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A FIRST PRINCIPLES APPROACH TO THERMAL CONDUCTIVITY MEASUREMENTS OF SOLIDS*

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Although knowledge of heat conduction is crucial to the understanding of many practical everyday phenomena, the exposure of university students at the undergraduate level to this subject is often limited. With the intent of improving this situation, we describe the design of a simple apparatus for measurement of the thermal conductivity of materials, using components that could be found in most undergraduate laboratories. Use of this apparatus clearly illustrates the basic principles of heat conduction, as the data collected enable the determination of the thermal conductivity of a material directly from the defining equation. To demonstrate the use of this apparatus in determining the thermal conductivity of materials, we describe the result obtained from measurements of a plate of aluminium alloy.

Bien que la connaissance de la conduction de la chaleur soit critique à la compréhension de plusieurs phénomènes pratiques journaliers, l'exposition de ce sujet aux étudiants universitaires au niveau non-diplômé est souvent restreinte. En vue d'améliorer cette situation nous décrivons le plan d'un simple appareil qui mesurerait la conductivité thermale de matériaux, avec les composants que l'on trouve dans la plupart des laboratoires. L'usage de cet appareil démontre clairement les principes fondamentaux de la conduction de la chaleur, puisque les données qu'on relève permettent la détermination de la conduction thermale du matériau soumis à l'examen directement de l'équation définissante. Afin de démontrer l'usage de cet appareil, nous décrivons aussi le résultat obtenu des mesures d'une plaque d'alliage d'aluminium.

Introduction

Thermal conductivity is a fundamental and important property of matter. As the name implies, the thermal conductivity of a substance is a quantitative measure of how perfectly the substance conducts heat. Thermal conductivity values for different materials can vary over several orders of magnitude, and this fact has many practical applications in everyday life. For example, the high thermal conductivity of metals such as iron and copper make these substances useful in the construction of pots and pans for cooking, since heat will be distributed evenly throughout the metal and food will cook uniformly. However, coffee mugs are normally made from low thermal conductivity ceramic materials to minimize the heat exchange between the coffee in the mug and its surroundings, to keep the coffee warm.

Despite its fundamental and practical importance, the concept of thermal conductivity usually receives only brief mention in undergraduate chemistry classes. Although the basic concept can be introduced with the kinetic theory of gases, a thorough study of heat conduction in materials would require a working knowledge of the detailed theories of solid-state physics and chemistry which are normally beyond the scope of undergraduate courses. Experiments illustrating the basic principles of thermal conductivity measurements could introduce students to the idea of thermal conductivity at an undergraduate level, and an experimental determination of the thermal conductivity of gases in the undergraduate laboratory has been published (Shoemaker and Garland 1967). The wide range of thermal conductivities of technologically important materials would make a simple experimental method for determination of

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thermal conductivities of solids a useful addition to the undergraduate physics or physical chemistry laboratory.

Very accurate thermal conductivity measurements require that the system of interest be thermally isolated to prevent unwanted heat exchange between the system and the surroundings. Such measurements would require the design and construction of a sophisticated piece of apparatus, and typical methods have been summarized (Berman 1976; Touloukian 1970). However, our concern in the development of the present experiment was not high accuracy, but rather to design a simple experimental procedure that would allow a good estimate of the thermal conductivity of a material.

Experimental Method

Thermal conductivity (κ) is a transport property that is defined by the following equation:

$$\dot{q} = -\kappa(dT/dx) \qquad (1)$$

where $\dot{q}$ is the heat flux through the material in the measured direction (represented as the x-direction in this case) and dT/dx is the corresponding temperature gradient. Heat flux is the rate of heat flow per unit area (*i.e.* $\dot{q} = \dot{Q}/A$ where $\dot{Q}$ is the rate of heat flow and A is the cross-sectional area). There are many other equations describing thermal conductivity which are derived from equation 1. However, our approach to thermal conductivity measurements uses the definition (equation 1) directly.

