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Comments on the Measurement of Thermal Conductivity and Presentation of a Thermal Conductivity Integral Method

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A discussion is presented regarding the significance of the spatial temperature gradient approximation normally used in thermal conductivity measurement. Examples are presented illustrating the magnitude of temperature differences allowed for conductivity integral (TCI) method of analysis is presented as an alternative method which totally eliminates the need to impose temperature difference restrictions on the measurement process, so long as other errors, such as radiative heat losses, do not become excessive.

KEY WORDS: Thermal conductance; thermal conductivity; thermal conductivity integral.

1. INTRODUCTION

Thermal conductivity, $k(T)$, is a temperature dependent property of a homogeneous material defined in terms of heat transfer through and the temperature gradient within a specimen of the material. The definition for unidirectional heat flow (planar isotherms) is given by

$$Q = -k(T)A(dT/dx) \quad \text{or} \quad k(T) = -Q(A\,dT/dx)^{-1} \tag{1}$$

where Q is the heat transfer per unit time, through cross-sectional area, A, and dT/dx is the temperature gradient in the direction of heat transfer. The negative sign simply indicates that the heat transfer direction is opposite to that of the temperature gradient. The one-dimensional case is

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used here for simplicity. However, this analysis can readily be extended to other simple heat transfer geometries, such as the radial or spherical cases.

The commonly used experimental or operational definition of thermal conductivity, $k_0(\bar{T})$, for this case, is

$$k_0(\bar{T}) = -Q(\Delta x/A\Delta T) \tag{2}$$

where Δx is the length of the specimen across which the temperature difference, $\Delta T = T_2 - T_1$, occurs, and the temperature to which this observation is usually assigned is $\bar{T} = (T_2 + T_1)/2$. This measured value, $k_0(\bar{T})$, is normally taken to be the true thermal conductivity of the specimen at the mean temperature, i.e., $k(\bar{T})$. This, of course, is an approximation of the true conductivity, $k(\bar{T})$, since $(dT/dx)^{-1}$ has been replaced by $\Delta x/\Delta T$. As ΔT approaches zero, $\Delta x/\Delta T$ approaches $(dT/dx)^{-1}$ and, in the absence of experimental errors, $k_0(\bar{T})$ approaches $k(\bar{T})$.

Most experimenters take great pains, often at the expense of accurate ΔT values, to utilize very small temperature differences to assure that the above derivative approximation is valid. This approach is essential when thermal conductivity is a strong function of temperature and especially when one is working near a phase transition where thermal conductivity may be discontinuous with temperature. One objective of this paper is to show that in all other cases, which include most measurements reported in the literature, small temperature differences are not essential for highly accurate results.

The objectives of this paper are (1) to show that relatively large temperature differences may be used experimentally, in most cases, without incurring excessively large errors, and (2) to describe a thermal conductivity integral (TCI) method, which totally obviates the need for restrictions on the size of experimental temperature differences. It should be noted that consideration is given only to the analytical aspects of the measurement process and not various experimental errors which may occur simultaneously. For example, it is not claimed that this method will account for the errors caused by stray heat losses, such as radiative heat transfer. These losses may, in fact, increase in a relative sense as excessively large temperature differences are used.

2. ERRORS CAUSED BY THE DERIVATIVE APPROXIMATION

The following discussion assumes the existence of a unique temperature dependent function, $k(T)$, describing the thermal conductivity of a specimen. The temperature average of this function from T_1 to T_2 is denoted as $\bar{k}(T_2, T_1)$.

