Benzene: A Further Liquid Thermal Conductivity Standard

M. J. Assael

Department of Chemical Engineering, Aristotle University, Thessaloniki, GR54006, Greece

M. L. V. Ramires and C. A. Nieto de Castro

Departamento de Química, Faculdade de Ciências da Universidade de Lisboa, R. Ernesto de Vasconcelos, Bloco C1, 1700 Lisboa, Portug

W. A. Wakeham

Department of Chemical Engineering, Imperial College, London SW7 2BY, United Kingdom

Received May 24, 1989

The available experimental liquid-phase thermal conductivity data for benzene have been examined with the intention of establishing a further liquid thermal conductivity standard along the saturation line. The quality of the available data is such that new standard reference values can be proposed with confidence limits better than ± 1% for most of the normal liquid range.

Key words: benzene; reference material; standard reference data; thermal conductivity; transient hot wire.

Contents

1. Introduction

In a recent paper,[1] we have proposed standard reference values for the thermal conductivity of liquid toluene, liquid water, and liquid *n*-heptane for most of the normal liquid range. The literature data, available up to 1985, was assessed by a careful analysis of the experimental methods and equipment used and was subsequently divided into primary and secondary data. The primary data were used to develop primary correlations of the thermal conductivity of toluene and water along the saturation line as a function of temperature and a secondary data correlation was prepared for *n*-heptane.

This effort[1] was developed under the auspices of
Subcommittee on Transport Properties of the Internati
Union of Pure Applied Chemistry and later publishe
part of a complete set of recommendations on the diffe
physical properties of fluids by IUPAC.[2]

Benzene was a chemical initially included in the st
However, no results were presented at that time because
literature data available were too discordant to permit
definitive statement. Since then, several new sets of dat
the thermal conductivity of liquid benzene became a
able[3–5] and it is now possible to propose standard refere
data for the thermal conductivity of benzene.

We report in this paper the results of such an anal
The format of our previous report[1] is maintained and
reader is referred to this paper for a complete discussio
experimental techniques, the criteria for standard refere
materials, and experimental data selection. We will only
scribe here briefly the procedure adopted for benzene.

Reprints available from ACS; see Reprints List at back of issue.

2. Experimental Techniques

The experimental methods used to measure the thermal ductivity of fluids may be divided into two groups: ady-state and transient methods. For an overall discus- n of the techniques and the accuracy attainable with them reader is referred to monographs on the experimental thods for the measurement of transport properties of ids.[6,7] Here, we only need to say that the most accurate thod for the measurement of the thermal conductivity of ids is the transient hot-wire technique which, when cor- tly used, can obtain data with an accuracy of 0.5%. This a result of the existence of a working equation for this thod, together with a consistent set of corrections and to fact that it can avoid other modes of heat transport, mely convection and radiation.

When the full conditions of the method are met, the truments based on it generate primary data with an accu- y of 0.5% or better. In this study the primary data subset benzene was chosen to have a maximum uncertainty of 1.5% at ambient temperatures.

3. Experimental Data

The recommendations previously made by Nieto de stro *et al.*[1] for the subdivision of experimental data into imary and secondary data were followed. The primary ta were identified by the following criteria:

(i) Measurements must have been made with a primary perimental apparatus, i.e., a complete working equation st be available.

(ii) The form of the working equation should be such at sensitivity of thermal conductivity to the principal vari- les does not magnify the random errors of measurement.

(iii) All principal variables should be measurable to a h degree of precision.

(iv) The published work should include some descrip- n of purification methods and a guarantee of purity.

(v) The data reported must be unsmoothed data. hilst graphs and fitted equations are useful summaries for reader, they are not sufficient for standardization pur- ses.

(vi) The lack of accepted values of the thermal conduc- ity of standard reference materials implies that only abso- e and not relative measurement results can be considered.

(vii) Explicit quantitative estimates of the uncertainty reported values should be given, taking into account the ecision of experimental measurements and possible sys- natic errors.

(viii) Owing to the desire to produce high-accuracy ref- nce values, limits have been imposed on the accuracy, as termined by the present authors, of the primary data sets. r primary standard reference materials the accuracy of imary data is required to be better than ± 1.5%.

3.1. Primary Data

A summary of the primary data for benzene, together th their estimated uncertainty is given in Table 1. The tistical treatment of the data is the same adopted in Ref. 1.

TABLE 1. Primary experimental data sources for thermal conductivity.

