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THERMAL CONDUCTIVITY OF 13 FLUOROCARBON LIQUIDS*

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SUMMARY

Experimentally measured values of the thermal conductivity of five fluorobenzenes, three fluorotoluenes, and five perfluoro compounds are presented for the range -50°C to 150°C. Easily-used equations are proposed for representing these data.

INTRODUCTION

Thermal conductivity is an important physical property since it is required for calculations of almost all forms of heat transfer, including forced convection. Fluorocarbons are finding more and more applications and the fully fluorinated (perfluoro) compounds, which have high thermal stability coupled with low viscosity, are particularly useful as coolants and as working fluids for heat engines; but designers are severely hampered because of the lack of the essential data on thermal conductivity. Apart from those on fluorobenzene, no other conductivity data on the fluorobenzene series are to be found in the literature. In an effort to alleviate this shortage, the National Engineering Laboratory has undertaken measurements on a cross-section of fluorobenzenes. For similar reasons, measurements were also made on some fluorotoluenes and on perfluoro-alkanes and perfluoro-naphthenes. In addition to reported experimental data on fluorocarbons, straightforward equations which describe thermal conductivity as a function of temperature are provided in this paper to assist designers or other users.

Thermal conductivity is a difficult property to measure accurately, and this is reflected in the literature where it is found that while the

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TABLE 1

Measured thermal conductivity of fluorocarbons (mW m^{-1} K^{-1})

Fluorobenzenes	Temperature °C						Melting point °C	Boiling point °C
	0	25	50	65	75			
o-difluorobenzene	123.5	–	108.8	–	109.7		-47	93.9
1,2,4-trifluorobenzene	112.6	–	102.6	–	96.1		-35	88.0
1,2,4,5-tetrafluorobenzene	–	103.9	104.8	–	96.2		+4	90.3
1,2,3,5-tetrafluorobenzene	104.9	–	96.7	–	90.3		-48	84.8
hexafluorobenzene (perfluorobenzene)	–	94.4	91.8	85.5	–		+5	80.3

Fluorotoluenes	Temperature °C						Melting point °C	Boiling point °C
	-50	0	50	75	90	100		
o-fluorotoluene	133.3	125.3	114.0	–	–	102.6	-80	114
p-fluorotoluene	132.6	123.7	113.2	–	–	102.2	-56.7	117
octafluorotoluene (perfluorotoluene)	–	90.7	82.3	80.1	76.9	–	-98	80.5

Perfluoro-alkanes and -naphthenes (Flutec No)	Temperature °C						Melting point °C	Boiling point °C
	0	25	45	70	95	100		
perfluoro-n-pentane (PP50)	65.7	65.7*	–	–	–	–	-140	29
perfluoro-n-hexane (PP1)	66.9	64.8	64	–	–	–	-70	57
perfluoro-methylcyclohexane (PP2)	61.4	–	60.0	56.5	–	–	-50	76
perfluoro-1,3-dimethylcyclohexane (PP3)	61.8	–	–	56.8	56.3	–	-70	102
perfluoro-1-methyldecalin (PP9)	58.6	–	–	56	–	51.7	-70	160

*Believed high

majority of modern data for organic liquids have an accuracy within 2 to 5%, older data in handbooks often have errors of ±20% or more. Conductivity data within 5% are quite acceptable for most present-day design methods.

RESULTS

Measurements of thermal conductivity in the temperature range -50 to 150°C are reported for five fluorobenzenes, three fluorotoluenes, and five perfluoro compounds. The results are given in Table 1 where, in addition, the normal liquid range of each fluid is given by its melting point and boiling point.

The method of measurement is by the steady-state hot-wire technique where a platinum filament acts both as a heater and as a resistance thermometer. This relative method, operating at 1000 Hz, is described in a previous paper [1] and is accurate to within ±3%.

DISCUSSION

The conductivity of the fluorobenzenes is less than that of benzene itself, and the more fluorine atoms, the less is the conductivity, which means that fluorobenzene has a higher conductivity than hexafluorobenzene. As with most liquids, thermal conductivity is essentially a linearly decreasing function of temperature between melting point and boiling point. The fluorobenzenes exhibit this behaviour as do all the other fluoro compounds measured. In Fig. 1 the relative conductivities of benzene and the fluorocarbons are clearly seen.