For convenient calculations of the derivative approximation errors, the following derivation will show that the operational definition, Eq. (2), is equal to the temperature average of the true thermal conductivity from T_1 to T_2, $\bar{k}(T_2, T_1)$, and not the conductivity at the average temperature, $k(\bar{T})$, as normally assumed. Note that $\bar{k}(T_2, T_1)$ is simply the mathematical definition of the average value of $k(T)$ from T_1 to T_2, as given by

$$\int_{T_1}^{T_2} k(T)\,dT \Big/ \int_{T_1}^{T_2} dT$$

Proof: Integrating Eq. (1) with respect to temperature and assuming that Q and A are independent of x and T, one obtains

$$\int_{T_1}^{T_2} k(T)\,dT = -Q\Delta x/A \tag{3}$$

Dividing both sides of Eq. (3) by $\int_{T_1}^{T_2} dT$, to form the mathematical definition of the average, yields

$$\bar{k}(T_2, T_1) = -Q(\Delta x/\Delta T)/A \tag{4}$$

Note that the right side of Eq. (4) is the definition of $k_0(\bar{T})$ and, therefore, $\bar{k}(T_2, T_1) = k_0(\bar{T})$, and in general, these are not equal to $k(\bar{T})$. Thus, the error caused by the derivative approximation, $k(\bar{T}) - K_0(\bar{T})$, is equal to the difference between $\bar{k}(T_2, T_1)$ and $k(\bar{T})$. The relative error caused by the derivative approximation is

$$\% \text{ error} = \left[\bar{k}(T_2, T_1) - k(\bar{T})\right] 100/k(\bar{T}) \tag{5}$$

In this section, several cases will be analyzed to illustrate the magnitude of the error caused by using the operational equation to estimate the true thermal conductivity. In each case, Eq. (5) will be used to estimate the errors. Prior to looking at specific materials, two special cases, $k = a$ and $k(T) = a + bT$, where a and b are constants, will be considered.

2.1. Special Cases

The first special case is for a thermal conductivity that is constant, i.e., independent of temperature, $k = a$. Referring to Eq. (5), we see that there is no error in the operational definition, since both $\bar{k}(T_2, T_1)$ and $k(\bar{T})$ are equal to "a" for all temperatures.

The second case is for a thermal conductivity which varies linearly with temperatures from T_1 to T_2, i.e., $k = a + bT$. Referring to Eq. (5), we

again see that the operational definition is perfectly valid, since

$$\bar{k}(T_2, T_1) = \int_{T_1}^{T_2} (a + bT)\, dT \Big/ \int_{T_1}^{T_2} dT = a + b\bar{T} = k(\bar{T})$$

For higher order thermal conductivity equations, values of $\bar{k}(T_2, T_1)$ and $\bar{k}(T)$ are not generally equal, and the operational definition is incorrect except in the limit as ΔT approaches zero. The above results are not trivial, however, since for certain temperature ranges, the thermal conductivity of many materials approximate either a constant or linear temperature dependence. For example, the thermal conductivities of most amorphous dielectrics and metallic alloys vary approximately linearly from cryogenic to high temperatures. Pure metals at very low temperatures often approximate linear behavior while at high temperatures they vary quite slowly with temperature. Next, the experimentally determined functional form of $k(T)$ for several real materials will be analyzed to further illustrate these points.

2.2. Iron

Figure 1 illustrates the thermal conductivity of a moderately pure iron, exhibiting the usual linear behavior at very low temperatures, the peak at

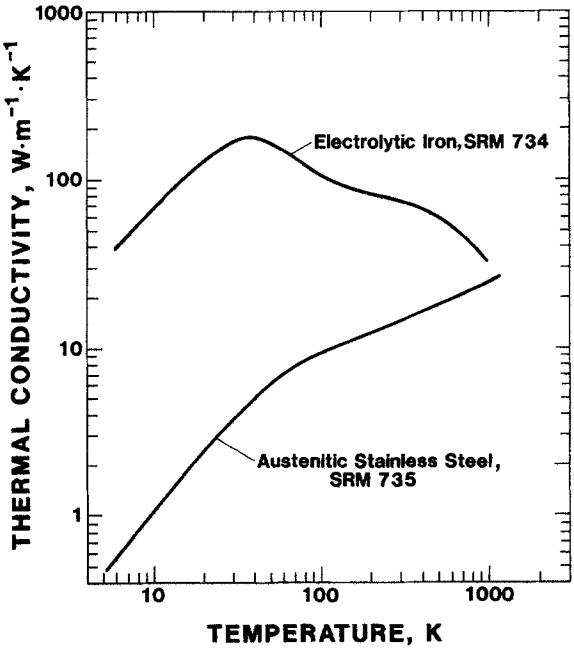

Fig. 1. Thermal conductivity of electrolytic iron, SRM 734, and of austenitic stainless steel, SRM 735.

