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# Thermal Conductivity of *n*-Octadecane

## New Measurements and a Critical Appraisal of the Article by Sutherland, Davis, and Seyer

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SUTHERLAND, Davis, and Seyer, investigating the thermal conductivity of *n*-octadecane with a horizontal, unguarded plate apparatus reported a remarkable and hitherto unknown dependence of the thermal conductivity on the thickness of the liquid film (*3*). By varying the width of the gap in their apparatus between 0.69 cm. and 0.01 cm. the thermal conductivity appeared to fall from $3.5 \times 10^{-4}$ to $0.45 \times 10^{-4}$ cal./cm. °C., sec. This unusual phenomenon was ascribed to the existence and depth of penetration of orientating forces between the copper surface of their apparatus and the fluid in contact with it.

These observations seemed to cast severe doubt not only on the reliability of determinations by previous observers of the thermal conductivity of hydrocarbons of high molecular weight, but also might have general repercussions on the validity of all data obtained by the thin-film method. To clarify this situation, independent measurements were made on *n*-octadecane by Powell and Challoner (*1*) using a guarded, horizontal plate apparatus, the surfaces of which were nickel plated. Their results for film thicknesses of 0.2 and 0.3 cm, were practically identical and thus failed to reveal any measurable influence of surface phenomena on thermal conductivity. Furthermore, for these film thicknesses the data of Powell and Challoner were about 2.6 times higher than the corresponding ones of Sutherland, Davis, and Seyer.

Despite this remarkable disagreement it appears from their reply that the observations by Powell and Challoner were not regarded as conclusive by Sutherland, Davis, and Seyer mainly because the metal in contact with the fluid in Powell's apparatus was different from that in Sutherland's apparatus, and that the range of variation of film thickness from 0.2 to 0.3 cm. was inadequate. Further tests with film thicknesses as low as 0.02 cm. were therefore suggested to provide a final proof.

At this stage Dr. Powell brought the matter to the attention of this laboratory where for several years a guarded, coaxial cylinder apparatus employing film thicknesses of 0.02 cm. was used for studying the thermal conductivity of various fluids. In view of the considerable theoretical, and undeniable practical importance of the phenomenon described by Sutherland, and the failure by Powell and Challoner to confirm it, further independent measurements seemed justified and were carried out at this laboratory on a sample of *n*-octadecane supplied by Dr. Powell. The two conductivity cells employed in these tests were:

A guarded, coaxial cylinder apparatus which had been used in many previous studies by the senior author and which has been described in detail in a previous article (*5*). It allowed absolute determinations of the thermal conductivity on a liquid film of slightly less than 0.02 cm. thickness.

An unguarded conductivity cell of the same type but much simpler in design than the first precision cell mentioned. To ensure a high degree of reliability this cell was calibrated over the entire temperature range of these experiments with three test liquids of sufficiently well known thermal conductivity,—viz., with carbon tetrachloride, using the data by Schmidt and Leidenfrost (*2*), with toluene, using the best average data from six independent investigations (*4*), and with kerosine, using the results obtained earlier in this laboratory (*6*) with the first precision cell described. The values of the cell constant evaluated from these three independent calibrations agreed well, and the observed variation of about 2% is consistent with the experimental accuracy claimed for the data of the individual test fluids.

Both conductivity cells were made of a 97 to 3% copper to nickel alloy. The cells were mounted in suitable containers and were immersed in a thermostatically controlled water bath giving a temperature stability of better than 0.02° C. per hour.

The results of these tests on *n*-octadecane are given in Figure 1. The two series of determinations for film thicknesses of 0.02 and 0.1 cm. agree within about 1% which is the order of accuracy claimed for these experiments. Between 35° and 70° C. the data obtained with both cells were correlated by a single linear equation

$$10^4 \times k = 3.616 - 0.00584\, t \qquad (1)$$

where $k$ is the thermal conductivity in cal./cm. ° C. sec, and $t$, the temperature in ° C.

Two points, one at 29.2° C. and one at 30.9° C., indicate a more rapid increase of the thermal conductivity with falling temperature than predicted by the proposed equation. This is believed due to fractional crystallization of impurities of higher melting point. Visual observation on a sample of the substance studied showed the beginning of an increasing cloudiness at about the same temperature at which a deviation from the linear relation can first be noticed.

In view of the evidence provided by this research and by the earlier concurring results of Powell and Challoner, it seems conclusively established that within the ranges of film thicknesses employed (0.02 to 0.3 cm.) the nature of the two metal surfaces used (nickel and copper) had no measurable influence on the thermal conductivity of *n*-octadecane.

In order to explain the phenomenon observed by Sutherland, Davis, and Seyer (*3*) one must obviously look for other causes; it seems not unlikely that deficiencies in the experimental technique or, as Powell has pointed out, the presence of a thin gas film on or between the plates has been largely responsible for this anomalous effect. This latter argument gains weight when one considers that Sutherland's value of the thermal conductivity of *n*-octadecane for a film thickness of 0.01 cm. is of the same order as the anticipated thermal conductivity of the vapor phase of this substance.