The fluorotoluenes exhibit a similar pattern to the fluorobenzenes in that thermal conductivity decreases with increase of fluorine atoms. The conductivities of ortho- and para-fluorotoluene are so close that they can be considered to have identical values.

The Flutec compounds all have conductivities which fall within the narrow band 51 to 66 mW m^{-1} K^{-1}. It is unusual for liquids to have such a low conductivity in this temperature range. The conductivities of the perfluoro-n-pentane and -n-hexane compounds are so close as to be indistinguishable, and the same applies to the perfluoro-methylcyclohexane and -1,3-dimethylcyclohexane compounds.

TREATMENT OF RESULTS

The measurements of di-, tri-, tetra-, and hexafluorobenzene cover five of the twelve members of the fluorobenzene series, which, coupled with the literature values for (mono)fluorobenzene, enable this series to be examined systematically.

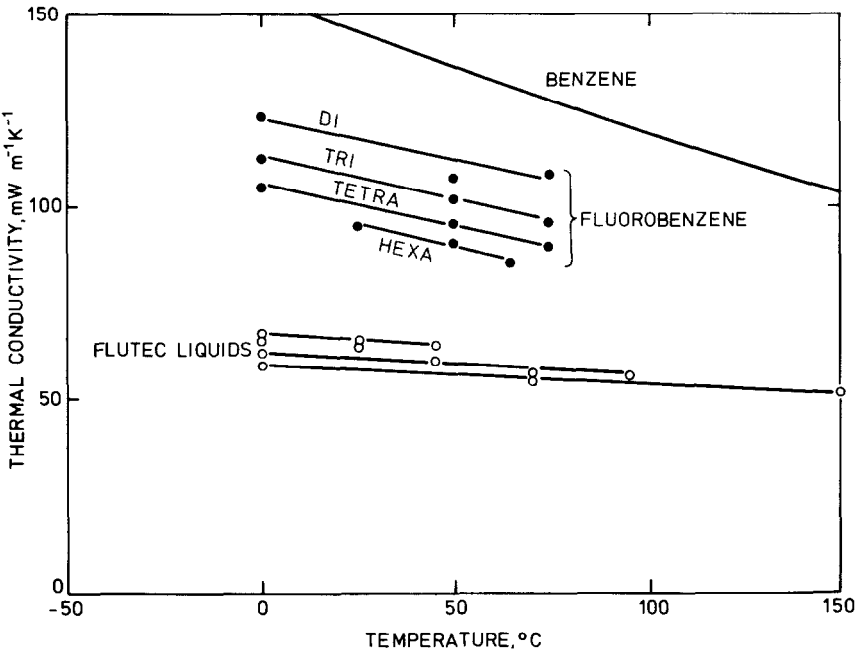

Fig. 1. Thermal conductivity of fluorocarbons

Before the members of any series can be compared, the data must be rationalized in some way. This may be done for liquid thermal conductivity by using the well-known equation of Riedel [2]

$$\lambda = A\left\{1 + B\left(1 - \frac{T}{T_c}\right)^{\frac{2}{3}}\right\}, \qquad (1)$$

where T_c is the critical temperature (K). This equation allows a better representation of data over a wider temperature range than a straight line, and the coefficients A and B form a consistent set of values. The coefficient A is dominant and in practice A and B were found by a least-squares procedure for each compound; smoothed values of B were found from a plot of B as a function of the number of fluorine atoms, and then these fixed B values used to re-optimize for A. This in turn gave new values for A, which were also plotted as a function of the number of fluorine atoms and, where

necessary, A values were adjusted to form a smooth curve. This smoothing was achieved without adversely affecting the overall fit to the experimental data. The functions of A and B then allow a graphical interpolation to be made for the missing fluorobenzenes.

The above explains in simple terms a method for deriving a consistent set of values for the coefficients A and B in Equation (1) from experimental data on the fluorobenzene series. In the derivation of these coefficients, account was also taken of existing data for the chlorobenzene, bromobenzene and iodobenzene compounds [3]. Data exist for ten out of twelve of the chlorobenzenes and a few measurements have been made for the bromobenzenes and iodobenzenes. The values of A and B were in fact found for all the halogenated benzenes where data exist and examined collectively to arrive at an overall optimum. As already described, Equation (1) is relatively insensitive to variations in B, and it was found that a single set of values was sufficient for all the halogen series. This is shown in Fig. 2.

