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THE THERMAL CONDUCTIVITY OF TOLUENE. NEW DETERMINATIONS AND AN APPRAISAL OF RECENT EXPERIMENTAL WORK

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Abstract—New, absolute determinations of the thermal conductivity of toluene in the temperature range −20° to +112°C are reported. These results were compared with the best data published during the last 10 years, and as a result of a subsequent analysis a linear relation between the thermal conductivity and temperature is proposed, which predicts the thermal conductivity of toluene within better than 1 per cent between −20° and +112°C. In the absence of comprehensive experimental evidence from −20°C to the f.p. at −95°C, it is tentatively suggested to use this equation for extrapolations which will probably fall within 2–3 per cent of the real values.

The accuracy and consistency of the results of the various investigations from which the above relation was derived, and the favourable physical and chemical properties of toluene justify making a strong recommendation for using this substance for calibration purposes in relative determinations, or for control measurements in absolute measurements of the thermal conductivity of fluids.

Résumé—Les nouvelles determinations absolues de la conductivité thermique du toluène (entre −20 et +112°C), sont données ici. Ces résultats sont comparés avec les meilleures données publiées au cours de ces dix dernières années, une étude consécutive a permis de proposer une relation linéaire entre la conductivité thermique et la température qui donne la conductivité du toluène à mieux de 1% entre −20 et +112°C. En l'absence de données expérimentales de −20°C au point de congélation à −95°C, il est suggéré d'essayer d'extrapoler cette équation qui permettra probablement d'obtenir des valeurs à 2–3% près.

La précision des résultats des nombreuses recherches à partir desquelles la relation ci-dessus a été établie, et les propriétés chimiques et physiques favorables du toluène justifient la recommandation d'utiliser cette substance pour les étalonnages relatifs ou pour des mesures de contrôle dans les mesures absolues de la conductivité thermique de fluides.

Zusammenfassung—Durch neue Absolutmessungen wurden die Wärmeleitfähigkeiten für Toluol im Temperaturbereich −20° bis +112°C bestimmt. Ein Vergleich mit den besten anderen während der vergangenen zehn Jahre veröffentlichen Werten führte analytisch zu einer linearen Beziehung zwischen Wärmeleitfähigkeit und Temperaturen.

Die vorgeschlagene Gleichung ermöglicht es, die Wärmeleitfähigkeit von Toluol im Bereich von −20° bis +112°C mit weniger als 1% Unsicherheit zu berechnen. Solange umfassende Versuchswerte zwischen −20°C und dem Gefrierpunkt bei −95°C fehlen, kann die Gleichung für diesen Bereich extrapoliert werden. Die Unsicherheit dürfte dabei 2–3% betragen.

Die Genauigkeit und innere Konsistenz der der oben erwähnten Gleichung zugrundegelegten Forschungsergebnisse und die günstigen physikalischen und chemischen Eigenschaften von Toluol lassen es als Eichsubstanz bei der relativen Bestimmung und als Kontrollsubstanz bei der Absolutbestimmung der Wärmeleitfähigkeit von Flüssigkeiten sehr geeignet erscheinen.

Аннотация—Приведены результаты определения абсолютного значения коэффициента теплопроводности толуола в интервале температур от −20° до +112°C. Эти результаты сопоставлялись с данными, опубликованными за последние 10 лет. Установлена линейная зависимость коэффициента теплопроводности от температуры и предложена формула, позволяющая с точностью до 1% вычислять значение этой теплофизической характеристики в интервале от −20° до +112°C. В связи с недостаточным количеством экспериментальных данных по коэффициенту теплопроводности толуола от −20°C до точки плавления при −95°C предлагается и в этом температурном интервале использовать указанную формулу. Точность определения коэффициента теплопроводности для температур $-95°$ до $-20°C$ будет, по-видимому, в пределах 2–3%.

Достаточная точность и совпадение результатов исследований, на основании которых была получена предлагаемая формула, а также благоприятные физические и химические свойства толуола позволяют рекомендовать это вещество для тарировки при измерениях коэффициента теплопроводности жидкостей как относительными, так и абсолютными (в контрольных опытах) методами.

