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COMMISSION ON PHYSICOCHEMICAL MEASUREMENTS
AND STANDARDS*

RECOMMENDED REFERENCE MATERIALS FOR REALIZATION OF PHYSICOCHEMICAL PROPERTIES

(Recommendations 1977)

EDITOR: K. N. MARSH

SECTION: THERMAL CONDUCTIVITY OF FLUID SUBSTANCES

COLLATOR: H. ZIEBLAND

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INTRODUCTION

The symbol for thermal conductivity recommended by the IUPAC is λ (or sometimes k) (Ref. 1). In SI units thermal conductivity is expressed as watt per meter per kelvin ($\text{W m}^{-1} \text{K}^{-1}$) and it is defined as the time rate of transfer of energy by conduction through unit thickness across unit area for unit difference in temperature.

In the experimental determination of the thermal conductivity of fluids, conditions are required under which the energy transferred by molecular interaction can be determined. The effects of other coexistent energy transport processes such as thermal radiation through the fluid layer or, in the case of partially absorbing substances, within the fluid itself, must be known and accounted for.

Likewise natural convection, which is caused by the bulk movement of the fluid enclosed within the conductivity cell, must be minimized by choosing appropriate operating conditions. With the correct conditions, which involves relatively small temperature differences and simple geometric configurations of the solid surfaces surrounding the fluid layer, simple solutions of the Laplace equation exist which allow the absolute determination of the thermal conductivity from the measurement of the energy flow through the fluid film, the temperature difference between the bounding walls, and the linear dimensions of the apparatus.

Reliable absolute measurements of thermal conductivity require a carefully constructed apparatus and the precise and accurate measurement of the various quantities given above. Further, equally precise determinations, or proof of their absence, of possible secondary energy transfers are also necessary. In many cases it is difficult to justify the time consuming procedures required for an absolute determination when making routine or occasional measurements.

The thermal conductivity of a fluid may be obtained with a relatively simple apparatus by comparing the observed measurement with that obtained with a reference material. The linear dimensions of a cell can be compounded into a single term called the 'geometric cell constant' but when calibrating the conductivity cell with materials of known thermal conductivity, this 'geometric cell constant' is combined with the effects of energy losses or gains into another constant called the 'cell constant'. It is desirable that the chosen reference material should have a thermal conductivity similar to that of the substance to be examined, and that the rate of energy dissipation be about the same during both the calibration and the actual experiment.

The precision attainable with relative measurements is often quite adequate for technical requirements, but successful application of the relative measurement technique is frequently impeded by the lack of suitable reference materials. Further, even for absolute determinations, the occasional need arises to test some specific property of the apparatus, to check the experimental procedure employed, or to check the proper performance of the entire measuring system under the operating conditions. This can most readily be done using critically selected reference materials. It is the purpose of this report to examine a number of substances which have been proposed as reference materials for the calibration and the testing of cells to be used for the measurement of thermal conductivity and to present for these substances a set of results which have been critically evaluated.

Requirements in choosing a reference material which are specific to thermal conductivity measurements: Transfer of energy by radiation and convection are the two main sources of error associated with the measurement of the thermal conductivity of fluids. Energy transfer by radiation depends on the molecular properties of the test fluid and on those of the confining solid surfaces and thus will always be present to some degree in the measurement of thermal conductivity. Convective energy transfer is a hydrodynamic phenomenon and it occurs when there is a bulk movement of fluid due to density gradients in and around the conductivity cell.

The accurate calculation of the radiant energy flux requires a detailed knowledge of the properties of the surface and the properties of the fluid under test. The three distinguishable cases are: (1) the test fluid is completely opaque to infrared radiation, (2) the test fluid is completely transparent to infrared radiation, or (3) the test fluid possesses selective absorption bands in the infrared. There is no problem in the first case and simple solutions exist for the second case. For the third case, however, the correct solution for simultaneous conductive and radiative transport leads to complex non-linear integro-differential equations which require the knowledge of the absorption spectrum of the fluid concerned. Given an option one would tend to select as reference materials fluids which are either transparent or opaque to infrared radiation.

True values of the thermal conductivity of fluid substances can be obtained only if the energy transferred by convection is sufficiently small or are accounted for. Because a density difference is always set up in the fluid by the difference in temperature between the hot wall and the cold wall, the bulk transfer of energy that occurs by fluid motion may become large enough to influence the observations. This phenomenon has been extensively studied (Ref. 3) and it has been shown that in a cylindrical annuli such as a hot wire cell or a coaxial cylinder cell, convection becomes significant when a critical value of the product of the Grashof number (Gr) and the Prandtl number (Pr) is exceeded, i.e. when

$$(Gr \cdot Pr)_{crit} = g_n l^3 \alpha \rho^2 (\Delta T) c_p / \eta \lambda > 800$$

where g_n is the acceleration of free fall, l is a characteristic linear dimension of the conductivity cell which is the thickness of the fluid layer traversed by the measured energy flow, α is the cubic expansion coefficient $V^{-1}(\partial V/\partial T)_p$, ΔT is the temperature difference between the bounding solid walls, ρ is the density, η is the viscosity, λ is the thermal conductivity, and c_p is the specific heat capacity of the fluid at constant pressure.

