

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  $\lambda_i$  by extrapolation to  $t_f$ , small experimental deviations occur to depress the actual  $\lambda_a$  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,  $\lambda_s/\lambda_a$ , 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  $\pm 1.5\%$ .

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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  $\pm 1.5\%$  and the overall accuracy is  $\pm 3\%$  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

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

Table I. Experimental Data on Alcohols

liquid alcohol	purity, <sup>a</sup> %	temp, °C	thermal conductivity, mW m <sup>-1</sup> K <sup>-1</sup>	diff from eq 2, %
methyl	>99.8	0	209.6	0.13
		50	191.2	-0.06
sec-propyl	>99.8	0	139.8	-0.07
		50	129.1	-0.14
		65	142.7	-0.09
n-butyl	>99.8	0	154.0	0
		50	142.7	-0.09
		65	139.6	-0.11
		75	136.8	-0.19
isobutyl	>99.5	0	137.7	0.08
		50	127.0	-0.03
		65	125.7	0.06
sec-butyl	>99.0	0	139.7	0
		65	128.6	0.08
tert-butyl	>99.7	0 <sup>b</sup>	114.3	0
n-pentyl	>98.0	0	153.0	-0.01
		50	142.6	-0.06
n-hexyl	>99.0	0	152.6	-0.07
		50	145.3	0.08
		65	143.1	0
n-heptyl	>99.0	0	153.3	-0.10
		50	144.7	-0.07
		65	143.1	0
		120	132.0	-0.17
		150	129.2	-0.03

<sup>a</sup> By gas chromatography and then dried over molecular sieve.

<sup>b</sup> Supercooled liquid below normal melting point.

where  $\tau = 1 - T/T_c$ ,  $T_c$  is the critical temperature,  $B$ ,  $C$ , and  $D$  are constants,  $A$  is the pseudocritical thermal conductivity, and  $\lambda$  is the thermal conductivity at atmospheric pressure or saturation pressure where this is greater. When data are correlated as a function of both temperature and chemical structure, it is necessary to relate the constants to structure, but since it is impractical to attempt to relate all four constants to structure, a simplified version of eq 1, referred to as 1a, was developed in which  $C = 1 - 3B$  and  $D = 3B$ . This equation was shown (1) to be effective with various series of liquids including alkanes, alkenes, and dienes, aromatic hydrocarbons, naphthenes, aliphatic and aromatic esters, aliphatic and aromatic ethers, and halogenated aliphatic and aromatic hydrocarbons. None of these liquids is associated though they may be polar or nonpolar.

With the associated liquids described in this paper, eq 1 was confirmed as being capable of smoothing the data to within their claimed experimental accuracy, but the simplified version (eq 1a) in which the three terms  $B$ ,  $C$ , and  $D$  are reduced to a single constant did not represent accurately the experimental data. This was to be expected since with associated liquids the degree of association will vary with temperature and this will influence the ability of the liquid to conduct heat. However an empirical attempt was made to simplify eq 1, and the following equation was developed for associated liquids

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

where  $C = 1 - 2.6B$  and  $D$  is constant for a single chemical series with a value of 6.5 for alcohols and 6.0 for alkyl- and dialkylamines.

For many series of associated chemicals  $B$  and hence  $C$  are also constants independent of chain length as shown in Figure 1. The pseudocritical thermal conductivity,  $A$ , varies smoothly with the number of carbon atoms, but it has been found that it is simpler to smooth the thermal conductivity at a reduced temperature of 0.6 ( $\tau = 0.4$ ) and calculate  $A$  from this. Figure 2 shows how  $\lambda_{0.6}$  varies with chain length for the alcohols and amines. By use of the values given in Figures 1 and 2 with eq 2, the thermal conductivity of the alcohols and the primary and secondary amines can be represented to within their experi-

Table II. Experimental Data on Primary and Secondary Aliphatic Amines

liquid	purity, %	temp, °C	thermal conductivity, mW m <sup>-1</sup> K <sup>-1</sup>	diff from eq 2, %
Primary Aliphatic Amines				
n-propylamine	>99.0 <sup>a</sup>	-50	187.8	-0.21
		0	178.9	1.19
		25	172.4	0.23
n-butylamine	>99.0 <sup>a</sup>	0	165.9	-0.24
		25	156.8	-3.0
		50	154.1	-2.28
n-pentylamine	>99.0 <sup>a</sup>	-50	171.6	1.12
		0	160.4	0.31
		50	152.2	0.33
n-hexylamine	>99.0 <sup>a</sup>	0	157.0	0.58
		25	151.7	-0.13
		50	147.6	-0.34
n-octylamine	>99.0 <sup>a</sup>	100	142.8	0.78
		25	150.3	-1.44
		50	144.1	-0.55
n-decylamine	>99.0 <sup>a</sup>	100	137.5	-0.72
		150	134.2	0.6
		25	150.3	-0.73
		100	140.3	-0.64
		175	134.7	0.82
isopropylamine	>99.5 <sup>a</sup>	-50	163.7	5.6
		-50	162.2	4.6
		0	145.3	-0.2
		0	147.0	0.96
		25	138.2	-2.54
allylamine	>99.0 <sup>a</sup>	-50	206.8	0.78
		0	192.6	-0.16
		50	183.5	0.27
Secondary Aliphatic Amines				
diethylamine	99.5 <sup>b</sup>	0	142.0	0.5
		0	142.3	0.71
		25	137.0	2.23
di-n-propylamine	99.0 <sup>a</sup>	40	128.6	-0.85
		-50	153.8	3.36
		0	133.7	-1.4
di-n-butylamine	99.0 <sup>a</sup>	50	122.4	-0.73
		-50	151.1	-0.33
		0	137.0	-1.72
diisopropylamine	99.0 <sup>b</sup>	50	124.7	-2.5
		100	119.4	1.88
		-50	132.3	0.99
		0	116.7	-1.60
		0	116.5	-1.77
		50	108.4	1.12

<sup>a</sup> By gas chromatography. <sup>b</sup> By acidimetry.