INTRODUCTION

EXPERIMENTAL determinations of the thermal conductivity of fluids can be made with the aid of relative or absolute methods. Common prerequisites for all absolute determinations are the accurate knowledge of certain characteristic dimensions of the conductivity cell and the absence of noteworthy heat losses or gains from, or to, the cell.

High precision is required in the manufacture and in the assembly of conductivity cells for absolute determinations and in many instances the resulting high cost of the equipment cannot be justified for determinations of a routine character requiring less accuracy. Apparatus of simpler design, and greater ease and higher speed of operation have often been used in the past, in which determinations were made relative to another fluid of established thermal conductivity. The accuracy of such measurements depends therefore in the first place on the reliability of the values of the calibration fluid.

With the exception of several substances whose thermal conductivity has been well established in the gaseous state (nitrogen, air, hydrogen etc.), there is, liquid water excluded, no other substance whose thermal conductivity is sufficiently accurately known over a wide range of temperature in order to recommend it as a calibration, or control fluid.

Until a few years ago reliable measurements of the thermal conductivity of liquids were very scarce and a study of the relevant literature showed that discrepancies of up to 30 per cent between different observers' values for a certain substance are by no means a rarity. In principle, any liquid whose thermal conductivity has been sufficiently well established could be considered as a calibration fluid. A substance recommended for general use should possess in addition the following physical and chemical properties:

(a) the temperature interval between the freezing point and the normal boiling point, i.e. the extent of the liquid range, should be large and should preferably include the ice point and/or some other thermometric fixed point,
(b) the liquid should be non-toxic and non-corrosive with respect to the usual engineering materials, and
(c) it should be obtainable at reasonably low cost and guaranteed high purity.

A substance that adequately meets these requirements is toluene. It has a low f.p. of $-95°C$ and an atmospheric b.p. of 110·8°C; the liquid phase extends therefore over a temperature interval of about 206°C and includes the ice point and the b.p. of water as thermometric fixed points. It is also non-corrosive, non-toxic and inexpensive.

The use of toluene as a calibration fluid in thermal conductivity determinations was first suggested by Riedel [1] in 1951 who also made a plea to other workers for further studies of the thermal conductivity of this liquid to complement and substantiate his own observations, and thus to arrive at an internationally agreed set of values. Since then several other observers have published values of the thermal conductivity of toluene [2–4].

It is the purpose of the present paper to discuss and analyse some of the earlier work on the thermal conductivity of toluene, to compare it critically with measurements carried out during the past two years at the Explosives Research and Development Establishment, Waltham Abbey, and to propose on the basis of this analysis new values of adequate accuracy to justify the use of toluene as a calibration or control liquid in determinations of the thermal conductivity of fluids.

EXPERIMENTAL

For several years absolute determinations of the thermal conductivity have been carried out at the Explosives Research and Development Establishment (E.R.D.E.), Waltham Abbey, on a variety of fluids. These experiments often extended over considerable periods of time during which the conductivity cell was exposed to the effects of high temperature and elevated pressures. To ascertain that no changes of the alignment of the cell, or of its absolute dimensions had taken place during the period of experimentation, it had become established practice to carry out control measurements on a reference substance at a fixed temperature at the beginning, and at selected intervals during a series of tests. For convenience, toluene was chosen as this reference fluid. The primary object of these measurements was simply to demonstrate the reproducibility of the results on the reference fluid, from which in turn the absence of permanent changes of the cell or other disturbing effects was inferred. In course of time many individual results were thus obtained which, however, in view of their purpose, were rather non-uniformly distributed over the temperature range of interest. When the need for reliable and internationally acceptable data on the thermal conductivity of a standard substance was realized, the available data on toluene

Table 1. *Experimental determinations of the thermal conductivity of toluene* (*this research*)