Alternatively, the effect of the transport of energy by convection, if it is laminar, can be avoided in a vertical coaxial cell where the energy is supplied by a guard electrode situated below the metering section and the energy is released into the region above the metering section. It should be noted that the appropriate choice of the Grashof-Prandtl product depends on the sensitivity of the apparatus and the acceptable uncertainty in the final result. The terms in the Grashof-Prandtl product can be separated into those which are physical constants or characteristic dimensions of the system and those which are typical fluid properties so that

$$Gr \cdot Pr = [\alpha \rho^2 c_p / \eta \lambda] \times [g_n l^3 \Delta T].$$

The magnitude of the first term is a useful criterion for assessing different fluids with respect to their relative sensitivity towards the onset of natural convection in narrow fluid filled gaps. Table 1 contains values of the first term for some selected fluids. A low value indicates a lesser tendency towards the onset of convective fluid motion.

TABLE 1. Properties of various fluids at 300 K and atmospheric pressure

Substance	$(\alpha\rho^2c_p/\lambda\eta)\times 10^{-8}/s^2\ m^{-4}\ K^{-1}$	$\lambda/W\ m^{-1}\ K^{-1}$
Argon	0.16	0.01787
Nitrogen	0.14	0.0259
Neon	0.021	0.0493
Helium	0.0021	0.151
Water	13	0.613
Toluene	190	0.147

It will be noticed that the gases, largely on account of their low density, are distinctly less susceptible to significant levels of energy transfer by convective fluid motion. On the other hand, toluene, because of the large value of the first term, is very prone to energy transfer by convective fluid motion, hence it is not suitable as a reference material. By using either helium or neon as the calibrating fluid as opposed to toluene, the requirements are less stringent on either the geometry of the cell (the gap width) or the operating conditions (large temperature differences are permissible). However, when using a cell which has been calibrated with either helium or neon to measure the thermal conductivity of organic compounds care must still be taken to ensure that the transfer of energy by convective fluid motion is sufficiently small.

Fluids can be divided with respect to their thermal conductivity into three broad groups: (1) Gaseous substances (excluding hydrogen and helium) which have thermal conductivities ranging from 0.018 to 0.05 $W\ m^{-1}\ K^{-1}$, (2) Organic liquids and their mixtures have thermal conductivities in the range 0.05 to 0.15 $W\ m^{-1}\ K^{-1}$, and (3) Water, aqueous solutions and ammonia which have thermal conductivities in the range 0.3 to 0.7 $W\ m^{-1}\ K^{-1}$. Table 1 includes values of the thermal conductivities of some substances at 300 K and atmospheric pressure. Throughout this document the term 'atmospheric pressure' is used to indicate that the data refer to a sample at a nominal pressure of 10^5 Pa.

In the gaseous phase argon, nitrogen, and neon are recommended as reference materials. Their respective thermal conductivities at 300 K and atmospheric pressure range from 0.017 to 0.049 $W\ m^{-1}\ K^{-1}$. All so-called permanent gases and vapours of organic materials lie within this range. For the middle range, which embraces most liquid organic substances whose thermal conductivities range between 0.05 and 0.15 $W\ m^{-1}\ K^{-1}$ either gaseous neon or helium are recommended as reference materials. Also dimethylphthalate is recommended as a reference material for the calibration of cells to be used with liquids in this range. For liquids which possess still higher thermal conductivities, such as liquid ammonia and aqueous solutions, liquid water is recommended as the reference material.

The choice of the four reference gases can be justified on the following grounds: (1) they are free from absorption bands in the infrared, thus no corrections for partial absorption or re-emission in the fluid layer are necessary. The direct radiative transfer of energy between two bounding surfaces can be calculated from the emissivities of the wall materials and the geometry of the cell. (2) They are chemically inert, they have very low boiling temperatures, and a number of measurements and evaluations have been published. (3) Gases, because of their low densities, are much less susceptible to the transfer of energy by convective motion in the fluid layer, thus there is a greater freedom in the choice of experimental conditions. (4) The gases recommended are commercially available at very high purity (better than 99.999 mole per cent), their cost is moderate, and they have an unlimited storage life. For fluids with a high thermal conductivity there is no alternative to water as a reference material. It is much less susceptible to convection than most organic liquids and further it possesses very strong absorption bands in the infrared, a situation which at least in thick fluid layers (i.e. about 0.5 mm) completely obviates the need to correct experimental results for radiative energy transfer between the bounding walls.

Dimethylphthalate is also recommended as a reference material. It possesses strong absorption bands in the infrared and thus minimal corrections are required for radiative energy transfer. The recommended values for dimethylphthalate result from a joint programme between the Physikalisch-Technische Bundesanstalt, West Germany and the Thermo-Physical Property Laboratory of the Propellants, Explosives, and Rocket Motor Establishment, United Kingdom.