Literature source	Technique	Temp. range	No. of data pts.	Assigned accuracy
M. L. V. Ramires *et al.* (Ref. 5)	THW[a]	298–350	25	± 1.0
S. F. Y. Li *et al.* (Ref. 10)	THW	310–345	3	± 1.0
E. Charitidou *et al.* (Ref. 3)	THW	298–336	11	± 1.0
J. K. Horrocks *et al.* (Ref. 11)	THW	295–346	5	± 1.5

[a] THW—transient hot wire technique.

The reasons for the assigned accuracies in Table 1 are as follows:

(i) Measurements presented by Ramires *et al.*[5] and Charitidou *et al.*[3] were obtained with the most recent versions of automatic computer controlled bridges, and using liquids well purified and degassed.

Although both works claim an accuracy of 0.5%, a systematic deviation of 0.7% was found between the two sets of data. Therefore, they were both assigned an accuracy of 1%.

(ii) The data presented by Li *et al.*[10] were obtained from extrapolation of high-density data along an isotherm to saturation density. Due to this fact the extrapolated data have been assigned with an accuracy of 1%.

(iii) The data reported by Horrocks *et al.*,[11] were obtained with an old version of the transient hot wire instrument, using a single wire with potential leads to monitor the temperature change in the hot wire. It is less precise than the more recent versions of the transient wire technique. Therefore, they were assigned the accuracy of 1.5%.

4. Correlations Procedures and Results

4.1. Equation Form

The temperature dependence of the thermal conductivity has been represented by a linear function

$$\lambda = b_0 + b_1 T, \qquad (1)$$

where λ is the thermal conductivity and T the absolute temperature.

The data have been fitted to this equation, using the method of least squares with weighting factors reflecting the accuracy of the data given in Table 1. The assumptions made in Ref. 1 to assign relative weights to the different data sets are adopted here.

4.2 Correlation

In order to establish recommended standard reference data we use a correlation to take account of differences between the various sets of primary data. This correlation relates the thermal conductivity as a function of temperature.

From this correlation we recommend for the thermal conductivity of benzene at 298.15 K and 0.1 MPa the value:

$$\lambda(298.15\ \mathrm{K}) = 0.1411 \pm 0.0011\ \mathrm{W\,m^{-1}\,K^{-1}},$$

where the uncertainty is given at a 95% confidence level (2 standard deviations).

Using the convention of the IAPS formulation for the transport properties of water substance,[8,9] we have expressed the correlation in terms of dimensionless variables λ^* and T^*, defined as:

$$T^* = T/298.15 \tag{2}$$

and

$$\lambda^*(T^*) = \lambda(T)/\lambda\ (298.15), \tag{3}$$

where λ (298.15) is the adopted standard value for the thermal conductivity of benzene at 298.15 K and 0.1 MPa, given above.

The correlation obtained is given, in reduced form, in Eq. (4) covering the range 295 K$\leqslant T \leqslant$350 K.

$$\lambda^* = 1.69572 - 0.695716\ T^*, \quad 295\ \text{K} \leqslant T \leqslant 350\ \text{K}. \tag{4}$$

The maximum deviation of the primary experimental data from Eq. (4) is 1.4% with a standard deviation of 0.00061 W/(m K).

This correlation reproduces all primary data sets within their assigned uncertainty.

The deviations of the primary data from the correlation represented by Eq. (4) are plotted in Fig. 1.

4.3. Tabulations

Table 2 gives recommended values for thermal conductivity of benzene, along the saturation line.

The recommended values are given to four significant figures but it should be emphasized that the uncertainties in the tabulated data must be based in the analysis presented in Sec. 4.2 and we estimate the accuracy of these recommended values to be 1%.

TABLE 2. Recommended thermal conductivity for benzene.

T K	λ W/(mK)
290.00	0.1438
300.00	0.1405
310.00	0.1372
320.00	0.1339
330.00	0.1306
340.00	0.1273
350.00	0.1240

4.4. Comparison of Correlation with the Seconda Data

As already stated in a previous publication,[1] the cor lation outlined in preceding section should, ideally, repr duce all the secondary data, if the latter are assigned a real tic experimental uncertainty. This, however, would be a ve difficult and tedious task and would not serve any importa purpose. We therefore content ourselves with a plot of t deviation of these secondary data from the correlation. T deviation plot is shown in Fig. 2 and includes only the da for which the deviations are less than ± 5%, although son of the data excluded by this condition depart from the repr sentation by as much as 15%.