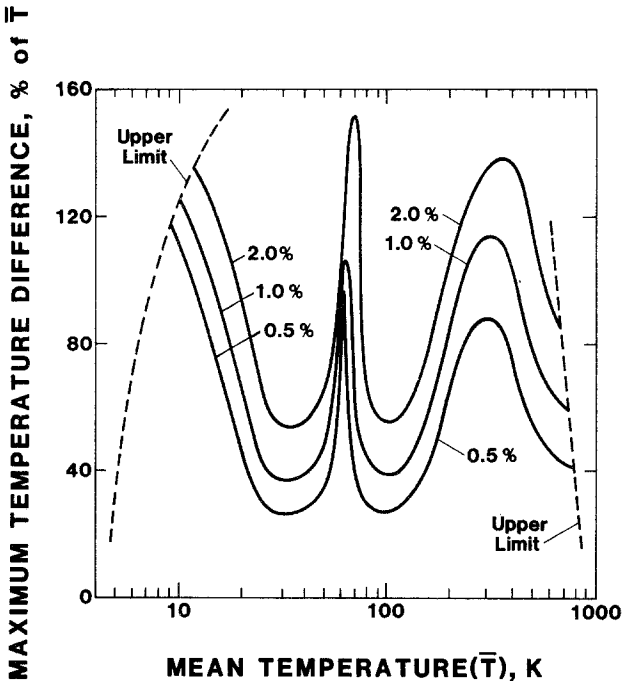

Fig. 2. Maximum temperature differences allowed in a thermal conductivity experiment upon SRM 734 for various error limits caused by errors in the temperature gradient approximation. The upper limits, indicated by dashed lines, are caused by the limits of validity of the equation, 4 to 1000 K.

intermediate temperatures, and the decrease to a slowly varying function at high temperatures. The $k(T)$ function used here is for electrolytic iron, SRM 734, from 4 to 1000 K [1]. From the empirically determined thermal conductivity function of this SRM, values of $\bar{k}(T_2, T_1)$ and $k(\bar{T})$ were calculated for various values of T_2 and T_1, yielding the percentage errors according to Eq. (5). From these calculated values, maximum values of $\Delta T = T_2 - T_1$ were obtained for error limits of 0.5, 1.0, and 2.0%. The resulting lines of constant error are plotted in Fig. 2 and illustrate that comparatively large temperature differences are experimentally valid, even for the 0.5% error band, which is near state-of-the-art measurement capability.

2.3. Steel

Figure 1 also illustrates the thermal conductivity of the second example, a stainless steel exhibiting a lower order temperature dependence, which is typical of alloys and impure dielectrics. The $k(T)$ function used is