The use of gases as reference materials requires certain precautions which, if ignored, can lead to substantial errors. If the molecular mean free path of the gas approaches the thickness of the gas layer in the conductivity gap, a noticeable temperature discontinuity will occur at the bounding surfaces of the cell which results from the imperfect energy exchange between the impinging molecules and those of the wall material. Mathematically, this phenomenon is accounted for by assuming that the temperature difference is that of the bounding solid surfaces and that the energy is transferred through a uniform temperature gradient. This is possible only by adding to the distance of the conductivity gap fictional extensions known as the 'temperature jump distances'. For a gas at low density the energy transferred q over an area A between two infinite parallel plates separated by a distance d is

$$q = A\lambda\Delta T/(d + g_1 + g_2),$$

where g_1 and g_2 are the temperature jump distances associated with the particular gas and surfaces 1 and 2. The temperature jump distance depends on the thermal accommodation coefficient and is related to the mean free path L by

$$g = (2 - \alpha)4C\lambda L/[a(\gamma + 1)\eta c_v]$$

where α is the thermal accommodation coefficient, γ is the ratio of the heat capacity at constant pressure to that at constant volume, η is the viscosity, c_v is the specific heat capacity at constant volume, and C is a constant having a value of 0.49. For helium at 10^5 Pa and 293 K, $\lambda/\eta c_v = 2.5$ and $L = 1.7 \times 10^{-7}$ m so that for an accommodation coefficient $\alpha = 0.37$ then $g \sim 8L$. Assuming the two walls to be of similar material the relative increase in length $2g/d$ becomes $16L/d$ which for a gap width of 0.2 mm leads to an increase in length due to the inclusion of a temperature jump distance of $(16 \times 1.7 \times 10^{-7})/(2 \times 10^{-4}) = 1.4$ per cent (Ref. 3). This same equation is approximately correct for a coaxial cylinder cell. The effect of the temperature jump can be calculated and approximately corrected for, or avoided by working in an adequate pressure range or using an adequate gap between the plates. The mean free paths of various gases at 293 K and atmospheric pressure are given in Table 2.

TABLE 2. Mean free path of various gases at 293 K and atmospheric pressure

Substance	Mean free path $\times 10^7/m$
Argon	0.62
Nitrogen	0.59
Neon	1.24
Helium	1.75

Detailed information as to the corrections which should be applied have been given for coaxial cells (Ref. 4) and for hot wire cells (Ref. 5). There is a further aspect which should be considered when using either helium or neon as a reference material. Because of the large difference between the thermal conductivity of either of these two gases and that of the most likely contaminant in the cell, atmospheric air, careful cleaning of the cell and the prevention of ingress of air during the measurement is imperative. Repeated flushing and evacuation followed by filling the cell with the reference material at a pressure above atmospheric should adequately deal with this practical problem. Where possible, flushing and evacuation should be carried out at an elevated temperature in order to displace any contaminating gas layer adsorbed on the surface of the cell.

The thermal conductivities of gases and liquids are given at a nominal pressure of 10^5 Pa. The thermal conductivity of gases vary from between 0.02 and 0.04 per cent for a pressure change of 10^5 Pa so that normal changes in the atmospheric pressure will be immaterial when using gases as a reference material. The thermal conductivities of liquids have about the same pressure dependence.

The following provisos apply to information on reference materials: (a) the recommended materials have not been checked independently by the IUPAC, (b) the quality of the material may change with time, (c) the quoted sources of supply may not be the exclusive sources because no attempt has been made to seek out all possible alternative sources and (d) the IUPAC does not guarantee any material that has been recommended.

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REFERENCE MATERIALS FOR THE MEASUREMENT OF THERMAL CONDUCTIVITY

1.

Physical property: Thermal Conductivity, λ

Unit: $\text{W m}^{-1} \text{K}^{-1}$

Recommended reference material: Argon, (Ar)

Range of variables: 80 to 2000 K, 10^5 Pa

Physical state within the range: gas

Class: Calibration and Test Material

Contributor: H. Ziebland

Intended usage: Argon can be used for the calibration of thermal conductivity cells of arbitrary geometry and/or for the testing of the proper functioning of the apparatus and its ancillary equipment within the temperature range 80 to 2000 K.

Sources of supply and/or methods of preparation: Argon of high purity is commercially available from many firms supplying industrial gases. The research grade argon supplied by supplier (A) has a guaranteed purity of 99.9997 mole per cent. High purity material is also available from suppliers (B), (E), (F), and (G).