A compilation of literature data sources for which v were able to obtain copies is given in the Appendix.

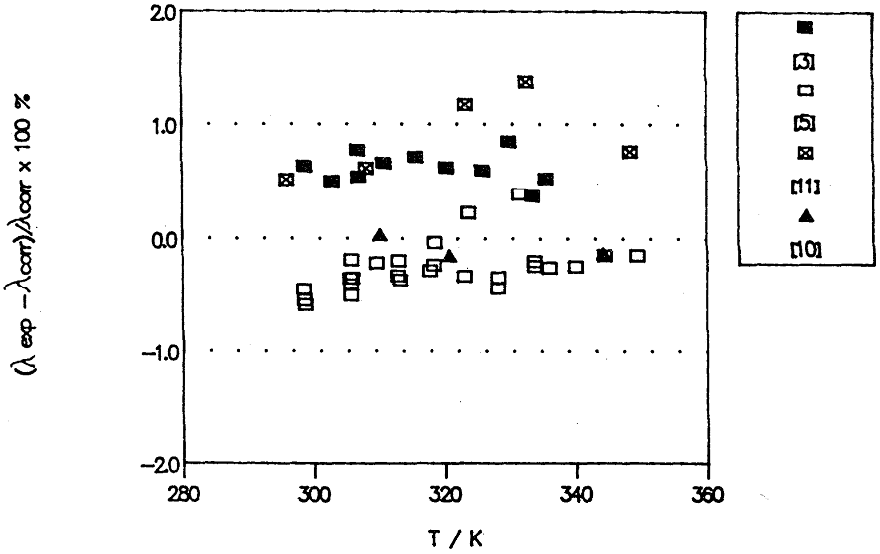

FIG. 1. The deviations of the primary data for the thermal conductivity of Benzene from the correlation of Eq. (4).

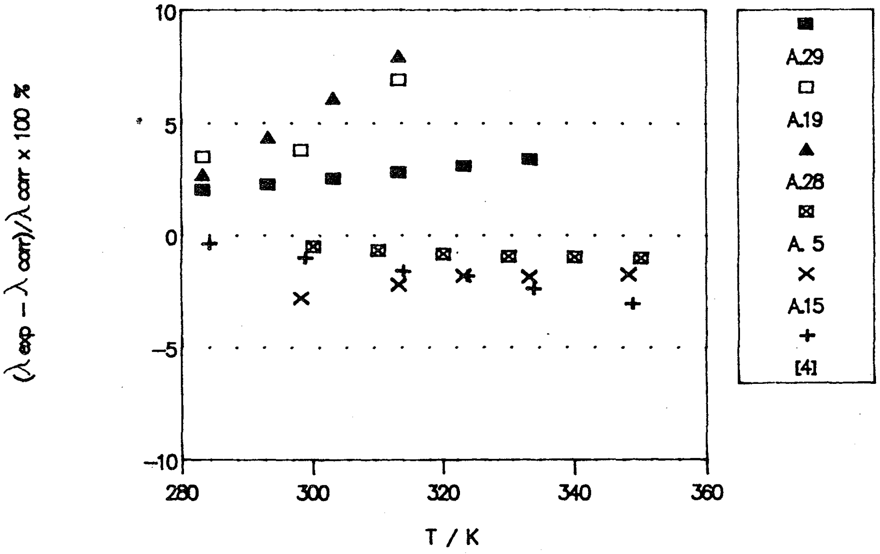

FIG. 2. The deviations of the secondary data for the thermal conductivity of Benzene from the correlation of Eq. (4).

4.5. Cautions for Use of the Tabulated Recommended Thermal Conductivities

As mentioned earlier, recommended standard values e two purposes: (i) they act as the test of the accuracy of absolute instruments, and (ii) they are means of cali- ing instruments for which the full working equation is available. It is for the latter use that caution must be l, as the use of benzene alone for the calibration of such ruments may lead to erroneous results for other systems, re the radiation contributions to the measured thermal ductivity will be different. Thus it is stressed that any tive instrument should be calibrated with at least two ls with very different thermal conductivities and radi- n properties. It is emphasized that the tabulated values ulated from Eq. (4) are radiation free, i.e., true thermal ductivities.

5. Conclusions

Standard reference data for thermal conductivity are posed for the system benzene, over the normal liquid ge along the saturation line. These recommendations are ed on the most accurate available literature data up to including 1988, and as such are considered to be of high- ccuracy than any correlations presently available in the ature.

