the thermocouple wells were made so that pressure fittings for electrical leads were unnecessary, and the thermocouple junctions in rubbing contact in the wells were movable in the apparatus.

In the lower plug was a small hole for connection to a pressure gage, rupture-disk assembly, and needle valve (Figure 3). The gage was a Helicoid Test Gage (American Chain and Cable Co.) having a stainless steel Bourdon tube. Its full-scale range was 1500 p.s.i. and after calibration it was accurate to ±2 p.s.i. in the range 0 to 1000. The phosphor-bronze rupture disk was specified to burst at 1400 p.s.i. The needle valve permitted slow bleeding of the apparatus to desired pressures. All fittings and the tubing were of stainless steel.

To maintain the high temperatures an automatically controlled oil bath was used. The fluid was standard Fisher bath wax having a melting point of about 60° C. and a flash point above 300° C. An Aminco bimetal thermoregulator controlled the bath temperature closely enough so that its small cycling had no effect on the temperature drop across the test section. Two submerged flexible steel-sheathed heaters were used in the bath, which was contained in a brass vessel of annular shape. This vessel was in turn surrounded by a layer of glass wool insulation.

Regulated direct current was supplied to the heater in the test section from a 110-volt a.c. line, a Stabiline automatic voltage regulator, Type IE51002, a Powerstat variable voltage transformer, No. 116, and a 2-ampere selenium rectifier with a filter choke. The a.c. input to the rectifier was regulated to ±0.1%. The current and voltage in the test heater were measured with a Leeds and Northrup Type K-2 Potentiometer in conjuction with a Leeds and Northrup No. 7581 Voltbox and No. 4205 Secondary Standard 1-ohm resistor.

For orientation bath temperatures were noted on an ordinary glass thermometer, but all other temperatures were measured with copper-constantan thermocouples made from 10-foot lengths of No. 30 B. and S. Gage Duplex wire from Leeds and Northrup spool No. 67117-10. The thermocouples were calibrated at three points on the International Temperature Scale with special apparatus (*20*).

CALIBRATION

The best way of obtaining reliable thermal conductivities with the apparatus described above was to calibrate with substances whose conductivities have been well established in the temperature range of interest. Because of the extraneous thermal resistances in the radial conduction path and the dissymmetry of the apparatus about the central horizontal plane, direct calculation of conductivities was not considered. Calibration with fluids of known conductivity reduced the effect of the longitudinal heat losses by an order of magnitude, since the measure of error was not the ratio of heat loss to the radial heat flow, but the differences between this quantity for the calibration fluids and the unknown fluids. The essence of the calibration procedure was to measure the radial temperature drops with the calibrating fluids over a range of conditions sufficient to establish constants of the apparatus which give a measure of the two factors mentioned: extraneous resistances in series with the liquid films and longitudinal heat losses.

The error introduced by uncertainty in the values of conductivity for the calibrating fluids must be small compared with the other errors. In this work water and air were used as calibrating fluids. Several empirical equations have been proposed (*9, 12, 15*) for extrapolation to the higher temperatures. Since air, unlike liquids, is transparent to thermal radiation, a correction (*20*) amounting to as much as 10% had to be applied to previous values.

The conductivity of water has been less extensively measured at temperatures above 100° C. Recent careful measurements by Challoner and Powell (*7*) have confirmed within 1 or 2% the earlier data from 0° to 82° C.

PROCEDURE

Runs with calibration fluids and with unknowns had the same procedure. The two removable steel tubes were first cleaned with water and acetone or methanol and dried, then inserted into the vessel. The upper plug assembly, including the central heater well, was screwed into place, but not tightened. The outlet tube from the bottom plug was connected to a buret containing freshly distilled liquid, which was allowed to run slowly into the system until it appeared at the vent hole outside the upper plug (Figure 2). The reproducibility of the buret reading at this point for different trials was taken as evidence of complete filling. The plug was then tightened so that the cell and its outlet tube were filled with liquid. This total volume was 37.3 ml., including some of the volume outside the upper gasket. The pressure gage and the other connections were also filled with the freshly distilled liquid, and the vessel was then immersed in the bath to the point shown in Figure 3. The initial bath temperature was usually 80° to 90° C.

Thermocouples were then inserted into the wells, so that the temperature drop across the films and tubes was measured directly, as well as the absolute temperature in one of the outer wells. The three junctions in the vessel were pushed to a point midway between the ends of the test section with the help of external scales.