Pertinent physicochemical data: Experimental values of the thermal conductivity of gaseous argon exist between 90 and 1373 K. The more recent and probably more accurate experimental results are in reasonable accord. The values recommended by Powell *et al.* (Ref. 1) were obtained by drawing a smooth curve through the results derived from all sources. Their uncertainty was estimated to be 1 per cent between 100 and 500 K and five per cent below 100 K and between 500 and 1500 K. Vargaftik and Filippov (Ref. 2) has derived an interpolation formula for the prediction of the thermal conductivity between 200 and 2000 K. For the less well explored temperature range between 90 and 200 K their recommended values were obtained by graphical interpolation. The estimated uncertainty of their values are: 2.5 per cent between 90 and 200 K, 1.5 per cent between 200 and 600 K, 2 per cent between 600 and 1400 K, and 3 to 4 per cent between 1400 and 2000 K.

More recently Hanley (Ref. 3) critically evaluated the measurements on the thermal conductivity and viscosity of argon and other rare gases. His tables were based on the more recent experimental results for the viscosity of these gases and values were generated using the kinetic gas theory in conjunction with the experimental results for all the transport properties. This approach leads to a rational representation of the thermal conductivity of any given monatomic gas and enables one to verify that such values are consistent with those of the other transport properties.

The values recommended by Vargaftik and Filippov (Ref. 2) were presumably based on a least square analysis of experimental results leading to a fourth order polynomial in the absolute temperature for the thermal conductivity. It is gratifying to note that the more sophisticated approach used by Hanley more or less confirms the values given by Vargaftik and Filippov. Between 200 and 1300 K the disagreement between the two sets is less than 1 per cent. Above 1300 K the values calculated by Hanley increase somewhat more steeply with temperature and at 2000 K the difference is approaching 3 per cent. There are insufficient experimental results above 2000 K so the recommendations are only made up to that temperature. For reasons of better internal consistency the critically evaluated results derived by Hanley (Ref. 3) have been used in compiling the recommended values. The estimated uncertainties of the values are: 2.5 per cent between 90 and 200 K, 1.5 per cent between 200 and 600 K, per cent between 600 and 1400 K, and 4 per cent between 1400 and 2000 K.

Recommended values for the Thermal Conductivity of Argon between 80 and 2000 K:

T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$
80	0.00517	650	0.03243
100	0.00638	700	0.03417
120	0.00763	750	0.03585
140	0.00886	800	0.03748
160	0.01008	850	0.03906
180	0.01129	900	0.04061
200	0.01246	950	0.04212
220	0.01360	1000	0.04359
240	0.01472	1050	0.04504
260	0.01580	1100	0.04645
280	0.01685	1150	0.04784
300	0.01787	1200	0.04921
320	0.01887	1250	0.05055
340	0.01983	1300	0.05187
360	0.02078	1350	0.05317
380	0.02170	1400	0.05444
400	0.02260	1450	0.05571
420	0.02348	1500	0.05696
440	0.02434	1550	0.05818
460	0.02517	1600	0.05940
480	0.02600	1650	0.06060
500	0.02680	1700	0.06178
520	0.02760	1750	0.06296
540	0.02837	1800	0.06412
560	0.02914	1850	0.06526
580	0.02989	1900	0.06640
600	0.03063	2000	0.06864

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2.

Physical property: Thermal Conductivity, λ
 Unit: $W m^{-1} K^{-1}$
 Recommended reference material: Nitrogen (N_2)
 Range of variables: 80 to 1400 K, 10^5 Pa
 Physical state within the range: gas
 Class: Calibration and Test Material
 Contributor: H. Ziebland

Intended usage: Nitrogen can be used for the calibration of thermal conductivity cells of any geometry and/or for the testing of the proper functioning of the apparatus and its ancillary equipment within the temperature range 80 to 1400 K.

Sources of supply and/or methods of preparation: Nitrogen of high purity is commercially available from many firms supplying industrial gases. The research grade nitrogen supplied by supplier (A) has a guaranteed purity of 99.9992 mole per cent. High purity material is also available from suppliers (B), (E), (F), and (G).

Pertinent physicochemical data: Since 1966 there have been three extensive data compilations published on the thermal conductivity of gaseous nitrogen at atmospheric pressure (Refs. 1-3). The smoothed values obtained by graphical or numerical smoothing of experimental results agree to better than 2 per cent between 80 and 800 K (Refs. 1,2). The values recommended by Powell *et al.* (Ref. 1) however, are consistently lower than those recommended by Vargaftik and Filippov (Ref. 2). This is probably due to the fact that, in order to take into account the increasing discrepancy between theory and experiment, Powell *et al.* selected values to lie midway between the experimental and the theoretical values, whereas Vargaftik and Filippov obtained values from an analysis of the experimental results only.

The tables due to Hanley and Ely (Ref. 3) were calculated from the kinetic theory using the $m - 6 - 8$ model potential with non-spherical contributions. Between 80 and 800 K the values agree adequately with the previous values (Refs. 1,2). At temperature higher than 800 K the values recommended by Hanley and Ely are consistently higher than those recommended by Powell *et al.* and Vargaftik and Filippov. To assist in arriving at a comprehensive recommendation, the most recent experimental results reported by Faubert and Springer (Ref. 4) were also taken into consideration. Within the range 800 to 1400 K the results of Faubert and Springer agree with those of Vargaftik and Filippov. Although the results reported by Faubert and Springer extend to nearly 2000 K it was thought advisable to restrict the recommended values to a temperature not exceeding 1400 K until further corroborative experimental evidence becomes available.