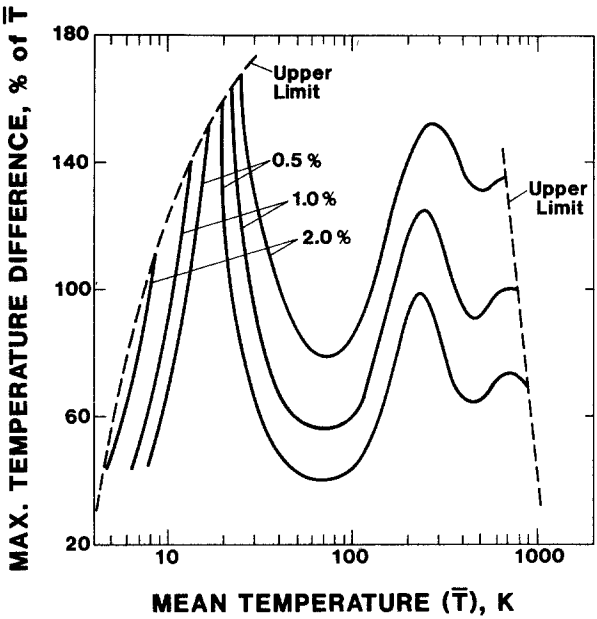

Fig. 3. Maximum temperature differences allowed in a thermal conductivity experiment upon SRM 735 for various error limits caused by errors in the temperature gradient approximation. The upper limits, indicated by dashed lines, are caused by the limits of validity of the equation, 4 to 1200 K.

for austenitic stainless steel, SRM 735, from 4 to 1200 K [2]. Calculations are performed as for the previous example, and the results are shown in Fig. 3 for the same error bands. The size of the allowable temperature differences is larger than for iron, as expected, and much larger than those used by experimentalists.

3. THERMAL CONDUCTIVITY INTEGRAL METHOD

The previous section has demonstrated that relatively large temperature differences can be used by the experimenter without introducing unduly large errors. As a matter of fact, overall errors may be reduced because the measurement of small temperature differences often, in itself, leads to large experimental errors. This section describes an alternative method of measurement/analysis which totally eliminates the need for any temperature difference restrictions, a thermal conductivity integral (TCI) method. The analytical method is based on only one assumption, that the thermal conductivity to be measured is representable by an integrable function of temperature over the temperature range of the measurements.

Clearly, this again eliminates from consideration $k(T)$ functions which are discontinuous, such as occur through a phase change.

First, for simplicity, assume that the actual thermal conductivity can be written as

$$k(T) = \sum_{i=1}^{n} A_i T^i \tag{6}$$

A function linear in the parameters A_i has been chosen, but a nonlinear function can also be used so long as it is integrable, either mathematically or numerically. Substituting $k(T)$ from Eq. (6) into Eq. (3) and integrating with respect to T yields

$$\sum_{i=1}^{n} A_i \left(T_2^{i+1} - T_1^{i+1}\right)/(i+1) = -Q\Delta x/A \tag{7}$$

Equation (7) contains only the set of n undetermined parameters (A_i) and the experimentally determined set of variables (Q, T_2, T_1, Δx, and A). Thus, from a set of at least n experimental runs over the temperature range $T_{\min}$ to $T_{\max}$, one can evaluate the A_i and, therefore, the original $k(T)$ function, Eq. (6), is defined. Although n runs are, in principle, sufficient for this process, as in any least squares process, considerably more runs are necessary. A personal rule of thumb is to have considerably more than $2n$ runs spaced uniformly over the temperature range $T_{\min}$ to $T_{\max}$. This rule of thumb is, however, strongly dependent on the nature of the function $k(T)$ selected to represent the data. For power series with large n (say above 5), careful attention must be given to selecting the number and spacing of points and the interpretation of the final results. The method allows some simplification of experimental arrangements and instrumentation but requires more expertise in data acquisition planning and in numerical analysis techniques.

It is convenient to point out here that Eq. (7), which is applicable to one-dimensional heat flow, can readily be extended to include other common geometries. Only the right side of Eq. (7) is affected. For a radial heat flow configuration, the right side becomes

$$\frac{Q}{2\pi} \ln \frac{r_2}{r_1}$$

For spherical heat flow, the right side of Eq. (7) becomes

$$\frac{Q}{4\pi}\left(\frac{r_2 - r_1}{r_2 r_1}\right)$$

where r_2 is the radius at T_2 and r_1 is the radius at T_1.