Table III. Experimental Data on Tertiary Aliphatic Amines

liquid	purity, %	temp, °C	thermal conductivity, mW m <sup>-1</sup> K <sup>-1</sup>	diff from eq 1a, %
triethylamine	99.0 <sup>a</sup>	-50	135.6	-1.17
		0	121.2	-2.34
		0	122.1	-1.61
tri-n-propylamine	98.0 <sup>b</sup>	50	111.7	0.18
		-50	137.6	4.2
		0	119.7	-2.12
		0	121.2	-0.9
		50	112.1	-0.62
tri-n-butylamine	99.0 <sup>a</sup>	100	107.4	3.67
		125	100.5	1.41
		-50	131.3	-0.98
		0	123.2	-1.28
		25	120.2	-0.66
		50	117.3	0.09
		150	102.8	0.59

<sup>a</sup> By gas chromatography. <sup>b</sup> By acidimetry.

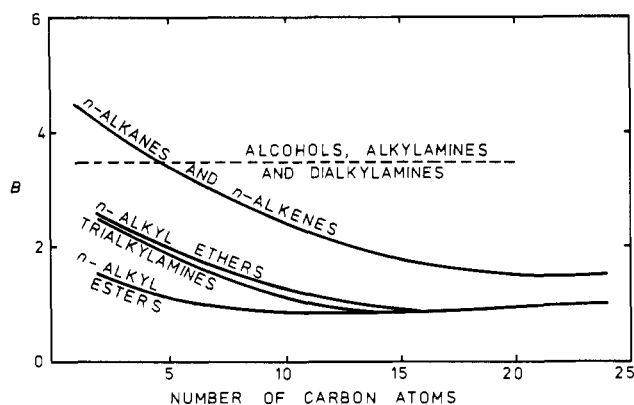


Figure 1.  $B$  as a function of the number of carbon atoms.

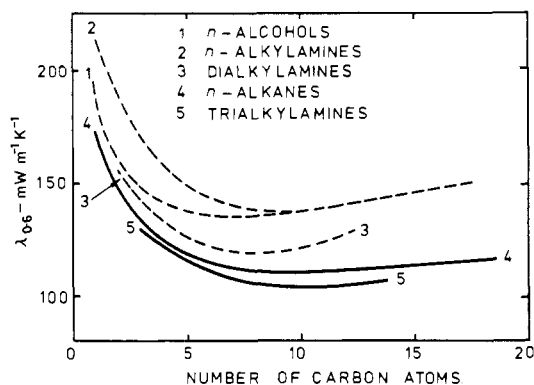


Figure 2.  $\lambda_{0.6}$  as a function of the number of carbon atoms.

mental uncertainty. Tables I and II give the percentage deviation of eq 2 from the new experimental data presented in this paper.

The trialkylamines are not represented by eq 2 since they are tertiary amines and as such are polar but nonassociating. This means that they should be represented by eq 1a. Figures 1 and 2 show how the terms  $B$  and  $\lambda_{0.6}$  compare with those from other

series of nonassociated liquids and Table III gives the individual percentage deviation of each measurement from that predicted by eq 1a.

Detailed tabulations using eq 1a and 2 have been prepared by the authors under the sponsorship of ESDU and may be found in ref 4 and 5 for 30 alcohols, 20 primary alkylamines, 5 secondary alkylamines, and 5 tertiary alkylamines. The necessary critical temperature data were taken from ref 6 and 7.

### Conclusion

Experimental thermal conductivity data are presented for series of alcohols and primary and secondary amines. All of these fluids associate by the formation of hydrogen bonds. Experimental values are also presented for a series of tertiary amines which, while polar, do not form hydrogen bonds and so are classed as nonassociating.

An equation developed previously (1) to correlate the thermal conductivity of nonassociated liquids has been modified, and an alternative form is presented which correlates the thermal conductivity data for these associated liquids.

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## Viscosity and Density of Aqueous $\text{Na}_2\text{CO}_3$ and $\text{K}_2\text{CO}_3$ Solutions in the Temperature Range 20-90 °C and the Pressure Range 0-30 MPa

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The paper presents new experimental measurements of the viscosity of aqueous  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  solutions in the temperature range 20-90 °C and the pressure range 0-30 MPa. The measurements cover the concentration range 0-1.7  $m$  for the first salt and 0-2.5  $m$  for the second and are believed to be accurate to  $\pm 1\%$ . The effect of pressure on the density of these solutions has also been measured. The paper contains correlations of the density and viscosity of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  in terms of temperature, pressure, and concentration. The correlations reproduce the experimental results to within their quoted accuracy.

### 1. Introduction

In a number of earlier publications (2, 3, 6) we reported the viscosity of the aqueous solutions of NaCl and KCl and their mixtures over the temperature range extending to 150 °C, pressure range extending to 30 MPa, and composition range extending from zero to near saturation. These measurements are believed to be the only ones covering ranges of pressure, temperature, and concentration which correspond to those prevalent in liquid-dominated geothermal reservoirs. The present paper is the sixth in a series (2, 3, 6-8) that is intended to provide data on the viscosity of the most important constituents of geothermal fluids and, together with the other papers in this