In view of the above, the values given by Vargaftik and Filippov form the basis for the recommendations given here. For the temperature dependence of the thermal conductivity of nitrogen between 200 and 1200 K the following polynomial equation was derived from a least square analysis of the known experimental results.

$$\lambda/W m^{-1} K^{-1} = 0.825 \times 10^{-3} + 0.959 \times 10^{-4} T/K - 0.428 \times 10^{-7} (T/K)^2 \\ + 0.250 \times 10^{-11} (T/K)^3 + 0.915 \times 10^{-14} (T/K)^4.$$

Between 80 and 100 K and 1200 and 1400 K graphical smoothing was employed. According to the authors (Ref. 2) the estimated uncertainty in the recommended values is 2.5 per cent between 80 and 300 K, 1.5 per cent between 300 and 800 K, and 2.5 per cent between 800 and 1400 K.

Recommended values for the Thermal Conductivity of Nitrogen Between 80 and 1400 K:

T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$
80	0.00782	360	0.0301	680	0.0488
100	0.00958	380	0.0314	720	0.0509
120	0.0113	400	0.0327	760	0.0529
140	0.0130	420	0.0340	800	0.0548
160	0.0148	440	0.0353	840	0.0568
180	0.0166	460	0.0365	880	0.0588
200	0.0183	480	0.0377	920	0.0607
220	0.0200	500	0.0389	960	0.0627
240	0.0214	520	0.0401	1000	0.0647
260	0.0229	540	0.0412	1100	0.0700
280	0.0244	560	0.0424	1200	0.0758
300	0.0259	580	0.0435	1300	0.0810
320	0.0273	600	0.0446	1400	0.0874
340	0.0287	640	0.0467		

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3.

Physical property: Thermal Conductivity, λ Unit: $W \text{ m}^{-1} \text{ K}^{-1}$

Recommended reference material: Neon (Ne)

Range of variables: 273 to 1100 K, 10^5 Pa

Physical state within the range: gas

Class: Calibration and Test material

Contributor: H. Ziebland

Intended usage: Neon can be used for the calibration of thermal conductivity cells of any geometry and/or for the testing of the proper functioning of the apparatus and its ancillary equipment within the temperature range 273 to 1100 K.

Sources of supply and/or methods of preparation: Neon of high purity is commercially available from many firms supplying industrial gases. The research grade neon from supplier (A) has a guaranteed purity of 99.999 mole per cent. High purity material is also available from suppliers (B), (E), (F), and (G).

Pertinent physicochemical data: Three critical tabulations of the thermal conductivity of neon at atmospheric pressure have been reported in the literature. Those by Vargaftik and Filippov (Ref. 1) and by Jody and Saxena (Ref. 2) were based on the evaluation of experimental results between 273 and 1100 K, and 320 and 3000 K, respectively, whereas the values given by Watson (Ref. 3) were derived from experimental values of viscosity using the rigorous kinetic theory expression for a monatomic gas,

$$\lambda = aF\eta/M$$

where λ is the thermal conductivity, η is the viscosity, M is the molar mass, a is a constant, and $F = f_{\lambda}^k(T^*)/f_{\eta}^k(T^*)$ is the ratio of the k -th order approximation terms to the thermal conductivity and the viscosity coefficients at reduced temperature T^* which is defined in terms of the parameters of the intermolecular potential.

An unpublished set of experimental values between 273 and 500 K (Ref. 4) has also been considered in arriving at the final recommendation. Between 273 and 500 K the agreement between the three sets of recommended values and the new experimental values is excellent. The average deviation of individual results from all four sources from their respective arithmetic average is less than 0.5 per cent. This is slightly less than the experimental uncertainty claimed by the various authors. In fact, the average values within the temperature range are almost identical with those calculated by Watson (Ref. 4) so it seems justified to consider these average values as the most probable ones and to assign them an uncertainty of 1 per cent.

Above 500 K the values recommended by Watson tend to rise more steeply with temperature than those recommended by either Jody and Saxena or Vargaftik and Filippov and at 1100 K the values given by Watson are almost 5 per cent above those recommended by Vargaftik and Filippov. The values of Jody and Saxena lie about midway between these two sets so the difference from the two sets at 1100 K is about 2.5 per cent. This is the uncertainty claimed by the respective authors. In view of the increasing uncertainty of the results at elevated temperatures the compilation of recommended values was terminated at 1100 K. The recommended values between 500 and 1100 K were computed from the correlation equation proposed by Jody and Saxena,

$$\lambda/W \text{ m}^{-1} \text{ K}^{-1} = 0.1446 + 0.1276 \times 10^{-2} T/K - 0.3610 \times 10^{-6} (T/K)^2 + 0.5593 \times 10^{-10} (T/K)^3,$$

with an estimated uncertainty of 2.5 per cent. There are insufficient measurements to confirm the values recommended by Vargaftik and Filippov between 90 and 273 K so no values in this temperature range are recommended.

