k, k_{sb}, k_{cb} = thermal conductivity
k_{sb} for soybean oil meal
k_{cb} for carbon black
α = thermal diffusivity
L, L_1, L_2 = length of path for heat transfer
r = radius of cylinder
t = time
T = temperature at geometric center of finite cylinder except as noted
T_0 = initial temperature of cylinder
T_1 = surface temperature of cylinder at time θ (forcing temperature)
u = "theoretical" temperature, $T_1 - T/T_1 - T_0$
ρ = density

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Thermal Conductivity of Some Organic Liquids High Temperature Measurements

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Although thermal conductivity values are becoming more numerous in the literature, they represent for the most part values determined at relatively low temperatures—i.e., below 100° C. Engineers desiring to use these data for high temperature problems must extrapolate low temperature values to the desired temperature. In many cases, only one value exists and this must be used for all calculations. Such extrapolations are obviously questionable.

This report deals with the extension of a technique for determining absolute values of thermal conductivity (*1*) to temperatures as high as 200° to 250° C. This work does not represent a limit for thermal conductivity measurements but serves to illustrate how values at higher temperatures can be determined.

EXPERIMENTAL

The method used [described in detail elsewhere (*1*)] is a highly refined modification of the hot-wire technique. The thermal conductivity cell proper employs a four-lead arrangement analogous to a four-lead platinum resistance thermometer, thereby eliminating end effects. All constants necessary for thermal conductivity measurements are determined from the dimensions of the cell. The determined thermal conductivity values are thus absolute.

Of prime importance in the success of this method is the constancy of the temperature of the thermostated bath. In the previous low temperature work, simple on-off control of the thermostated bath provided a temperature which was constant to within about ± 0.003° C. Duplicate measurements at 30° C. had shown an average deviation from the mean of ± 0.3%, and this deviation had increased to ± 0.5% at 80° C. These data demonstrate one of the inherent faults of on-off control—namely, that progressively less satisfactory performance is obtained as the desired operating temperature differs more widely from ambient temperature. For this reason other types of controls and thermostating were considered. The final choice for the high

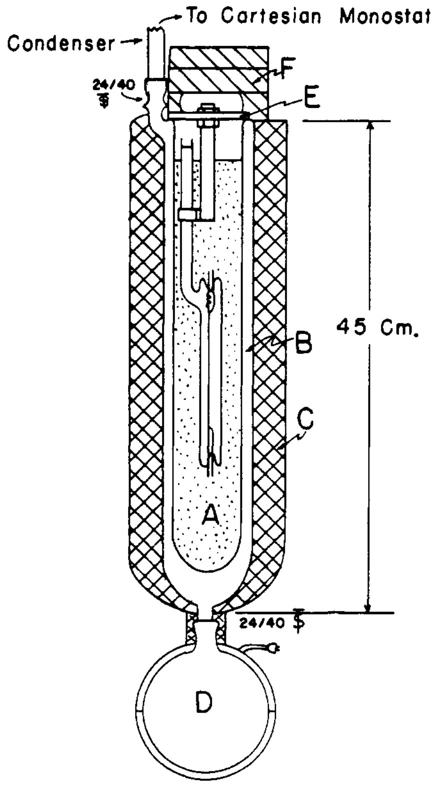

Figure 1. Thermal conductivity cell and condensing vapor thermostat

A. Silicone oil reservoir
B. Condensing vapor jacket
C. 1¼-inch thick magnesia insulation
D. 1-liter pot heated with spherical mantle
E. Transite top and cell holder
F. Glass wool insulation

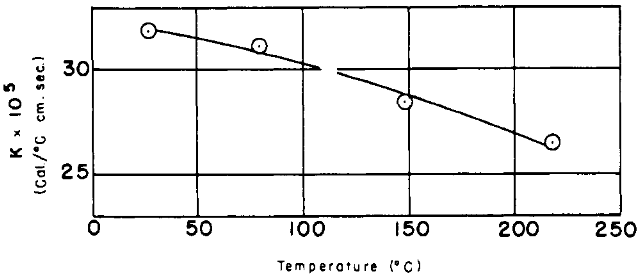

Figure 2. Thermal conductivity of tricresyl phosphate

temperature work was a condensing vapor bath. It was compact in size and relatively simple to design and construct. The upper temperature limit for this type of thermal conductivity measurement is governed by the availability of a suitable inert nonvolatile bath fluid which retains high electrical resistivity at the desired operating temperature.