However, in view of recent improvements in both the ory and experimental techniques, further experimental k should allow even more accurate correlation to be de- nined for the system studied here. Thus it is envisaged t the recommendations for Standard Reference Data will periodically updated as new experimental data become ilable.

6. Acknowledgments

The work described in this paper has been carried out under the auspices of the Sub-Committee on Transport Properties of Commission I.2 of the International Union of Pure and Applied Chemistry. The authors are grateful to the members of the subcommittee for their valuable advice. The authors are also indebted to Prof. A. Nagashima for enlightening discussions and comments in earlier stages of this work. Partial financial support for the work was provided by NATO Grant Research No. 85/0311.

7. References

[1] C. A. Nieto de Castro, S. F. Y. Li, A. Nagashima, R. D. Trengove, and W. A. Wakeham, J. Phys. Chem. Ref. Data **15**, 3 (1986).

[2] *Recommended Reference Materials for the Realization of Physico-Chemical Properties*, edited by K. N. March (Blackwells Scientific, London, 1986).

[3] E. Charitidou, Ch. Molidou, and M. J. Assael, Int. J. Thermophysics **9**, 37 (1988).

[4] Y. Tanaka, T. Hase, H. Kubota, and T. Makita, Ber. Bunsenges. Phys. Chem. **92**, 770–776 (1988).

[5] M. L. V. Ramires, F. J. Vieira dos Santos, U. V. Mardolcar and C. A. Nieto de Castro, Int. J. Thermophysics **10**, 1005 (1989).

[6] *Measurements of Transport Properties of Fluids*, edited by A. Nagashima, J. V. Sengers, W. A. Wakeham (Blackwells, London, 1989) (in preparation).

[7] C. A. Nieto de Castro, JSME Int. J., Series II, **31**, 387 (1988).

[8] J. V. Sengers, J. T. R. Watson, R. S. Basu, and B. Kamgar-Parsi, J. Chem. Ref. Data **13**, 893 (1984).

[9] J. Kestin, J. V. Sengers, B. Kamgar-Parsi, and J. M. H. Levelt Sengers, J. Phys. Chem. Ref. Data **13**, 175 (1984).

[10] S. F. Y. Li, G. C. Maitland, and W. A. Wakeham, Int. J. Thermophysics **5**, 351 (1984).

[11] J. K. Horrocks and E. McLaughlin, Proc. Roy. Soc. Ser. A., **273**, 259 (1963).

Appendix. Results of the Literature Survey of the Thermal Conductivity of Benzene

This is a summary of all the thermal conductivity data sources, for benzene, of which it was possible to obtain copies. The temperature and pressure range covered together with the estimation of the experimental accuracy of the experimentalists is given whenever possible and if any information is missing it is because it was not reported.

A.1. Abas-Zade, A. K., Dokl. Akad. Nauk. SSSR, 68(4), 665–668 (1949). Paper in Russian, no statement of uncertainty. Benzene: 283–461 K; 0.1–4.8 MPa.

A.2. Atalla, S. R., El-Sharkawy, A. A., Gasser, F. A., Int. J. Thermophys., 2(2), 155 (1981). Apparatus for multiproperty measurement, thermal conductivity, thermal diffusivity, thermal activity, and heat capacity. Benzene: 293 K; 2.2%.

A.3. Briggs, D. K. H., Ind. Eng. Chem., 49(3), 418 (1957). Concentric cylinder apparatus. Benzene: 293–333 K; <3%.

A.4. El'darov, F. G., Zh. fiz. Khim., 32 (10), 2443–2447, (1958). Paper in Russian. Calibrated instrument. Benzene: 298 K.

A.5. Fischer, S., Obermeier, E., High Temp—High Press., **17**, 699–705 (1985); rotating concentric cylinders .25%.

A.6. Frontasev, V. P., Zh. fiz. Khim., 20(1), 91 (1946). Paper in Russian. Benzene: 293 K.

A.7. Frontasev, V. P., Zav. Lab., 22(7), 812 (1956). Yofle's optical method. Paper in Russian. Benzene: 293 K.

A.8. Frontasev, V. P. and Gusakov, M. Y., Zh. Tekhn. Fiz., 29(10), 1277 (1959).Yofle's optical method. Paper in Russian. Benzene: 293 K.

A.9. Goldschmidt, R., Phys. Z., 12(11), 417 (1911). Hot wire apparatus. Benzene: 288–307 K.