Recommended values for Thermal Conductivity of Neon between 273 and 1100 K:

T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$
273	0.0463	650	0.0837
300	0.0493	700	0.0880
350	0.0547	750	0.0922
400	0.0600	800	0.0963
450	0.0651	900	0.1041
500	0.0699	1000	0.1116
550	0.0747	1100	0.1186
600	0.0792		

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4.

Physical property: Thermal Conductivity, λ

Unit: $\text{W m}^{-1} \text{K}^{-1}$

Recommended reference material: Helium (He)

Range of variables: 80 to 2000 K, 10^5 Pa

Physical state within the range: gas

Class: Calibration and Test Material

Contributor: H. Ziebland

Intended usage: Helium can be used for the calibration of thermal conductivity cells of arbitrary geometry and/or for the testing of the proper functioning of the apparatus and its ancillary equipment within the temperature range 80 to 2000 K.

Sources of supply and/or methods of preparation: Helium of high purity is commercially available from many firms supplying industrial gases. The research grade helium supplied by supplier (A) has a guaranteed purity of 99.9997 mole per cent. High purity material is also available from suppliers (B), (E), (F), and (G).

Pertinent physicochemical data: Measurements of the thermal conductivity of helium have been made between 80 and 2000 K with the majority of the measurements between 200 and 600 K. In this latter range there is relatively good agreement between the results of different workers. The agreement is somewhat less satisfactory at temperatures between 600 and 1200 K and even less so between 1200 and 2000 K where only three sets of measurements have been published.

Based on the experimental results available to them, Powell *et al.* (Ref. 1) and Vargaftik and Filippov (Ref. 2) have published tables of recommended values with estimated uncertainties. These recommended values were obtained by a selection and a numerical smoothing of the experimental values. In contrast the values given by Watson (Ref. 3) were derived from viscosity measurements using the rigorous kinetic theory expression for a monatomic gas (for details refer to the section on neon).

There is disagreement on uncertainties claimed by the various authors of the recommended values (Refs. 1-3). However on the basis of a critical analysis of the individual discrepancies the following observations can be made: Within the temperature range 80 to 600 K the values selected by Powell *et al.* and by Vargaftik and Filippov are in good agreement as they are based on the same experimental results. The two sets do not differ by more than 1.5 per cent whereas the results reported by Kannuluik and Carman (Ref. 4) are up to 4 per cent lower than those in references 1 and 2, the discrepancy becoming greater at higher temperatures. The yet unpublished results (Ziebland and Erwood (Ref. 5)) in the range 273 to 400 K are in substantial agreement with previous recommended values (Refs. 1,2), the difference being less than 1 per cent. However Guildner (Ref. 6) has suggested that most of the results at low pressures in the temperature range 273 to 450 K are low due to contamination of the helium by gases of lower thermal conductivity that are degassed from the walls of the apparatus. The values measured recently by Guildner (Ref. 6) and by the Physikalisch-Technische Bundesanstalt (Ref. 7) are higher than the values recommended in references 1 and 2 by up to 3 per cent between 300 and 400 K. Between 600 and 2000 K the values recommended by Powell *et al.* are considerably higher than those recommended by Vargaftik and Filippov and by Watson. It is noteworthy that the results based on the kinetic theory (Ref. 3) agree in the range 600 to 2000 K within about 1.5 per cent with the values given by Vargaftik and Filippov which represent smoothed experimental values of the thermal conductivity from many different sources. Likewise the more recently published experimental results of Jain and Saxena (Ref. 8) extending from 400 to 2300 K are in good agreement with the values given by both Vargaftik and Filippov (Ref. 2) and Watson (Ref. 3).

On the basis of these observations the values given by Vargaftik and Filippov have been chosen for the temperature range 80 to 600 K and, for reasons of internal consistency, values recommended by Watson (Ref. 3) have been chosen for all temperatures above 600 K. An examination of the value of $\Delta\lambda/\Delta T$ in the region around 600 K shows that no discontinuity arises by combining the two sets of results based on these different evaluations. The uncertainty of the data between 80 and 600 K has been estimated by Vargaftik and Filippov to be less than 2 per cent. However, because of the uncertainties arising from the possibility of degassing and uncertainties in the theory of the temperature jump, the estimated uncertainty has been set at 3 per cent between 80 and 1200 K and from 3 to 5 per cent from 1200 to 2000 K. There is clearly a need for more precise measurements on the thermal conductivity of helium in the temperature range from 80 to 450 K.

As the molecular mean free path increases with rising temperature, attention is drawn to the need for verifying the absence of temperature jump conditions.