Temperature (°C)	*Pressure, (atm)	Thermal conductivity (10^{-4} . cal/cm °C sec)	Number of determinations	Temperature difference (°C)	Cell type	Thermostat
−14·9		3·46	3	1·57	3	H
−14·7		3·43	1	1·60	3	H
−12·0		3·44	1	2·16	3	H
−11·3		3·45	1	2·29	3	H
−10·0		3·47	1	1·60	3	H
−9·7		3·47	1	1·59	3	H
−3·1		3·34	2	1·68	3	H
15·2		3·24	4	1·97	2	F
17·3		3·21	3	1·96	2	F
33·9		3·12	1	1·74	3	G
34·3		3·14	7	2·39	2	E
34·9		3·09	1	1·71	3	G
36·4		3·09	7	2·05	2	E
38·1		3·10	1	1·89	3	G
44·4		3·08	3	2·40	2	E
49·7		3·06	4	3·74	1	B
55·2		2·95	4	2·08	2	E
57·4		2·94	3	4·27	2	E
57·7	3	2·93	5	3·13	1	A
66·1		2·87	5	2·32	2	E
71·9		2·85	4	2·43	2	E
77·5		2·80	1	3·12	1	A
81·6		2·79	1	2·75	1	D
90·7		2·80	4	4·10	1	C
111·8	4	2·62	1	2·90	1	D
111·8	4	2·58	2	2·90	1	D

* Atmospheric Pressure, except where stated otherwise.

Cell Types:
1 : silver emitting cylinder, Hidural 5 receiving cylinder; annulus width 0·0755 cm.
2 : all-silver conductivity cell; annulus width 0·0755 cm.
3 : all-Hidural 5 conductivity cell, gold plated; annulus width 0·0258 cm.

Thermostats:
A, B, C and D—various combinations of air cooled heat sinks.
E—thermostatically controlled water bath.
F—mains water bath.
G—electrically heated tubular thermostat.
H—Freon refrigerator.

from previous studies at this Establishment were complemented by new measurements in the temperature range $-15°$–$+110°C$.

A compilation of all experimental data obtained at different times at E.R.D.E. can be found in Table 1. The same basic type of apparatus, viz. a coaxial cylinder cell with independently heated guard rings, was used in all experiments. Naturally, bearing in mind the purpose of these determinations, changes in detail were made from time to time to the apparatus and those which appeared to be significant were recorded in columns 6 and 7 of Table 1. A detailed description of the apparatus and the experimental technique can be found in a previous publication [5] by the same author.

The substance studied in the present research was sulphur-free toluene of A.R. quality supplied under the standard specifications of the manufacturers, the General Chemical and Pharmaceutical Company Ltd.

The data obtained in this research were correlated by the following equation

$$10^4 \times k = k_0 - (dk/dt) \, . \, t = 3{\cdot}35 - 0{\cdot}0068\, t \quad \text{cal/cm °C sec}$$

where k and k_0 are the thermal conductivities at t°C and 0°C, respectively, (dk/dt) the temperature coefficient of the thermal conductivity and t the temperature in °C.

The constants in this equation, k_0 and (dk/dt), were found from a least square analysis. This relation is represented by the thin solid line in Fig. 1

DISCUSSION

A comparison of this research with earlier work was confined to data given in four papers published since 1950 [1–4] but also the results of two earlier studies [6, 7] which have been frequently quoted in the relevant literature will be briefly discussed, although they were not included in the final analysis. It was indeed a fortunate coincidence that most of the later determinations were absolute ones and were made with different types of conductivity cells employing different methods of temperature measurement. Greater confidence can obviously be put into average values which were derived from an analysis of data obtained by different methods, as the possibility of propagating inherent errors due to the use of only one experimental method is eliminated.

Each group of experimental values taken from one of the above references was subjected to a least square analysis. The constants of the resulting different linear equations (k_0 and dk/dt) were compiled in Table 2, where also a brief description of some significant details of the experimental method employed by the various authors can be found.

