within 1 to 2 °C of freezing (*7*).

The data for each strength were fitted to equations of linear form as shown in Table II.

The results obtained for water are reported in Table III and also shown in Figure 1. Agreement to IAPS (1977) (*6*) is better than 1.5%, the results reported here being slightly lower. Plotted also in Figure 1 are the smoothed data for dilute aqueous solutions of H_2SO_4 (*2*, *3*).

Conclusion

Absolute measurements of the thermal conductivity of oleum and water are reported in the temperature range 0-95 °C. The results are believed accurate to ±1.5%.

Acknowledgment

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Thermal Conductivity of Phenol (C_6H_5OH)

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The paper reports measurements of the thermal conductivity of solid and liquid reagent grade phenol over the temperature range 30-200 °C at pressures to 0.5 MPa, performed by means of an absolute transient line source instrument. At the melting point there is a depression of the expected conductivity of 0.02 mW/(cm K); the ratio of $\lambda_s:\lambda_a$ is 1.13:1. It is estimated that the overall uncertainty in the data is less than ±1.5% on the basis of measurements made of two samples with two different cells.

Introduction

Most empirical expressions relate the thermal conductivity of normal simple liquids as linear functions of temperature over their normal melting point to boiling point range. The majority of measurements to date support such a description, except for water. Past measurements on toluene did show a substantial prefreezing depression (*1*) which was attributed to molecular cluster formation. New measurements on solid and liquid phenol reported here also provide evidence of a slight prefreezing in addition to significant increase upon solidification.

Experimental Section

A modification of the absolute transient line source instrument (*2*, *3*) was employed by using samples of BDH and Fisher detached crystal reagent grade phenol. The two cells employed for the work were of 25 and 50 μm diameter platinum. The 25-μm cell (cell 2) was 10.65 cm long, used without potential leads; the 50-μm cell utilized a working length of 9.11 cm between potential leads. The measurements shown in Figure 1 and Table I are obtained with a precision of approximately 6000 ppm by measuring the voltage-time behavior of the platinum cell wire source immersed in the substance and pulsed with a constant current sufficient to produce temperature rises of 1 to 2 °C in 5 s. Experimental procedures are such that end conduction, convection, and radiation heat loss effects can be minimized (*2*).

Table I. Thermal Conductivity of Phenol (C_6H_5OH)[a]

temp, °C	λ, mW/(cm K)	comment
28.3	1.79_2	cell 2, solid (Fisher) anisotropic effects
41.9	1.56	cell 2, liquid (Fisher) anisotropic effects
43.2	1.57_8	cell 1, liquid (BDH)
49.2	1.57_0	cell 1, liquid (BDH)
58.1	1.55	cell 2, liquid (Fisher)
62.0	1.56_4	cell 1, liquid (BDH)
80.0	1.54_7	cell 1, liquid (BDH)
101.0	1.51_5	cell 1, liquid (BDH)
120.0	1.49_1	cell 1, liquid (BDH)
149.7	1.45_8	cell 1, liquid (BDH)
149.7	1.45_3	cell 1, liquid (BDH)
173.1	1.41_6	cell 1, liquid (BDH)
172.6	1.41_4	cell 1, 0.68 MPa nitrogen overpressure
197.8	1.39_2	cell 1, liquid (BDH) 0.4 MPa nitrogen overpressure

[a] $\lambda_i = 1.66 - 0.00143t$ mW/(cm K). $\lambda_a/\lambda_i = 1 - 0.0125 \exp(-1.4298/T^{*1/2})$. t, °C; T, K.

In all, 11 measurements with cell 1 and 3 measurements with cell 2 are reported. The results of cell 1 are considered more reliable, since they were obtained by using potential leads and hence are not subject to axial and radial conduction losses (*4*). Each experimental run was executed between 3 and 10 s; a digital voltmeter of the data acquisition system takes up to 200 readings, at time variable between 25 and 350 ms; the first reading can be adjusted to be from 1 to 350 ms from initiation of the experiment. Values above the normal boiling point were obtained by using a slight nitrogen overpressure. In order to determine the effects of this overpressure, we made duplicate measurements at 173 °C (Table I). The theory and its experimental application are described elsewhere (*2*).