Recommended values for the Thermal Conductivity of Helium between 80 and 2000 K:

T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$
80	0.0632	360	0.170	1000	0.360
100	0.0720	380	0.177	1100	0.385
120	0.0814	400	0.183	1200	0.410
140	0.0905	450	0.201	1300	0.434
160	0.0988	500	0.218	1400	0.457
180	0.107	550	0.234	1500	0.480
200	0.115	600	0.250	1600	0.502
220	0.124	650	0.266	1700	0.524
240	0.130	700	0.280	1800	0.546
260	0.138	750	0.294	1900	0.567
280	0.145	800	0.307	2000	0.587
300	0.151	850	0.321		
320	0.158	900	0.334		
340	0.164	950	0.347		

REFERENCES

1. R. W. Powell, C. Y. Ho, and P. E. Liley, *Thermal Conductivity of Selected Materials*, National Standard Reference Data Series, National Bureau of Standards 8, Washington D.C. (1966).
2. N. B. Vargaftik and L. P. Filippov, *Thermal Conductivity of Gases and Liquids (Data Book)*, Standards Press, Moscow (1970).
3. J. T. R. Watson, *Thermal Conductivity of Gases in Metric Units*, National Engineering Laboratory, Edinburgh, H.M. Stationary Office U.K. (1973).
4. W. G. Kannuliuk and E. H. Carman, *Proc. Phys. Soc. (London)* **65B**, 701 (1952).
5. H. Ziebland and Ch. Erwood, unpublished report of the National Physical Laboratory, Teddington, U.K.
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7. W. Ruhl, Physikalisch-Technische Bundesanstalt, West Germany (private communication) (1980).
8. P. C. Jain and S. C. Saxena, *Chem. Phys. Letters* **36**, 489 (1975).

5.

Physical property: Thermal Conductivity, λ

Unit: $\text{W m}^{-1} \text{K}^{-1}$

Recommended reference material: Water (H_2O)

Range of variables: 273 to 373 K, 10^5 Pa

Physical state within the range: liquid

Class: Calibration and Test Material

Contributor: H. Ziebland

Intended usage: Liquid water can be used for the calibration of thermal conductivity cells of any geometry and/or for the testing of the proper functioning of the apparatus and its ancillary equipment within the temperature range 273 to 373 K.

Sources of supply and/or methods of preparation: Distilled and degassed normal water is adequate.

Pertinent physicochemical data: The thermal conductivity of water has been extensively studied, there being approximately seventy publications giving experimental values. Powell *et al.* (Ref. 1) selected seven results which they considered the most reliable and obtained a correlation equation for the thermal conductivity of water between 273 and 373 K. It is claimed that this equation fits the selected experimental results with a standard deviation of less than 0.8 per cent. Recently Vargaftik and Filippov (Ref. 2) examined some 320 experimental results between 273 and 473 K and found that 92 per cent of all the values agreed to within 1 per cent and 98 per cent of all the values agreed to within 1.2 per cent with the equation proposed at the International Steam Tables Conference in 1963. The mean square deviation of these experimental values from that correlation equation is less than 1 per cent.

Between 295 and 373 K the agreement between the values calculated from the two equations (Refs. 1,2) is very good and lies well within the 1 per cent tolerance limit. However, in the range between 274 and 295 K values calculated from the equation given by Powell *et al.* are up to 1.5 per cent higher than those calculated from the equation used by Vargaftik and Filippov. This greater uncertainty (in this temperature range) is due to the lack of precision of the experimental values as exhibited by the deviation plot given by Vargaftik and Filippov.

Careful experiments by Fritz and Poltz (Ref. 3) have shown that, owing to the high infrared absorption of water, the effect of thermal radiation within the fluid layers investigated (0.5 to 2 mm) is negligible at 298 K and the observed thermal conductivity can be considered to be independent of the thickness of the fluid layer. According to Vargaftik and Filippov the correction is negligible up to 373 K and it may be assumed that the uncertainty due to the uncorrected thermal radiation transfer does not exceed 0.2 per cent.

The values in the table have been calculated from the equation proposed at the 1963 Steam Conference using the coefficients redetermined by Vargaftik and Filippov (Ref. 2). The uncertainty in the values is less than 1 per cent.

Recommended values for the Thermal Conductivity of Water between 273 and 373 K:

<i>T/K</i>	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	<i>T/K</i>	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$
273	0.569	330	0.650
280	0.583	340	0.659
290	0.599	350	0.667
300	0.613	360	0.673
310	0.626	370	0.678
320	0.638		

REFERENCES

1. R. W. Powell, C. Y. Ho, and P. E. Liley, *Thermal Conductivity of Selected Materials*, National Standard Reference Data Series, National Bureau of Standards 8, Washington D.C. (1966).
2. N. B. Vargaftik and L. P. Filippov, *Thermal Conductivity of Gases and Liquids (Data Book)* Standards Press, Moscow (1970).
3. W. Fritz and H. Poltz, *Internat. J. Heat Mass Transfer*, 5, 307 (1962).

