Nomenclature

W_m = weight of metal parts of specimen holder in ambient air = 63.078 g
W_s = weight of specimen in ambient air ≈ 50 g
W_{BE} = weight of bag and epoxy adhesive in ambient air = 1.328 g (a superscript "e" denotes weights in ethanol)
B_m = coefficient of volumetric expansion of metal = $-1/V_m\ \Delta Vm/\Delta T = -54 \times 10^{-6}$, °C^{-1}
B_{BE} = coefficient of volumetric expansion of bag and epoxy = -220×10^{-6}, °C^{-1}
m = mass, g = acceleration of gravity
ρ_m = density of metal at ambient = m_m/V_m = 8.9 g/cm^3
ρ_{BE} = density of bag and epoxy at ambient conditions = 0.94 g/cm^3
ρ_a = density of air at ambient conditions = 0.001 g/cm^3
ρ_e = density of ethanol

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Received for review October 28, 1974. Accepted August 6, 1975. Contribution of the National Bureau of Standards—not subject to copyright. Work sponsored by NASA, MSFC, Huntsville, Ala.

Thermal Comparator Measurements on Dimethyl Sulfite

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A thermal comparator was used to obtain a value of 0.178 W m^{-1} °C^{-1} for the thermal conductivity of a high-purity vacuum distilled sample of dimethyl sulfite having a specific density of 1.2083 at 24.8°C.

The thermal conductivity of the organic dimethyl sulfite is of interest because of its potential use as a nonaqueous battery solvent owing to its stability with high-energy density electrodes and its ability to dissolve electrolytes (*2, 8*). Yao et al. (*9*) have measured the melting point (−141°C), the dielectric constant ($\epsilon_{23.3}$ = 22.5), and the viscosity (0.7715 cP at 30°C and 0.4361 cP at 80°C). Kyrides (*4*) has reported a boiling point of 126°C at 760 mm Hg and 52°C at 45 mm Hg, a density of 1.2073 g/cc at 24°C, and an index of refraction of 1.4093 at 20°C for dimethyl sulfite. An exchange current density of 15 mA cm^{-2} for a 1.12 M LiClO$_4$ solution in dimethyl sulfite has been found by Tiedemann and Bennion (*8*).

Mahefkey and Kreitman have noted that the important thermal related properties of battery performance, viz., cell cycle life and cell capacity, as well as electrical efficiency, can be strengthened by operation at lower battery temperatures which they achieved with the introduction of an intercell heat pipe (*5*). The removal of waste heat from a battery is an important design characteristic; therefore, the thermal conductivity of the electrolyte solution is a significant factor in the design and operation of a battery. However, very little information exists on the thermal properties of dimethyl sulfite. To help fill this gap, we have used a thermal comparator to carry out measurements on the room temperature thermal conductivity of the liquid.

The thermal comparator method for obtaining rapid thermal conductivity measurements on solids was introduced by Powell (*6*) in 1957. Subsequent modifications (*7*) have led to the development of a commercial unit (available from the Thermophysical Properties Research Center, Purdue University Research Park, 2595 Yeager Road, W. LaFayette, Ind. 47906), a prototype of which was used in the measurements reported below. The purpose of this paper is to report the thermal conductivity measurement of dimethyl sulfite and to comment on the application of the comparator to the measurement of the thermal conductivity of liquids.

Sample

The liquid sample consisted of approximately 15 cc of commercial grade (Eastman Kodak Co.) dimethyl sulfite at 300K purified by two vacuum distillations. Equal volumes of calibrating liquids were used in the comparator. A westfall balance was used to obtain a value of 1.2083 at 24.8°C for the specific density of the liquid.

Experimental

The thermal comparator method offers a convenient way to obtain the thermal conductivity of an unknown sample to an accuracy of ±5% or better. The instrument registers the rate of cooling experienced by the thermocouple tip of a heated probe when it comes into contact with the surface of a test sample. In general, test samples of different material will draw different amounts of heat from the contact probe according to their thermal conductivity. To avoid undesirable effects which would arise form the probe coming into contact with a liquid sample, the heat conducting ability of the liquid is sensed by the probe through a thin mylar membrane. The membrane is stretched across the bottom of a shallow cylinder, approximately 1.375 in. in diameter, forming a cup ⅞ in. deep to contain the liquid.

As soon as the temperature sensing tip of the probe comes into thermal contact with the sample, heat is extracted from the tip and creates a temperature difference between tip and probe which is represented by an increasing microvolt reading on the comparator DVM readout control unit. For test samples which have a poor conductivity, the microvolt reading increases to a maximum within several seconds, and afterward it begins to decrease. The approach to the maximum represents an increase in the temperature difference between the probe and the tip. Because the temperature of the probe is carefully controlled, this increase in temperature difference results from a cooling of the tip and a corresponding warming of surface regions of the sample (in contact with the tip) due to heat which has been transferred through the tip.