Discussion

Previous measurements of phenol (*5-8*) are also shown in Figure 1; agreement is best (±2%) with ref 5, 6, and 7; the work of Jamieson (*8*) is 3.3% lower at 60 °C and in agreement at 160 °C.

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J. Chem. Eng. Data 1980, 25, 199-201

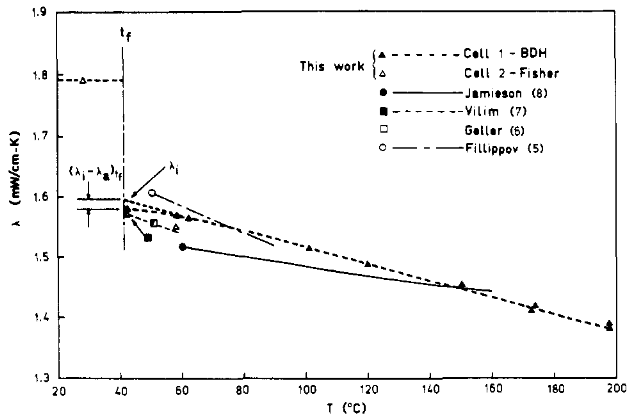

Figure 1. Thermal conductivity of phenol (C_6H_5OH).

At sufficiently high temperature the thermal conductivity of most fluids (water is an exception) can be characterized as decreasing linearly with increasing temperature in the interval between freezing and boiling.

$$\lambda = A' - B't$$

For phenol, sufficiently high temperature, that is, the temperature range wherein the behavior is linear, was observed to occur between 68 and 200 °C; over this range values of $A' = 1.66$ mW/(cm K) and $B' = 0.00143$ mW/(cm K^2) were found. If one allows this expression to yield the normal or expected value λ_i by extrapolation to t_f, small experimental deviations occur to depress the actual λ_a values. Previous work (*1*) has speculated that such deviation near t_f can be attributed to cluster formation and expressed as

$$\lambda_a/\lambda_i = 1 - A \exp(B/\sqrt{T^*})$$

where

$$T^* = [(T - T')/(T_f - T)]$$

Analysis of the data yields a t_f depression of 0.02 mW/(cm K) with $A = 0.0125$ and $B = -1.4298$. The temperature, T', at which the anomaly has been observed to vanish is estimated to be 341 K. The observed ratio of solid to liquid conductivity, λ_s/λ_a, is 1.13:1.

Conclusions

Absolute measurements of the thermal conductivity of solid and liquid phenol are reported in the temperature range 30–200 °C. The results are believed accurate to ±1.5%.

Acknowledgment

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Thermal Conductivity of Associated Liquids

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New experimental measurements are presented for the thermal conductivity of 9 alcohols and 15 primary, secondary, and tertiary alkylamines. An equation is also developed which correlates these data as a function of both temperature and chemical structure. This enables values to be estimated for other liquids with a similar chemical structure.

Introduction

Thermal conductivity is an important physical property which is required for calculations of almost all forms of heat transfer. Values are required over a wide range of temperatures and for such a large number of liquids that it would be impractical to attempt to provide experimental values over the whole range for each liquid. In an attempt to minimize this task, we developed an equation (*1*) which enables whole groups of liquids, from a single chemical series, to be handled together. The equation was tested and found to be effective with series of nonpolar liquids and with polar liquids which are not associated by forming strong hydrogen bonds (*1*). In this paper new experimental values are presented for a number of associated liquids, and these are used, with existing literature values, to assess the effectiveness of the authors' correlating equation.

Experimental Results

Thermal conductivities were measured with a hot-wire cell, using a 1000-Hz steady-state method. The cell was calibrated with water and argon, and the results were verified with several other fluids of known conductivity, as described elsewhere (*2*). The experimental technique involves passing known currents through the platinum filament of the cell and measuring the corresponding temperature. The repeatability is ±1.5% and the overall accuracy is ±3% over the full experimental range of -50 to +200 °C.

The values obtained for a series of nine alcohols are presented in Table I and those for eight primary, four secondary, and three tertiary aliphatic amines are given in Tables II and III. These values were supplemented with literature data given in ref 3, for the development and testing of the correlating equations.

Correlation of Data

It has been claimed (*1*) that experimental thermal conductivity data for all organic liquids may be smoothed by the following equation

$$\lambda = A(1 + B\tau^{1/3} + C\tau^{2/3} + D\tau) \qquad (1)$$

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