Excluding for the time being the results obtained by Bridgman [6] and those by Abas-Zade [7] which will be discussed later, the generally good agreement between the four previous observers, both with regard to their k_0-values, as well as to their temperature coefficients of the thermal conductivity is a noteworthy fact. However, on closer examination

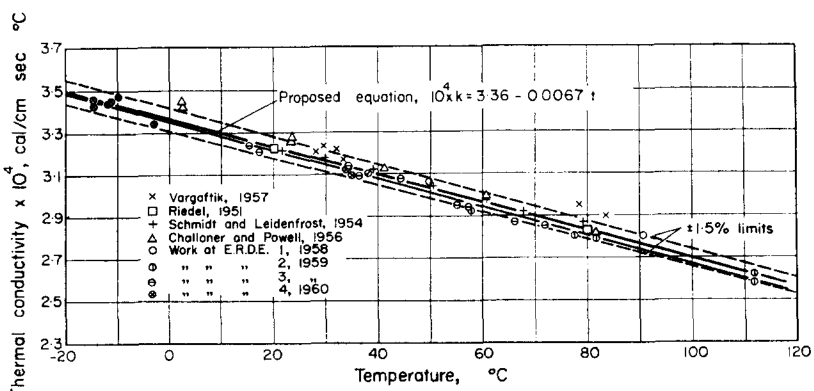

FIG. 1. The thermal conductivity of toluene.

Table 2. A compilation of some significant details of apparatus used for experimental studies of the thermal conductivity of toluene and the results of least square analysis of previous and present experimental work

Observer	Type of apparatus	Method of temperature measurement and range covered	Number of points	Standard deviation from proposed equation, (%)	Thermal conductivity at 0°C (k_0) 10^{-4} . cal/cm °C sec	Temperature coefficient, $-10^4\ dk/dt$
Bridgman [6]	Coaxial cylinders, 0·04 cm annulus	Copper–constantan thermocouples; 30° and 75°C	2	16·8	3·81	0·0056
Abas-Zade [7]	Hot-wire	Pt-resistance thermometer; 0°–320°C, 1 to 50 atm	18 (liquid phase)	18·5	3·90	0·0056
Riedel [1]	Coaxial cylinders	Thermocouples; −80°, +20° and +80°C		0·1 (for points above 0°C)		
	Flat plate 0·1 cm gap	Thermocouples; −80°, + 20° and +80°C			3·36	0·0065
	Concentric spheres 0·1 cm gap	Pt-resistance thermometer: 20°C		1·3 (including point at −80°C)		
Schmidt and Leidenfrost [3]	Coaxial cylinders, 0·1–0·4 cm annulus	Thermocouples; 20°–80°C	7	0·7	3·36	0·0062
Challoner and Powell [4]	Flat plate, 0·2 and 0·3 cm gap	Copper–constantan thermocouples; 0°–80°C	8	1·8	3·44	0·0075
Vargaftik [2]	Hot-wire	Pt-resistance thermometer; 25°–85°C	6	2·5	3·38	0·0057
This research	Coaxial cylinders, 0·026 cm and 0·076 cm annulus	Copper–constantan thermocouples; −15°–+112°C	29	1·1	3·35	0·0068

it is seen that excellent agreement exists between the results of Schmidt and Leidenfrost [3], of Riedel [1], and those of the present work. To establish a basis for a further analysis of all data, including those given in [2] and [4], the present results were combined with those of Schmidt and Leidenfrost, and of Riedel, and a second linear expression was established which differed only slightly from the one based solely on the present work. For the sake of clarity it has been omitted in the figure.

From the available evidence no justification could be found for assuming that any set or sets of experimental results were, as far as their absolute values are concerned, more accurate than the others, and in the final analysis they were all regarded as equivalent. To allow, however, for the random deviation of individual experimental points from the line of best fit based on [1], [3] and this work, the following system of weighting was introduced.

The area on either side of the straight line representing the reference equation was divided into 5 zones comprising points of the following respective percentage deviation: 0–0·5, 0·5–1, 1–2, 2–3 and 3–4. The weight attached to any individual point was the reciprocal of the upper limiting value of the deviation zone in which this particular point was located; e.g. all points located within the 0–0·5 per cent deviation zone were assigned a weighting factor of 1/0·5, those within the zone 0·5–1 a weighting factor of 1/1, etc. By using this method individual points farther removed from the reference relation were given a lower weight without, however, overweighting those very close to it.