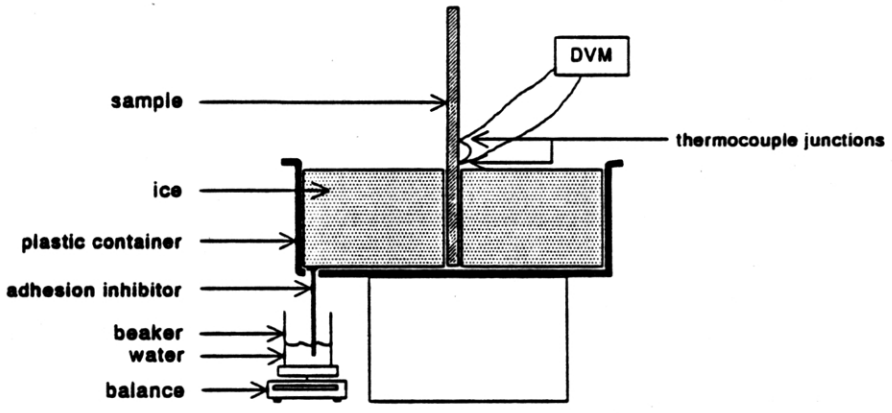

Fig 1 A schematic diagram showing the experimental set-up that was designed and used to measure the thermal conductivity of a plate of aluminium alloy. Dimensions are given in the text. DVM = digital voltmeter.

The experimental apparatus that was designed and used in this study is shown schematically in Fig 1. The basis of the experiment was the determination of the temperature gradient across a sample during conduction of heat from the room, through the sample, to melt ice in which the sample was imbedded. (The use of melting ice in thermodynamic determinations has a distinguished history, starting with the ice calorimeter designed by Lavoisier and LaPlace (1780)). The heat flux was determined by the rate of melting of ice (relative to the rate in the absence of the conducting material), and the thermal conductivity, κ, was determined from the direct use of equation 1.

The apparatus consisted of a rigid plastic container (a dish pan, 35 x 25 x 12 cm deep was used; better results were obtained when the pan was insulated) with a ~0.5 cm diameter hole in one corner. The material to be measured (in the form of a plate) was placed vertically in the centre of the plastic container, held in place by the ice which filled the plastic container. As the ice melted, the resulting water flowed out of the hole in the plastic container into a beaker which was resting on an analytical balance (0.1 g precision) below the pan. The rate of water production might be determined by volume, but this would need both 0.1 mL precision and calibration at the temperature of the water. A narrow piece of plastic tubing (~1 mm OD) was placed between the hole and the beaker to act as an "adhesion inhibitor" so that there was a steady flow of water between the plastic container and the beaker rather than an uneven dropwise flow; without the "adhesion inhibitor" mass measurements were uncertain. Once a steady flow of water was achieved, the mass of water in the beaker as a function of time was measured. The water mass increase rate (dm/dt) can be converted to rate of heat flow ($\dot{Q}$=dQ/dt) by multiplying by the enthalpy of fusion of water ($\Delta_{fus}H$ = 333.7 J g^{-1} (Adamson 1979)), i.e.

$$\dot{Q} = dQ/dt = \Delta_{fus}H(dm/dt). \quad (2)$$

There are two heat channels which cause melting of the ice in this configuration: (1) heat flow through the material being measured, and (2) heat flow through the remaining parts of the set-up. The measured increase in mass of water (which corresponds to the rate of heat flow, $\dot{Q}$) is made up of the contributions from both of these sources. To compensate for the melting of ice that would take place in the absence of the material being measured, mass flow measurements were initially taken without the material in the container. After steady-flow conditions were achieved (this took about 15 minutes), the mass of water was determined as a function of time (typically every 30s, for about 10 minutes). Then the material to be measured was placed in the container, a waiting time (*ca.* 15 minutes) for steady-state conditions was allowed, and mass measurements were again taken as a function of time. The difference between dm/dt with and without the sample, is the rate of mass change due to heat flow through the material, dm/dt of equation 2.