The thermostat assembly (Figure 1) consists of a vapor jacket, *B*, constructed from 60 - and 80-mm. tubing. The jacket, 45 cm. in height and insulated with 1.25 inches of magnesia pipe lagging, *C*, was connected at the bottom to a 1-liter flask, *D*, heated with a spherical mantle. At the top of the jacket a condenser (air or water depending on the boiling point of the liquid used) was attached. The large reservoir, *A*, was filled with silicone oil and heated by the condensing vapors. The thermal conductivity cell was immersed in reservoir *A*, so that the top of the 18-cm. filling arm was slightly above the oil level. The cell holder was connected to the Transite cover, *E*, on compartment *A*. The cover which also held a mercury-in-glass thermometer and a differential thermometer was insulated with 3 inches of glass wool batting, *F*.

The silicone oil served as a buffer to reduce effects of temperature variations of the condensing vapors. The outlet of the condenser was connected to a Cartesian manostat. A check of temperature uniformity in the bath made with a platinum resistance thermometer showed variations of ± 0.005° C. Point to point temperature differences were about the same.

Liquids used for the vapor source have included water, 2-methylpentanol, and primary decyl alcohol (Union Carbide Chemicals Co.).

External leads to the thermal conductivity cell were originally soft-soldered with a solder melting at 180° to 190° C. For the temperatures to which the authors proposed to submit the cell, the leads were resoldered with a high melting soft-solder (Erosin Multicore Comsol solder melting at 290° C., Multicore Sales Corp., 164 Duane St., New York 13, N. Y.). Other than the lengthening of the filling arm to 18 cm., no modifications of the cell were necessary.

DISCUSSION

Thermal conductivity values have been determined for a series of liquids of known or proposed industrial use, many of which were previously reported for a temperature range of 30° to 80°C. (*1*). Thermal conductivity-temperature relationships for the liquids over a range of temperatures up to 217° C. are given in Table I and Figures 2 through 6. The average per cent deviation of duplicate measurements for each determination is ± 0.4%. This is slightly greater variation than was observed in the authors' lower temperature work and probably reflects the slight difference in thermostat performance.

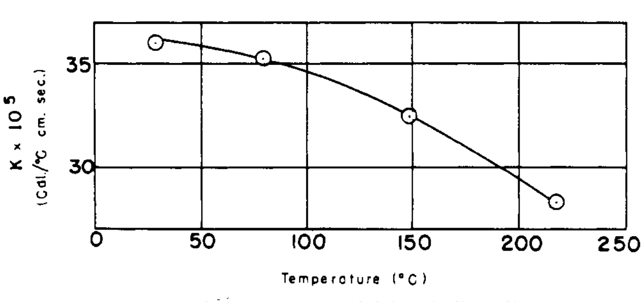

Figure 3. Thermal conductivity of di(2-ethylhexyl) sebacate

Table I. Thermal Conductivity of Biphenyl and Some Chlorinated and Alkylated Derivatives

Compound	$k \times 10^5$, Cal./Cm. °C. Sec.	Temp. Range, °C.	$dk/dt \times 10^5$, Cal./Cm. °C.
Aroclor[a] 1242	23.9	30-217	0
Aroclor 1248	23.5	30-217	0
Aroclor 1254	22.5	30-217	0
Biphenyl	31.6	98-217	0
Monoisopropyl-biphenyl	28.8	98-217	0
Diisopropyl-biphenyl	28.3 (150° C.)	98-217	0.0034

[a] Registered trade-mark of Monsanto Chemical Co.

The reliability of the method as applied to low temperature work has been demonstrated (*1*). The estimated accu-

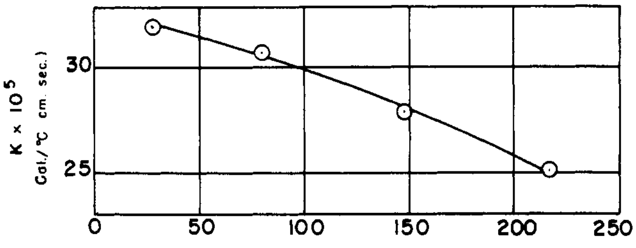

Figure 4. Thermal conductivity of tetra(2-ethylhexyl) silicate

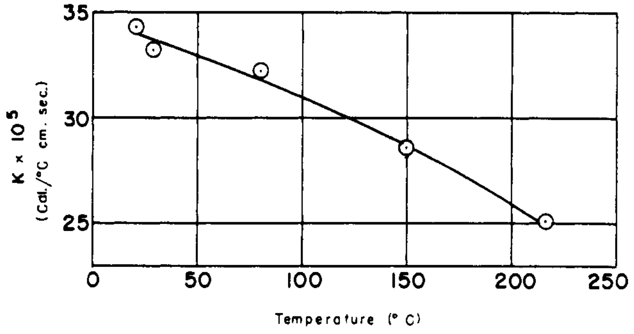

Figure 5. Thermal conductivity of OS-45 (Monsanto Chemical Co.)