4. APPLICATION OF THIS TCI METHOD

To demonstrate the application of this TCI method, thermal conductivity integral data from 2 to 80 K for aluminum were obtained from R. B. Roberts (see the paper by R. B. Roberts and R. S. Crisp [3]). Their TCI data, Q, T_2, T_1, and $A/\Delta x$ are given in Table I. Roberts and Crisp analyzed these TCI data using a segmented smoothing and derivative technique rather than fitting a single $k(T)$ function to the entire range. Their derived thermal conductivity values are also given in Table I and are for the T_2 temperatures. These derived thermal conductivity values along with the measured mean values obtained for each run are plotted in Fig. 4. There is, of course, a distinct difference between these two sets of values for a thermal conductivity curve of this shape.

Because of the difficulty of representing the shape of low-temperature pure metal thermal conductivity curves with a power series, we decided to use a rational fraction equation based partly on the results of the theory. The equation chosen to fit these data is

$$k(T) = \frac{T}{a + bT^f} \tag{8}$$

where $f = n + mT$.

This equation is nonlinear in the parameters to be determined, and so a nonlinear fitting technique was required. In addition, it is mathematically nonintegrable and, therefore, numerical integration was performed in solving the problem. The computer routine used minimized the sum of the squares of the TCI differences between the experimental data and corresponding values calculated from Eq. (8). The resulting parameters are

$$a = 0.08102$$

$$b = 1.301 \times 10^{-5}$$

$$n = 3.06$$

$$m = 0.00426$$

Thermal conductivity values calculated from Eq. (8) are shown in Fig. 4 as the solid line. Although this looks like a respectable fit of the k values derived by Roberts and Crisp [3], one must take a closer look to see the actual differences.

Figure 5 illustrates, first, the percentage deviations between the experimental TCI data, $Q\Delta x/A$, and the calculated TCI values. Second, this figure also shows the percentage differences between the thermal conductivities derived by Roberts and Crisp [3] and the results derived here. Both

Table I. TCI Data of Roberts and Crisp [3] (Helium Range Only)
$\Delta x/A = 2.1549 \times 10^6\ \mathrm{m}^{-1}$

T_2 (K)	T_1 (K)	$Q\Delta x/A$ ($\mathrm{W \cdot m^{-1}}$)	k ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)
2.723	2.158	29.01	3354
3.060	2.158	31.71	3786
3.391	2.158	33.88	4192
3.810	2.158	36.64	4688
4.249	2.158	39.26	5193
4.816	2.158	42.59	5822
5.421	2.158	46.11	6470
6.022	2.158	49.50	7098
6.597	2.158	52.68	7670
7.203	2.158	55.90	8245
7.725	2.158	58.54	8702
8.451	2.158	62.15	9300
9.131	2.158	65.56	9807
9.774	2.158	68.43	10235
10.916	2.158	73.13	10825
11.877	2.158	76.74	11113
12.410	2.158	78.54	11168
13.700	2.158	82.46	10903
14.742	2.158	84.26	10495
15.371	2.158	85.16	10358
16.450	2.158	86.28	10258
15.162	4.172	92.34	9821
16.485	4.172	93.44	9834
18.752	4.172	93.41	8886
20.529	4.172	92.72	8067
22.510	4.172	90.92	7137
25.476	4.172	87.28	5835
29.653	4.172	81.09	4229
31.876	4.172	77.63	3549
34.900	4.172	73.08	2803
38.261	4.172	68.26	2168
40.817	4.172	64.86	1813
45.036	4.172	59.74	1366
50.023	4.172	54.49	1007
55.883	4.172	49.27	719
63.031	4.172	44.04	488
69.874	4.172	39.94	395
77.810	4.172	36.08	391
83.024	4.172	33.87	422