The cross-sectional area of the material, A, was needed in order to calculate the heat flux through the material, $\dot{q}$. This value was determined using a ruler and a vernier calliper.

Measurement of the temperature gradient along the face of the material was carried out using a thermocouple. One junction of a 0.08-mm diameter AuFe (0.03 atom % Fe)/Chromel (Johnson Matthey; supplied and calibrated by Cryogenic Calibrations Ltd., HP22 4HT United Kingdom) differential thermocouple was attached to the sample close to the ice, to minimize the effects of lateral heat flow from the surroundings. The other junction was placed vertically above the first such that there was a reasonable distance (5-10 cm) between the two. The thermocouple junctions were covered with a thin layer of silicone grease (necessary for good thermal contact) and held in place with adhesive tape. The distance between the junctions was determined with a ruler. A fine-gauge AuFe/chromel thermocouple was used because of its known high accuracy and the low thermal conductivity along the thermocouple itself. Other thermocouples (*e.g.* copper-constantan or chromel-alumel) could function well for this set-up, but fine gauge wires should be chosen in order to make the heat flux through the sample dominate over that through the thermocouple wire. During the series of water mass measurements, the potential difference between the two

thermocouple junctions was constantly monitored with a digital voltmeter until a steady-state value was reached and this value was recorded. This voltage was later converted to a temperature difference using a calibration table for the AuFe/chromel thermocouple (Cryogenic Calibrations Ltd.).

A plate of aluminium alloy (≈ 350 mm x 200 mm x 3 mm) was measured as a test of the apparatus. An analysis of the plate by an electron microprobe with an energy-dispersive detector gave the following results: 97±1 atom% Al; 2.5±0.1 atom% Mg; 0.2±0.1 atom% Cr; 0.15±0.05 atom% Si; 0.15±0.01 atom% Fe.

Results and Discussion

Plots showing the mass of water flowing into the beaker as a function of time before and after insertion of the sample are shown in Fig 2. Both plots are linear and the slopes indicated on the graphs were obtained by linear least-squares fit. These slopes correspond to the water mass increase rate, and the difference between them (dm/dt after insertion of plate - dm/dt before insertion) gives dm/dt due to the heat flow through the plate. The thermal conductivity, κ, was calculated using equation 1. For the aluminium plate measured, $\kappa = 120 \pm 20\ W.m^{-1}.K^{-1}$ at $T = 280K$. The error range reflects the standard deviation on five measurements. One measurement was carried out with the pan and the ice surface insulated with 2.5 cm thick styrofoam block; the thermal