The bath temperature and cell heater voltage were adjusted to give approximately the desired temperature and temperature drop. If the liquid was above its boiling point, the system was bled carefully to adjust the pressure to a desired value a few pounds per square inch above saturation pressure.

Steady state was assumed to have been reached about an hour after the temperature drop across the cell ceased to vary. The thermocouple voltages and the heater voltage and current were measured with the potentiometer. Three or four different temperature drops were used at one temperature level. The total temperature drops were 1° to 4° C. in some of the early runs, but about 1° C. and less in most of the runs. After several temperature drops were taken at one temperature level, the bath temperature was increased, the system bled, and the procedure repeated. Usually readings were taken at five different temperatures up to 260° C. or the critical point, whichever was lower.

Accuracy of Measurements. The basic measurements were v, the voltage drop across the heater; I, the current in the heater; ΔT, the over-all radial temperature drop at the middle of the test section; and T, the temperature of the thermocouple in the outer well. The voltage was measured directly from taps at the ends of the heater coil. The heater current was measured by noting the voltage drop across the standard resistor in series with the heater. The accuracy of measurement of both v and I was limited by the fluctuations in line voltage. Usually the voltages were extremely steady; sometimes the maximum 0.1% fluctuation was observed. The product of v and I was known to ±0.2%; errors of the potentiometer, volt box, and resistor were negligible in comparison.

The procedure for calibration and use of the thermocouples has been described *(20)*. The error is estimated to be 0.3° C. in T and 1% in ΔT.

DATA ANALYSIS AND CALCULATION OF CONDUCTIVITY

The data for all fluids were plotted in the form shown in Figure 4, ΔT *vs.* $(W = vI)$, the power in the heater, for each temperature level. The analysis of the data is based on the fact that these plots were straight lines or could at least be reasonably approximated by a straight line.

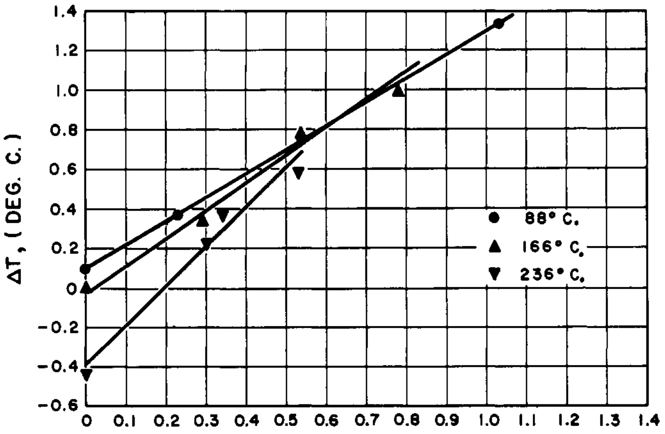

Figure 4. Temperature drop vs. power input for three temperatures

Calibrating with two fluids at one temperature level permitted determination of two correction factors characteristic of the apparatus. This method accounted for the effects of heat losses and extraneous resistances in the radial conduction path. Equation 1 results from integration of the ordinary steady-state equation for radical conduction. In this equation ΔT is the over-all temperature drop at the test section.

$$\Delta T = \frac{fW}{2\pi JL}\left(B + \frac{G}{k}\right) \tag{1}$$

The thermal resistance, B, is the combined thermal resistance in series with the fluid films, which have the resistance G/k. The correction factor, f, is to allow for longitudinal heat losses. In the final calculation f cancels out of the equations, and its numerical values are of interest only as an indication of the relative magnitude of the losses. If the losses were zero, the value of f would be unity. The temperature range, f, varied between 1.10 and 1.16.

The extra radial resistance, B, contributing to ΔT evidently could not be a function of the fluid films if convection were absent. Further, the ratio of conductivity of the metal to that of the fluids was great enough so that any axial heat losses could be ascribed to the steel parts of the apparatus, mainly to the relatively thick heater well. The two correction terms B and f were assumed to be functions only of temperature—i.e., the temperature level of the oil bath.