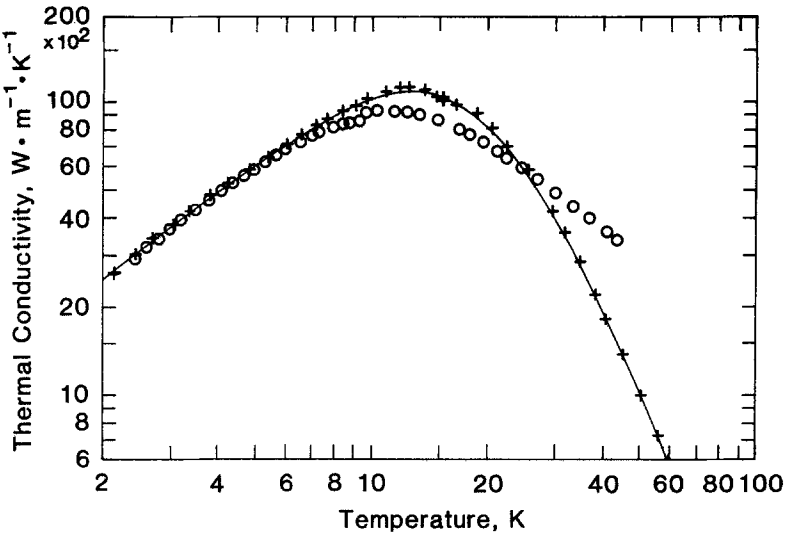

Fig. 4. Thermal conductivity values for aluminum: (+) as derived by Roberts and Crisp [3]; (∘) average values from Table I; (solid line) derived in this paper.

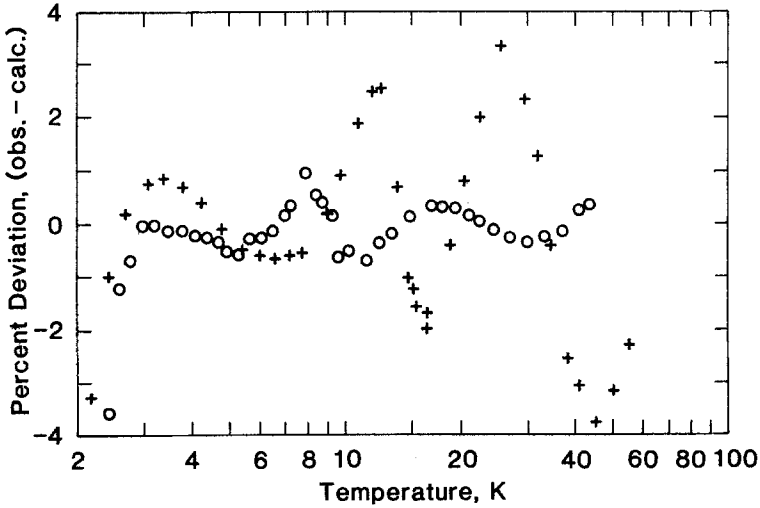

Fig. 5. Percent deviations: (+) thermal conductivity values from Roberts and Crisp [3], minus those of this research; (∘) thermal conductivity integral deviations (obs.–calc.)

differences are clearly systematic with seven crossings of the zero line. The correlation of the two deviation curves indicates that the method of Roberts and Crisp [3] yielded a better fit of their TCI data. Since Eq. (8) does not have the capability to oscillate in the above fashion, it can not account for these deviations. Assuming that these oscillatory deviations are physically real, one could repeat the above process with a power series to represent the remaining residuals.

5. SUMMARY

This paper has shown that for most conventional thermal conductivity measurements, relatively large temperature differences may be experimentally employed with little degradation of uncertainty due to the derivative approximation. Only in regions of rapidly changing thermal conductivity, primarily near phase transitions, is it essential that the temperature differences be small. The paper presents a TCI method of analysis which eliminates all analytical restrictions on the temperature difference. The method is useful because it allows considerable experimental simplification through the addition of some analytical complications. It can be used whenever the functional form of the thermal conductivity can be predicted in advance.

A TCI method has some advantages in analyzing data for the presence of nonconductive mechanisms, such as radiation and convection. These advantages occur because large temperature differences are valid in this analysis process while the large differences may simultaneously introduce increasingly large nonconductive mechanisms. The presence of these mechanisms often goes undetected except under large temperature difference conditions. Examples of such nonconductive mechanisms are radiation through partly transparent materials or radiation parallel to a longitudinal specimen.

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