A.10. Hase, T., Kashiwagi, H., Tanaka, Y., Kubota, H., and Makita, T., Fourth Japn, Symp. Thermophys. Prop. (1983), p. 183. Transient hot wire apparatus. Abstract in English, paper in Japanese. Graphical representation of experimental data only. Benzene: 283–373 K; 0.1–250 MPa; 1.0%.

A.11. Hashimoto, T., Oishi, M., Tanaka, Y., Kubota, H., and Makita, T., 1st Japan Symp. Thermophys. Prop. (1980) p. 75. Relative transient hot-wire apparatus. Abstract in English, paper in Japanese. Graphical and least squares representation of data only. Benzene: 303–348 K; 0.1 MPa; 2.0%.

A.12. Horrocks, J. K. and McLaughlin, E., Proc. Roy. Soc. A 273, 259, (1963). Transient hot-wire apparatus. Benzene: 295–346 K; 1.5%.

A.13. Horrocks, J. K., McLaughlin, E., and Ubbelohde, A. R., Trans. Faraday Soc., 59, 1110–1113 (1963). Transient hot-wire apparatus. Benzene: 295–348 K; 0.05 MPa at ambient temp.

A.14. Jamieson, D. T. and Tudhope, J. S., NEL Report No. *81 (1963). Steady-state hot wire apparatus. Benze* 298 K.

A.15. Kashiwagi, H., Oishi, M., Tanaka, Y., Kubota, and Makita, T., Int. J. Thermophys. 3(2), (198 Relative transient hot wire; instrument calibra with toluene data. Benzene: 303–348 K; 0.1 M 2.0%.

A.16. Le Neindre, B. and Tufeu, R., Techn. Ing. **10**, R29 (1979). Review with recommended values. Benze 283–353 K; 1.0%.

A.17. Li, S. F. Y., Maitland, G. C., and Wakeham, W. Int. J. Thermophys., 5(4), (1984). Transient h wire apparatus. Data needs to be extrapolated to MPa. Benzene: 310–360 K.

A.18. McLaughlin, E., Chem. Rev., 64, 389–428, (196 Review article with recommended values. Benze 283–363 K.

A.19. Nashima, T. and Yoshida, K., 1st Japn. Symp. Th mophys. Prop., (1980), p. 63. Steady-state hot-w apparatus: single wire apparatus treated as coax cylinder apparatus. Benzene: 283–313 K; 0.1 MPa

A.20. Poltz, H., 7th Thermal Cond. Conf. NBS (1967) p. Parallel-plate apparatus. Paper in German. Benze 298 K.

A.21. Poltz, H. and Jugel, R., Int. J. Heat and Mass Tra fer, 10, 1075–1088, (1967). Parallel-plate apparat *Benzene: 282–313 K; 0.5%.*

A.22. Potienko, N. F. and Tsymarnyi, V. A., Inzh.-Fiz. Z 20(4), 733 (1971). Non-steady-state method. A stract of deposited paper—in Russian. Benzene: 42 473 K; 0–49 MPa.

A.23. Riedel, L., Chem. Ingr. Techn. 23(13), 321 (195 Parallel-plate, concentric cylinder and concent sphere apparatus. Deviation between the three diff ent instruments <0.5%. Benzene: 293–323 K; 1.0

A.24. Scheffy, W. J. and Johnson, E. F., J. Chem. Eng. Da 6(2), 245 (1961). Concentric cylinder apparatus wi three concentric annular spaces. Benzene: 341–491

A.25. Schmidt, E. and Leidenfrost, W., Chem. Ingr. Tech 26(1), 35 (1954). Parallel-plate apparatus. Graphi representation only of experimental results. Benze 292–343 K.

A.26. Spirin, G. G., Inzh.-Fiz. Zh., 38(4), 656 (198 Transient hot-wire apparatus. Paper in Russian. Be zene: 293–393 K; 1.5%.

A.27. Stupak, P. M., Aizen, A. M., and Yapol'skii, N. Inzh.-Fiz. Zh., 19(1), 74–78 (1970). Concentric c inder apparatus. Paper in Russian. Benzene: 299–3 K.

A.28. Takizawa, S., Murata, H., and Nagashima, A., Bu JSME., 21(152), 273 (1978). Transient hot-wire a paratus. Benzene: 283–323 K; 0.1 MPa; 1.5%.

A.29. Tufeu, R., Le Neindre, B., and Johannin, P., C. Acad. Sc. Paris, 262, 229 (1966). Concentric cylind apparatus. Benzene: 278–353 K. 1%.