On this basis the differences in conductivities of various test fluids at one temperature are reflected completely in the differences at one temperature. Consider Equation 1 for one fluid at one temperature level. If W is changed by a very small increment, δW, the following holds:

$$\Delta T + \delta(\Delta T) = \frac{f(W + \delta W)}{2\pi JL}\left(B + \frac{G}{k}\right)$$

This equation depends on the fact that k, as well as B and f, varies only slowly with temperature and can be considered constant as long as the bath temperature remains constant. (The maximum change in ΔT was usually less than 1°.) Subtracting and rearranging,

Table I. Results of Conductivity Measurements

Substance	Temp., ° C.	10^6k, Cal. per (Sec. ° C. Cm.)
Acetone	83	310
(Fisher certified reagent)	119	337
	168	437[a]
	88	349
	118	306
	166	309
	206	185
	226	209
	236 (critical point)	174
Glycerol	78	819
(Fisher certified reagent	120	704
95% by volume	170	676
	220	770
Methyl siloxane polymer	89	264
(Dow Corning Fluid 200,	121	239
viscosity of 3 cs. at 25° C.)	170	228
	221	188
	276	175
Methyl siloxane polymer	74	393
(Dow Corning Fluid 200,	121	372
viscosity of 1000 cs.	169	367
at 25° C.)	219	359
	260	353
tert-Butyl alcohol	88	243
Eastman Organic Chemical	122	255
No. 820; distilled, 82.0° C.	170	264
fraction used)	209	232
Benzene	68	296
(Fisher analytical reagent;	117	273
distilled at 79.5-80.0° C.)	169	270
	76	312
	119	288
	169	261
	218	474[a]
Ethanol	88	343
(absolute; distilled at 78° C.)	117	354
	172	327
	212	451[a]
Methanol	118	426
(Fisher certified reagent	171	470[a]
99.5% by volume; distilled	212	516[a]
at 64°-65° C.)		

[a] Values discarded because of probable convection.

$$\frac{\delta(\Delta T)}{\delta W} = \frac{f}{2\pi JL}\left(B + \frac{G}{k}\right) \equiv A \qquad (2)$$

The slope A thus depends only on the fluid conductivity. Then, if subscript 1 refers to air, 2 to water, and n to any of the test liquids,

$$\frac{A_1}{A_2} = \frac{B + (G/k_1)}{B + (G/k_2)} \qquad (3)$$

$$\frac{A_1}{A_n} = \frac{B + (G/k_1)}{B + (G/k_n)}, \text{ and } \frac{A_2}{A_n} = \frac{B + (G/k_2)}{B + (G/k_n)} \qquad (4)$$

From Equation 3, B can be calculated, since k_1 and k_2 are both known. From either of Equations 4 the unknown conductivity, k_n, can be calculated at the temperature in question.

The slopes, A_1 and A_2, for air and water and the values of B determined from them were presumed to be continuous functions of temperature and were plotted against temperature to obtain values for calculations in which the unknown liquid was not tested at precisely the same temperature level as the calibrating fluids. In most cases only short interpolation was required.

RESULTS

Thermal conductivities for eight different pure liquids were determined over various parts of the temperature range of 70° to 270° C. (Table I). These determinations have extended the range of measurement because there was not always a previous experimental value for comparison. Where comparison was possible, there was fair agreement with previous data. The results in general confirm the picture of temperature variation (Figure 1).

Taking into account the uncertainty regarding heat losses, the possibility of convection, and the small uncertainty in the conductivities of the calibrating fluids, the maximum errors in the values of Table I are estimated to be between 10 and 15%.

Acetone. The only liquid for which conductivities were obtained up to the critical temperature was acetone (Figure 5). The values of Abas-Zade (*1-3*) were all measured at the critical pressure, and therefore are expected to be slightly higher than those measured at saturation pressures, except at the critical temperature.

Some of the values in Table I for acetone, benzene, ethanol, and methanol are marked as being discarded because of probable convection. In these cases even the small temperature drops used were great enough to cause instability. Unfortunately, the conditions under which this would occur could not be predicted precisely, because the product of Grashof and Prandtl numbers, which indicates the degree of free convection, involves quantities which could be estimated only roughly, as well as the unknown conductivity itself.

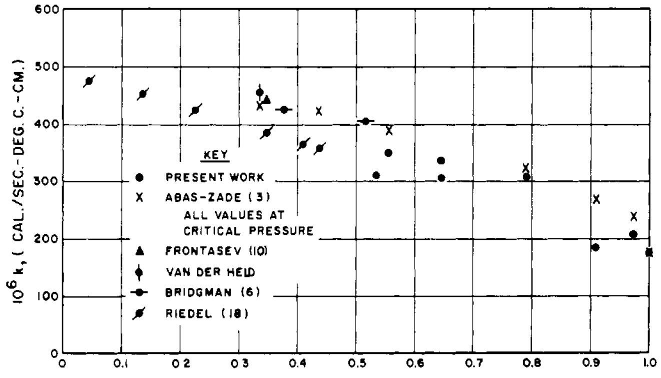

Figure 5. Thermal conductivity of acetone

The acetone conductivity at 168° C. was measured using values of ΔT up to 4° C. Reduction of ΔT to 1° C. or less yielded a lower conductivity, as the measurement at 166° C. indicates. All the conductivities for acetone above this temperature were obtained by the use of the smaller temperature drops.