The concluding statement by Sutherland, and others that only the thick-film method is a reliable method for determining the thermal conductivity of liquids can obviously not be upheld.

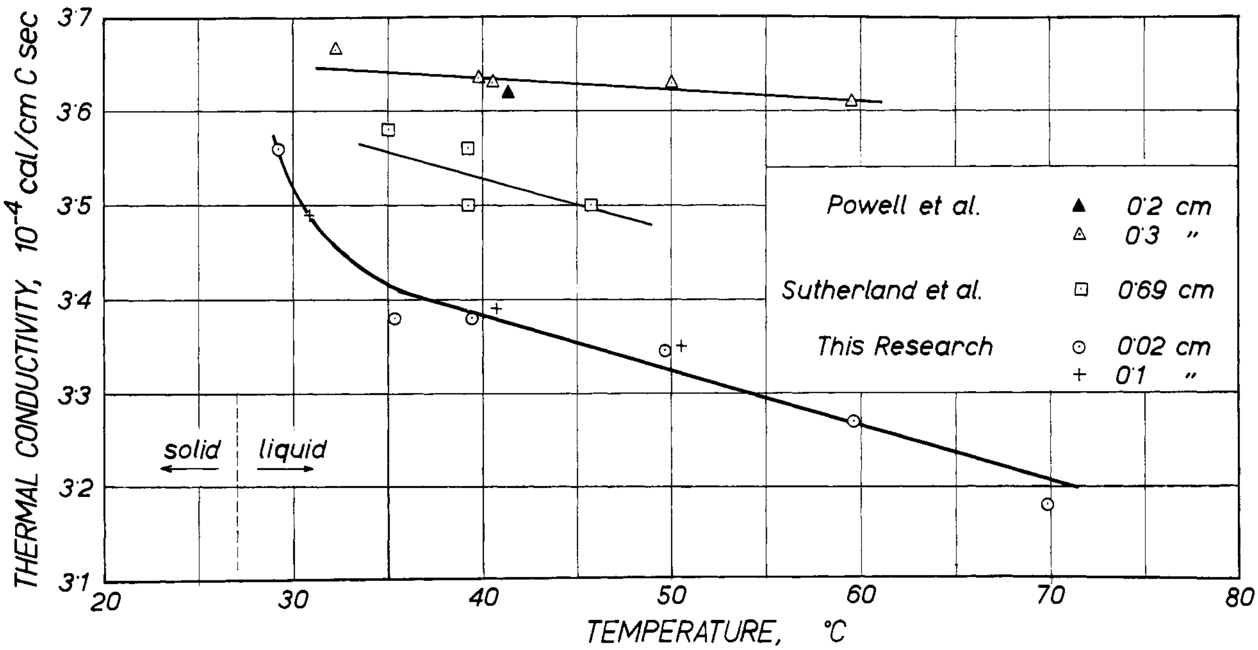


Figure 1. Three investigations of thermal conductivity measurements of *n*-octadecane are compared

The results of Sutherland and others, for the largest film thickness they investigated (0.69 cm.), are in fair agreement with those of Powell and Challoner and of this investigation, as shown in Figure 1. In view of the shortage of reliable data on high molecular weight liquid paraffins it appeared worthwhile to analyze the existing numerical results and their trends in order to establish the thermal conductivity of *n*-octadecane with a reasonable degree of accuracy.

Applying a least squares analysis to Sutherland's four points for a film thickness of 0.69 cm. (*1* Figure 4,) the following linear equation was evolved

$$10^4 \times k = 3.751 - 0.00556\, t \qquad (2)$$

The temperature coefficient of this equation is nearly identical with that of Equation 1. Absolutely, the data predicted by Equation 2 are about 4 % higher than those of this research.

The results of Powell and Challoner are about 6 to 7% higher and indicate a smaller temperature coefficient than those of this investigation. The reason for this discrepancy could not be established with certainty. Both investigations were conducted with care and both observers employed an apparatus which had proved reliable in past work. It only remains to suggest that the samples investigated differed in their purity. As the substance tested was obtained from the same manufacturer and the identical batch, contamination must have taken place before, or during the experiments. It is a matter of conjecture where and how this could have happened. The case for this research rests on the fact that two different conductivity cells were employed which gave identical results, and that the results obtained with the cell with the larger annulus were indirectly supported by the calibration with two control fluids of well established thermal conductivity (toluene and carbon tetrachloride).

Because of the close agreement between the temperature coefficients of the thermal conductivity derived from the work by Sutherland and coworkers and this research, one might consider the arithmetic mean value from both investigations $(0.00570 \pm 0.00014) \times 10^{-4}$ as more probable than the value of $0.00135 \times 10^{-4}$ derived from the experiments of Powell and Challoner. As far as the absolute values of the thermal conductivity are concerned, further tests are obviously needed to establish the thermal conductivity of *n*-octadecane with an accuracy better than indicated by the spread of the results of the three investigations.

## LITERATURE CITED


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