6.

Physical property: Thermal conductivity, λ
 Unit: $W m^{-1} K^{-1}$
 Recommended reference material: Dimethylphthalate ($C_{10}H_{10}O_4$)
 Range of variables: 283 to 493 K, 10^5 Pa
 Physical state within the range: liquid
 Class: Calibration and Test Material
 Contributor: H. Ziebland

Intended usage: Dimethylphthalate can be used for the calibration of thermal conductivity cells of any geometry and/or for the testing of the proper functioning of the apparatus and its ancillary equipment within the temperature range 283 to 493 K.

Sources of supply and/or methods of preparation: Material of suitable purity is available from suppliers (C) and (D). Dimethylphthalate is slightly hygroscopic and should be dried over 'Linde' type 4A molecular sieve prior to use.

Pertinent physicochemical data: Extensive studies have been made on the problem of selecting organic liquids which are suitable for use as reference materials for thermal conductivity. Poltz in 1967 (Ref. 1) noted that, because the correction term for radiative energy transfer through the fluid layer rises with the third power of the temperature, substances to be used at elevated temperatures should possess a high absorption coefficient in the infrared region. The phthalic esters possess this property and have relatively high chemical stability.

Since the suggestion by Poltz, samples of one of the candidate materials, dimethylphthalate, have been distributed amongst several research groups with the aim of establishing values of the thermal conductivity with sufficient precision to justify its use as a reference material. Experiments in the temperature range 273 to 493 K were conducted simultaneously at the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig and at the Thermo-Physical Laboratory of the Propellants, Explosives and Rocket Motor Establishment (ERDE) at Waltham Abbey, England. The two sets of measurements resulting from this collaborative programme were in excellent agreement which is of special significance as the two laboratories used different experimental methods and procedures.

The results and further details of this joint study have yet to be published but in view of the urgent need for carefully investigated reference materials, the results pertinent to this substance have been included in this recommendation.

The results presented are those obtained by the Thermo-Physical Laboratory of ERDE which differ from the values of the PTB by less than 0.7 per cent at the extremes of the temperature range. The correlation equation obtained by a least square analysis is

$$\lambda/W m^{-1} K^{-1} = 0.1501 - 1.0539 \times 10^{-4}(T/K - 273.15) - 2.23 \times 10^{-7}(T/K - 273.15)^2.$$

A useful correlation (Ref. 3) has been established between the thermal conductivity and the reduced temperature of a series of phthalates

$$\lambda/W m^{-1} K^{-1} = 0.6004[1 - 0.0376(1 - T/T_c)^{1/3} + 1.616(1 - T/T_c)^{2/3} + 0.531(1 - T/T_c)],$$

where T is the temperature and T_c is the critical temperature which is 760 K for dimethylphthalate. The values calculated from this equation agree well with the recommended values. The values given in the tables refer to a fluid film of 0.5 mm thickness and the estimated uncertainty is 0.8 per cent.

Recommended values for the Thermal Conductivity of Dimethylphthalate from 273 to 493 K:

T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	T/K	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$
273	0.1501	390	0.1348
280	0.1495	400	0.1330
290	0.1483	410	0.1313
300	0.1472	420	0.1296
310	0.1460	440	0.1260
320	0.1446	450	0.1241
330	0.1434	460	0.1222
340	0.1421	470	0.1203
350	0.1407	480	0.1184
360	0.1394	490	0.1164
370	0.1379	500	0.1142
380	0.1364		

REFERENCES

1. H. Poltz, *Proc. 7th Conf. Thermal Conductivity*, Gaithersburg (1967), National Bureau of Standards Special Publication 302, Washington D.C. (1967).
2. H. Ziebland, private communication of an unpublished report of the National Physical Laboratory, Teddington U.K.
3. *Thermal Conductivity of Liquid Aromatic Compounds Containing Oxygen*, Data Item 74032, Engineering Sciences Data Unit, London (1974).

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LIST OF SUPPLIERS

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|--|---|
| A. British Oxygen Co.,
Dear Park Rd.,
London, S.W.1 (UK) | E. Matheson Gas Products,
P.O. Box E, Lyndhurst,
N.J. 07071 (USA) |
| B. Messer Griesheim G.M.B.H.,
Industriegase,
4 Duesseeldorf 2,
Hombergerstrasse 12
(FEDERAL REPUBLIC OF GERMANY) | F. Union Carbide Corp.,
Linde Division
270 Park Ave.,
New York, N.Y. (USA) |
| C. BASF Aktiengesellschaft,
D6700,
Ludwigshafen/Rhein
(FEDERAL REPUBLIC OF GERMANY) | G. Airco Industrial Gases Div.,
Airco Inc.,
575 Mountain Ave.,
Murray Hill, N.J. (USA) |
| D. Physikalisch-Technische
Bundesanstalt,
D 3300, Braunschweig,
Bundesallee, 100
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