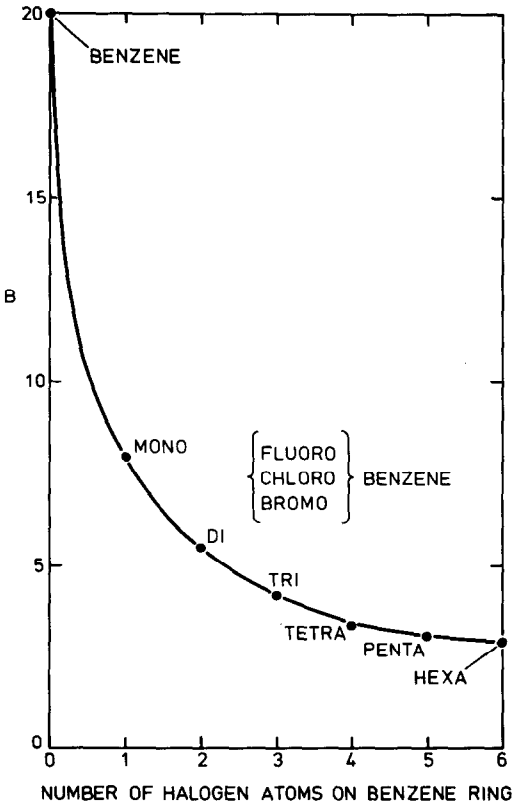

Fig. 2. Coefficient B as a function of number of halogen atoms

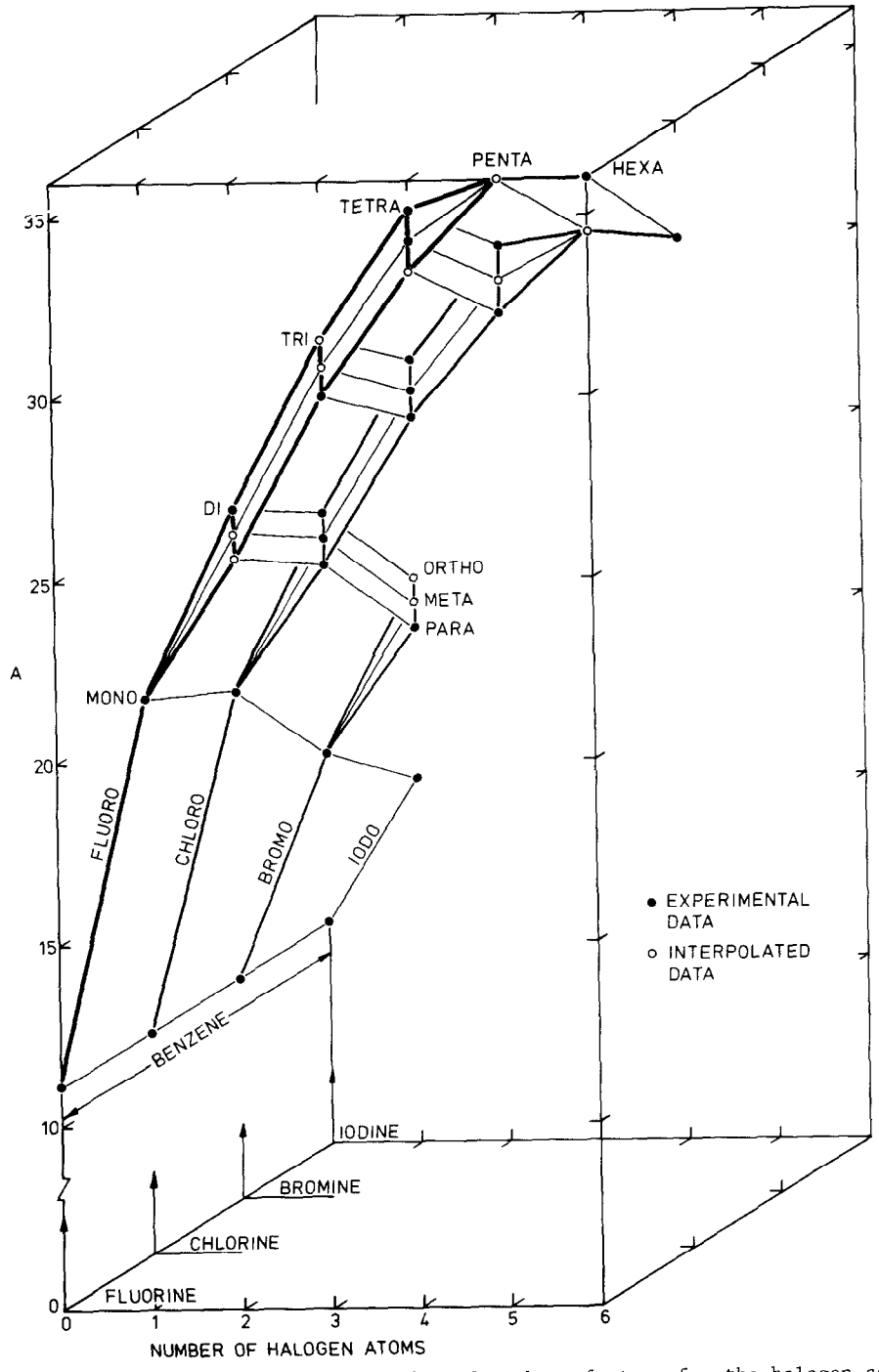

Fig. 3. Coefficient A as a function of number of atoms for the halogen series

The final values for A were also found from a comparison of the families of compounds, but a different set of values was required for each halogen series. The A values are in Fig. 3 where it is seen that they follow a regular pattern of behaviour. Points derived from experimental data are shown as solid circles, while interpolated values are shown as open circles.

The coefficients A and B are given in Table 2. Equation (1) describes the data within experimental error (±3%) and can be applied to each of the fluorobenzenes from the melting point to 100°C. If the equation is used for extrapolation, the accuracy is within ±5% up to 150°C.

TABLE 2

Coefficients of equation (1) for fluorobenzenes

Number of fluorine atoms	Liquid	Critical temperature °C	Equation (1) coefficients	
			A	B
0	benzene	289.01	11.1	20.0
1	fluorobenzene	286.95	21.77	8.0
2	o-difluorobenzene	292.2	27.00	5.5
	m-difluorobenzene*	275.5	26.35	5.5
	p-difluorobenzene*	284.6	25.65	5.5
3	1,2,4-trifluorobenzene	275.1	30.10	4.2
	1,3,5-trifluorobenzene*	258.8	31.65	4.2
	1,2,3-trifluorobenzene*	282.7	30.89	4.2
4	1,2,3,4-tetrofluorobenzene*	277.6	33.46	3.4
	1,2,4,5-tetrofluorobenzene	270.2	35.18	3.4