With the aid of this weighting method and by applying again a least square analysis to the individual points of all observers, the following final equation for the dependence of the thermal conductivity of toluene on temperature was established

$$10^4 \times k = 3{\cdot}36 - 0{\cdot}0067 . \, t \text{ cal/cm °C sec.}$$

This equation is represented by the thick solid line in Fig. 1. To enable a numerical comparison of the results of the various authors with the proposed equation, the standard deviations from this relation were computed and can be found in column 5 of Table 2. A fact worth pointing out is the excellent agreement of Riedel's two values at 20° and 80°C with the proposed equation, the standard deviations for these points being about 0·1 per cent. Also for the results of Schmidt and Liedenfrost and those of this research, comparatively small standard deviations of 0·71 and 1·1 per cent, respectively, were found. Somewhat higher deviations resulted for the data of Challoner and Powell and for those of Vargaftik. These two last mentioned studies exhibit a temperature coefficient somewhat different from the one derived for the proposed equation, that from the work of Challoner and Powell being higher, and the one from Vargaftik's study lower than the proposed one.

The somewhat higher temperature coefficient derived from the work by Challoner and Powell appears to be at variance with those of the other observers, and also indirectly, with one single value at −80°C due to Riedel. At this temperature the extrapolation of the linear relation correlating the data by Challoner and Powell yielded a value about 6 per cent higher than Riedel's experimental point. Although the proposed new equation does not reproduce the experimental value at −80°C within the limits of accuracy claimed by Riedel (1 per cent), the discrepancy is not excessive, the computed value being only about 2 per cent higher than the experimental one.

Differences of this order of magnitude are difficult to explain and two facts have to be considered here.

(a) The new equation was entirely based on experimental data obtained within the temperature interval −20°– +112°C and a simple linear expression between temperature and thermal conductivity was found to correlate them with adequate accuracy. It does not seem improbable, however, that deviations from linearity, so far perhaps masked by experimental scatter, could become more prominent at lower temperatures.

(b) The comparison to −80°C rests essentially on one single point obtained by one observer and until this value has been verified by further experiments there remains in theory the possibility of experimental error, although this explanation seems to be rather less likely than the first one in view of the excellent agreement of Riedel's values at higher temperatures. Work is in hand at E.R.D.E. to check the value near −80°C (carbon dioxide point) and at two other thermometric fixed points viz. at 0° and at 100°C.

Two more authors, Bridgman [6] and Abas-Zade [7], have reported data on the thermal conductivity of toluene which were also subjected to the usual analysis, the results of which can be found in the first two columns of Table 2. It is seen that the k_0-values of both authors lie considerably above those of all later workers, the corresponding temperature coefficients, however, are in fair agreement with those from the later studies. The causes which may have led to the relatively large discrepancies between Bridgman's determinations and those of later workers on toluene have been thoroughly discussed by Riedel [1] and need not be repeated here. The experimental evidence provided for toluene, and also for kerosene which was the subject of a recent study by the author of this paper, seems to confirm Riedel's criticism.

From the close agreement between the work by Abas-Zade and by Bridgman one could almost gain the impression that the former author's apparatus, a hot wire cell with a small annular gap, was calibrated with the aid of Bridgman's results. Although the hot wire cell permits in principle absolute determinations, several authors have remarked on their difficulties in centring the heated wire with the required precision in the surrounding glass tube, eventually forcing them to resort to some form of calibration with a liquid of known thermal conductivity for determining the true geometric constant of their apparatus. In view of the lack of confirmation and the consistency of later determinations, the results of these two authors were not considered in the final analysis.

Further references on the thermal conductivity of toluene dating back to 1911 can be found in the paper by Challoner and Powell [4] but much of the earlier work must now be regarded as superseded by the work carried out during the last ten years.

Considering all relevant circumstances it seems certain that the thermal conductivity of toluene is predicted by the proposed equation with an accuracy of better than 1 per cent between $-20°$ and $+110°C$, and probably within better than 2 to 3 per cent between $-80°$ and $+20°C$. The 1·5 per cent dispersion band with respect to the above equation includes 85 per cent, the 3 per cent band 100 per cent of all experimental points from five independent investigations. This is an excellent result when it is considered that these results were obtained by different observers using various types of apparatus.

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