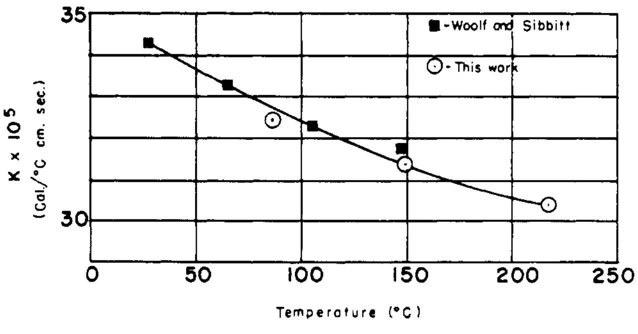

Figure 6. Thermal conductivity of Dowtherm A

racy of the low temperature work was within ± 2%. The reliability of the present work can only be inferred, since data for comparison are limited.

The smooth curves which can be drawn through the low and high temperature data can be taken as evidence that the new thermostat introduced no unsuspected bias in the high temperature data. A review of the basic principles of the hot-wire technique has revealed no reason for expecting progressive deviations from true values at higher temperatures, except perhaps from convection. Results presented earlier (*1*) indicated no convection, even with materials as fluid as chloroform. As the apparatus used in the present work was the same, the factor which would have the most significant contribution to convection would be viscosity. At the highest temperatures used, the viscosity of the most fluid compound considered only approached that of chloroform. Thus, there appears to be no cause for believing that convection was a factor in the present measurements.

Biphenyl and its chlorinated and alkylated derivatives show very little change in thermal conductivity with increasing temperature (see Table I). Phosphate, carboxylate, and silicate esters (see Figures 2 through 5) all show a steady decrease in thermal conductivity with increasing temperature.

A similar decrease is observed with Dowtherm A (Dow Chemical Co.) (Figure 6), considering the experimental data determined in this work to complement the work of Woolf and Sibbitt (*3*).

Available data on density and viscosity variations with temperature failed to show correlations which would have predicted this difference in behavior. Sakiadis and Coates (*2*) predict that positive, negative, and zero temperature coefficients of thermal conductivity are possible, but sufficient data on the heat capacity, velocity of sound, and intermolecular spacing in the liquid state were not available for the present compounds to permit use of their theoretical equation. The equation of Sakiadis and Coates predicts a linear variation of thermal conductivity with temperature. The curved lines which were obtained over wide temperature ranges, particularly with di-2-ethylhexyl sebacate, point up the need for modification of their treatment to explain these results.

The temperature coefficient data for Aroclor 1248 and Dowtherm A should be useful in the design of heat exchangers utilizing these important heat transfer fluids.

CONCLUSIONS

The success of this present work has shown that thermal conductivity values can be easily measured at high temperatures. If suitable liquids for the vapor bath and silver-soldered or spot-welded leads are used, the method discussed should be applicable at higher temperatures.

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Heats of Solution of Polyindene

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The physical-chemical behavior of high polymer–solvent systems has received a great deal of attention in recent years. On the other hand, the behavior of low molecular weight polymer solutions has not received much attention in spite of their commercial importance. The present study was undertaken to investigate the nature of the interaction of a low molecular weight polyindene type of polymer with solvents or plasticizers. Solubility measurements of this polymer have been reported elsewhere (*10*). Precise measurements of the heat of solution of polyindene are reported here and form the basis for a thermodynamic study of polyindene-solvent systems.

The usual expression for the energy of mixing of nonelectrolytes is given by the equation

$$\Delta E^M = V_m B\, V_2 (1 - V_2) \qquad (1)$$

where V_m is the volume of solution in cubic centimeters, V_2 is the volume fraction of polymer, and B is given by the expression:

$$B = (S_1 - S_2)^2 \qquad (2)$$

where S_1 and S_2 are the solubility parameters of solvent and polymer, respectively. The volume change on mixing may be considered to be negligible at low concentrations, so that the heat of mixing is equal to the energy of mixing. According to Equation 1 a plot of $\Delta E^M/V_m$ vs. $V_2(1 - V_2)$ should give a straight line with slope B. Since B is a squared term, it must be positive and thus this theory predicts that the heat of mixing of two nonelectrolytes must be endothermic. However, where specific interactions occur, the experimental value of B is not realized by Equation 2 but becomes more complex and often negative. Equation 1 may, however, still be applicable.

EXPERIMENTAL

Materials. Polymer. The polymer used in this study was a coumarone indene resin manufactured by the Pennsylvania Industrial Chemical Corp. Previous work in this laboratory on the molecular weight distribution, viscosity, and solubility of this resin (*5, 6, 10*) has been reported. [This resin corresponds to Pieski's (*5*) Resin II and to Vanderryn's (*10*) Resin IV.] The resin was fractionated into four fractions