Benzene. All the values for benzene (Figure 6) were measured using the larger ΔT of up to 4° C. Convection apparently began in the 218° C. run, as seen in Table I. The runs at lower temperatures give an indication of the reproducibility of the data, since the series at 68°, 117°, and 169° was measured with a different sample of benzene from the series at 76°, 119°, and 169°. The reproducibility is somewhat better than for acetone, which was also studied in two series.

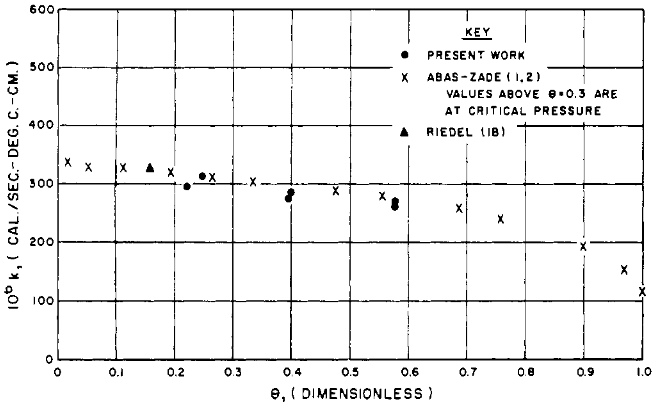

Figure 6. Thermal conductivity of benzene

Methanol, Ethanol, and *tert*-Butyl Alcohol. The runs involving the alcohols (Figures 7, 8, and 9) were all made with ΔT about 1° C. or less, but ethanol and methanol began to show apparent convective instability at relatively low temperatures. It is not likely that the apparent maximum in the conductivity of *tert*-butyl alcohol near 170° C. is real. It may be the result of convection, which always increases apparent conductivity.

Glycerol. Glycerol was of special interest because of its positive temperature coefficient at moderate temperatures (Figure 10). This may be attributed to the effects of hydrogen bonding, as in the case of water (*8*). Any liquid with a positive temperature coefficient must, like water, have a maximum in the curve, because the conductivity at the critical temperature must ultimately approach that of the gas. Although the data for glycerol are rather widely scattered, the maximum appears likely to occur at a temperature higher than 200° C.

Silicone Fluids. The silicone fluids were not pure molecular species, being composed of linear methyl polysiloxane molecules of varying length, identified in terms of their viscosities at 25° C. Bates (*5*) has measured the thermal conductivities of these and similar fluids at lower temperatures. The present data (Figure 11) agree fairly well with his values, and in fact might be used to extend his general correlation to higher temperatures.

ACKNOWLEDGMENT

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NOMENCLATURE

A_n = slope of ΔT *vs.* W graph for n^{th} fluid
B = apparatus correction term for extraneous thermal resistances in series with fluid films