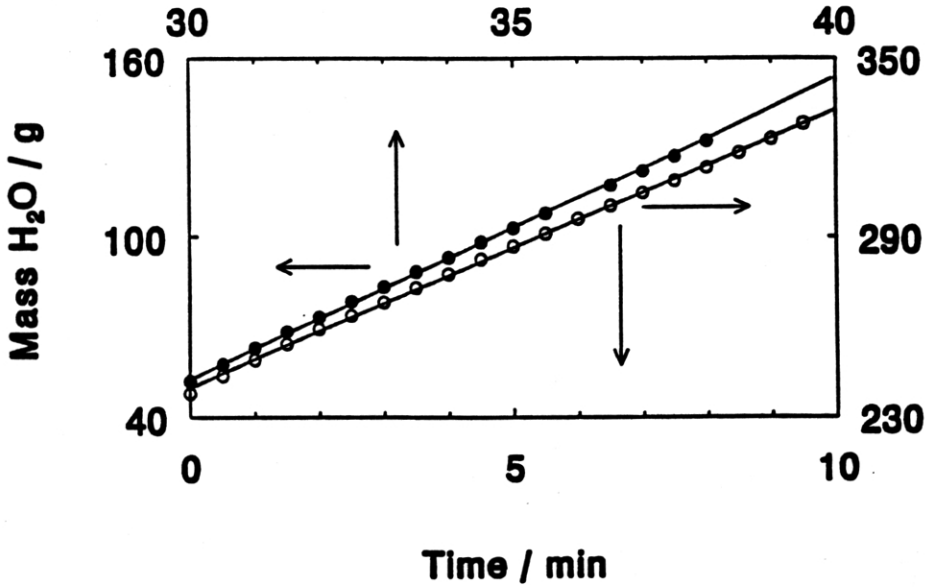

Fig 2 Plots of the measured mass of H_2O in the beaker *versus* time before (o) and after (•) the Al plate was inserted into the apparatus. The slopes, as indicated by the least-squares fit lines, are the rates of mass increase, dm/dt. (The later masses are less than the earlier ones because the beaker was emptied between run ◦ and run •.)

conductivity was essentially the same but the increase in dm/dt was more substantial (≈50% increase with insulation; ≈20% increase without insulation). Since a larger increase in dm/dt will reduce the uncertainty in the determination of the thermal conductivity, insulation is recommended.

This experiment has not been designed to provide the most accurate measurement of thermal conductivity, and there are sources of errors. The main sources of error are the thermal contact between the thermocouple junctions and the plate, and uniformity in water flow rate. Another error is that heat exchange by radiation and conduction between the material and the surroundings in the region between the thermocouple junctions is not taken into account; in principle, this would lead to steeper vertical temperature gradients closer to the ice than further out and the value of dT/dx in equation 1 could be inappropriate if the thermocouple junction separation were so great that lateral heat flux was important. However, we have carried out measurements with various thermocouple junction separations (5-10 cm) and do not find that this correlates with the measured thermal conductivity, showing that equation 1 is appropriate at these separations for this material.

Although the uncertainty in the determination is rather large (±17%), on the basis of measurements of thermal conductivities of Al alloys of similar composition (Touloukian 1970), the thermal conductivity of this sample at about 280K (the mean sample temperature) would be expected to be between 100 and 200 $W.m^{-1}.K^{-1}$ and the observed value is within this range. When making comparisons with literature values, it should be noted that the presence of even small amounts of impurities can reduce the thermal conductivity of metals significantly (Berman 1976): *e.g.* the thermal conductivity of very pure aluminium at about 280K is 235 $W.m^{-1}.K^{-1}$ (Touloukian 1970).

It is possible to use this method to measure thermal conductivities of other materials. In order to achieve meaningful measurements, the material to be investigated must sufficiently enhance the heat flux to the ice to produce a measurable increase in the rate of melting (compared to the absence of the material), while having a sufficiently large temperature gradient to be measured accurately with a thermocouple (preferably of the order of $1K.cm^{-1}$). The dimensions of the sample to be measured can considerably influence these factors.

Other possible aspects that could be explored include the effect of the material's colour (painting the plate black led to an enhanced heat flux), or the material's geometry (κ should be independent of geometry). Given the relevance of thermal conductivity to materials of technological significance, it is likely that students and teaching staff could help the experiment evolve in many different directions.

This experiment can introduce or enhance the following subjects in the undergraduate teaching laboratory: connections between thermodynamics and the "real world"; the use of thermocouples; error propagation; least-squares fitting; discussion of precision *vs.* accuracy of a measurement; quantitative effect of purity on a physical property. Given the simplicity of the experiment, these aims can easily be accomplished within the two- to three-hour timeframe of an undergraduate laboratory period.

Conclusions

This experimental procedure for measuring thermal conductivity is a rudimentary one, and yet leads to measurements of good accuracy. Furthermore, the determination is based on the defining equation for thermal conductivity. The set-up is so simple that

it could be used as an instructive undergraduate-level laboratory exercise to introduce students to the concept of thermal conductivity.

Acknowledgements

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