The maximum comparator reading represents the greatest difference in temperature between the warmer temperature-controlled probe and the tip which has been cooled by its contact with the sample. This maximum temperature difference between tip and probe is associated with an easily observed plateau (shown in the instrument operation manual) in the temperature increase of the test sample, and it represents a near steady state temperature level which is related to the material's thermal conductivity. When the thermal conductivity of the test sample is low, the heat transferred through the contact with the tip will cause the test sample's temperature to rise fast to a maximum. Because the heat cannot be conducted away so fast by a sample with poor conductivity, the temperature of the test sample will continue to rise so that the tip temperature will begin to approach the probe temperature. These effects, which cause the temperature difference of probe and tip to decrease, explain why the comparator reading decreases beyond its maximum as the test sample reaches a temperature plateau. The duration of time for the maximum microvolt reading was found to be less than 10 sec.

For a sample with good thermal conductivity, the temperature difference between probe and tip not only takes longer to reach a maximum, but the maximum is much greater because the tip is cooled much more by the surface of the test sample which, because of its good conductivity, is able to remove a large amount of heat from the tip. Therefore, the temperature of the test surface increases only a small amount, whereas the temperature of the contacting tip is decreased by a large amount. As the process continues, the tip continues to be cooled as more heat is drawn into the sample. These effects produce an initial rise in the thermal comparator reading followed by an upward drift.

Because of the upward drift, a procedure was established to record maximum comparator readings in a uniform way for different samples with good conductivities. Following the initial rise and the upward drift of the comparator reading described in the previous paragraph, that comparator reading was recorded, which was observable on the DVM without change (or with a change of less than 1 μV) after a duration of 5 sec. In other words, to establish a procedure for dealing equally with all samples and calibrations standards having good conductivities, the measurement was continued until the rate of increase in the microvolt meter decreased to less than 1 μV in 5 sec. The reading then shown was recorded as final. The duration of time required to reach this maximum was normally between 15 and 30 sec approximately. Further comment on the measuring method may be found in ref. *3*.

Kreitman (*3*) reported that the use of successive comparator readings can provide a criterion for rejection of erroneous data prior to data analysis, and thereby yield a value of conductivity with a lower percentage of error. However, this technique was not of great help in the present study because of the generally low value of the thermal conductivity measured and the associated small amount of scatter in the readings.

A calibration curve is formed when the cooling rates, registered in millivolts by the probe for the standard liquids, water, glycerol, methanol, and carbon tetrachloride, are plotted as a function of their thermal conductivities: 0.608, 0.288, 0.202, and 0.104 W m^{-1} K^{-1}, respectively. (These values for 300K were supplied by the Thermophysical Properties Research Center.) The curve allows easy determination of the thermal conductivity of an unknown liquid from a set of average millivolt values representing the liquids and the unknown. These average values are formed from the statistical analyses of multiple or additional readings on the standards and the unknown. From such a curve, it was possible to determine a value of 0.178 W m^{-1} C^{-1} for the thermal conductivity of dimethyl sulfite at 298K. Typical comparator calibration curves are available from the Thermophysical Properties Research Center and from the literature (*1, 7*).

Conclusion

Techniques of comparator measurement involving "additional" and "successive" readings developed in an earlier study of the thermal conductivity of semiconductor crystals (*3*) were applied to the measurement of liquid samples to obtain the thermal conductivity of the liquid dimethyl sulfite. Because of the low thermal conductivity values of the samples measured, the use of the successive readings was not as helpful in reducing error as in the previous study on solids where thermal conductivities were three orders of magnitude larger. However, there was no great need for an additional criterion to reduce error since the reproducibility of the readings in this experiment was well within 1% and the absolute error was measured to be less than approximately 4%. The lack of scatter in individual readings was probably due in part to the uniformity of the mylar surface supporting the liquid sample with which the probe contacted. In summary, the thermal comparator method as used is an effective technique which can be utilized to obtain thermal conductivities of liquids at room temperature with a minimum of difficulty.

Acknowledgment

It is a pleasure to acknowledge encouraging discussions with Donald C. Reynolds, Leonard Spialter, and Julius G. Becsey of the Aerospace Research Laboratories at Wright Patterson AFB, the latter having suggested the measurement and supplied the dimethyl sulfite and the calibrating fluids.

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Received for review April 9, 1975. Accepted July 18, 1975. Work performed at Aerospace Research Laboratories, Air Force Systems Command, under Contract F33615-71-C-1877.