	1,2,3,5-tetrofluorobenzene	262.0	34.34	3.4
5	pentafluorobenzene*	257.8	35.97	3.1
6	hexafluorobenzene	243.5	36.05	2.9

*Coefficients found by interpolation.

Thermal conductivity values were further extrapolated to $T_r = 0.9$ ($T_r = T/T_c$) by a reduced temperature plot using the accurate data of the aromatic hydrocarbons as a basis. The data were found to be well described by the equation

$$\lambda = A' + B'(1 - T_r)^{\frac{1}{3}} + C'(1 - T_r)^{\frac{2}{3}} + D'(1 - T_r)^{1}. \qquad (2)$$

This equation allows thermal conductivity to be calculated from melting point to $T_r = 0.9$. Equations (1) and (2) give values which differ by less than 1% over the range of temperature for which Equation (1) is applicable. The coefficients of Equation (2) for the fluorobenzenes are included in a more general report on halogenated aromatic hydrocarbons [4]. The extrapolated values from the second equation become more uncertain with increase in temperature reaching a maximum of about ±15% at $T_r = 0.9$.

The first equation should be used in the temperature range from the melting point to 100°C, and may be extrapolated to 150°C, while the second equation allows conductivity to be predicted up to $T_r = 0.9$. Both equations are easy to evaluate and can readily be incorporated in computer programs.

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