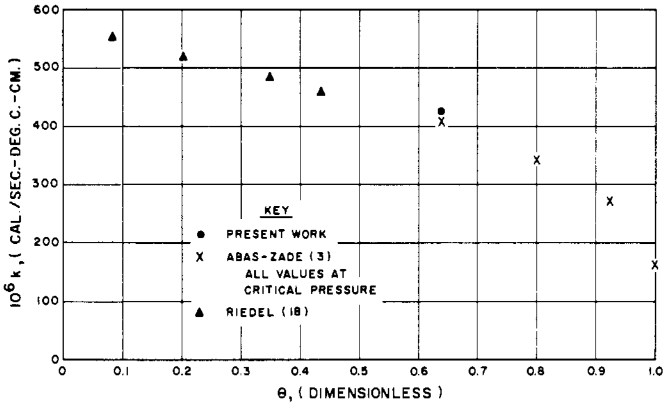

Figure 7. Methanol

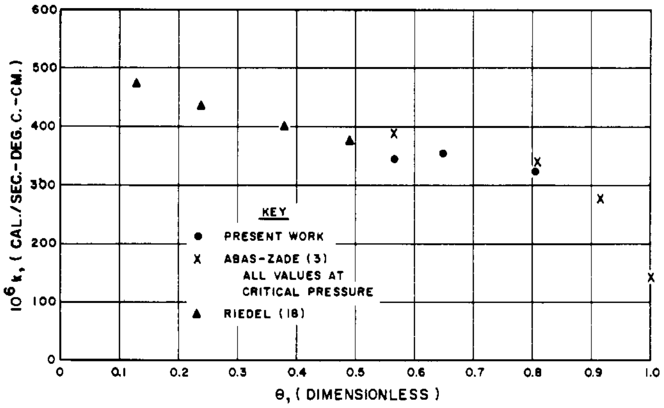

Figure 8. Ethyl alcohol

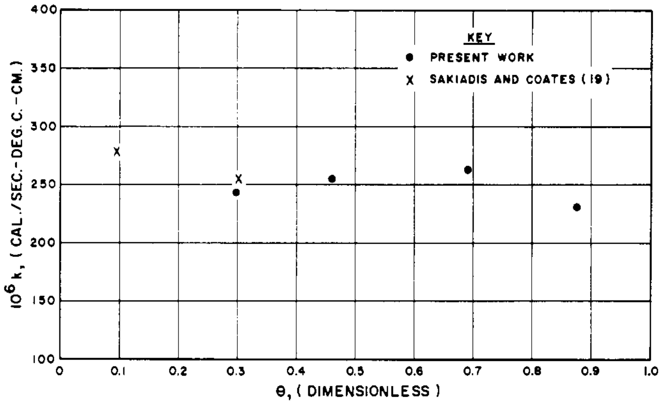

Figure 9. *tert*-Butyl alcohol

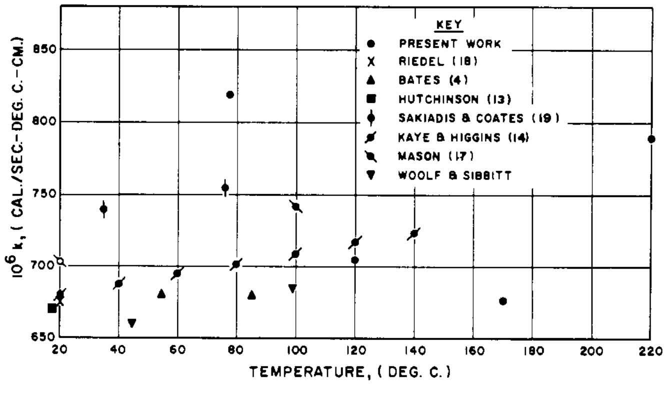

Figure 10. Glycerol

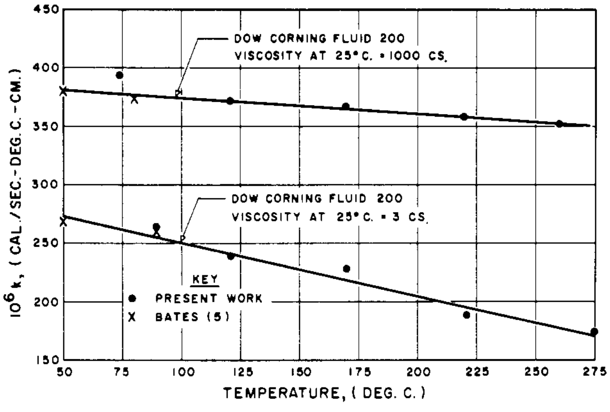

Figure 11. Two silicone fluids

f = apparatus correction factor

G = $\ln \frac{r_1 r_3 r_5}{r_0 r_2 r_4}$ apparatus geometrical factor

I = electric current in test heater

J = 4.183 joules/cal., mechanical energy equivalent to heat energy

k = thermal conductivity; k_c, at the critical point; k_m, at the melting point; k_n, of n^{th} fluid.

L = length of cylindrical heat transfer surface

r = radius of cylindrical surface bounding fluid film ($r_0 < r_1 < r_2 \ldots$)

T = temperature; T_c, critical temperature; T_m, melting point

v = apparatus heater voltage

W = vI, power output of test heater

ΔT = radical temperature drop across test section

δW, = $\delta(\Delta T)$, small increments in W and ΔT

θ = $\frac{T - T_m}{T_c - T_m}$, special reduced temperature for the liquid state

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