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The Thermal Diffusivity of Ice and Water Between −40 and + 60° C

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The thermal diffusivity α_s of triply-distilled deionised water, and α_L of single-crystal ice along the *c*-axis, have been measured by Angström's method. The temperature range covered was −40 to +60° C. The results for water compare well with published data for the thermal conductivity, but for ice there are unexplained discrepancies. The linear relationships $\alpha_s = (8.43 - 0.101\ T)\ 10^{-3}$ cm²/sec and $\alpha_L = (1.35 + 0.002\ T)\ 10^{-3}$ cm²/sec where T° C is the temperature, fit the data obtained.

1. Introduction

This investigation was undertaken to provide thermal property data necessary for a study of the solidification kinetics of ice [1]. In the present experimental technique (devised by Angström [2] in 1861) a sinusoidal temperature variation is impressed upon one end of a cylindrical specimen, and the thermal diffusivity is determined from the measured attenuation of this wave at several points along the specimen.

2. Theory

The differential equation for heat flow is

$$\alpha\,(\partial^2\theta/\partial x^2) = \partial\theta/\partial t + \mathrm{h}\theta \qquad (1)$$

in which θ is the temperature-difference between the specimen and the surrounding medium, at time t, at the point distance x measured along the specimen from the hot end; h is the coefficient of surface heat loss, and α is the thermal diffusivity. The constant h may be eliminated from the calculation of α by a method devised by Starr [3]. The attenuation of the thermal wave is determined from the ratio of the amplitudes of the thermal wave measured by thermocouples placed at intervals along the specimen. The thermal diffusivity is calculated from the measured attenuation for two periods. Substituting the appropriate boundary conditions in equation 1 gives

$$\alpha = \frac{\pi L^2}{\tau_1 \ln g_1 \ln g_2}\left(\frac{a^2 - b^2}{b^2 - 1}\right)^{1/2} \qquad (2)$$

where g_1 is the ratio of the wave amplitudes measured at two thermocouples for any one period τ_1, $a = \tau_1/\tau_2$, $b = \ln g_2/\ln g_1$, and L is the distance between thermocouples.

3. Experimental

Fig. 1 shows an apparatus designed to maintain a stable temperature gradient over a specimen length of approximately 15 cm. The water/ice system was contained in a polystyrene tube (1 cm diameter) which possessed a suitably low thermal conductivity and was also transparent and rigid. Liquid nitrogen was pumped through the copper helix at the lower end of the tube. The emf generated by a thermocouple attached to this helix was biased by a potentiometer, and the residual emf was amplified and fed into an anticipatory control unit, which actuated a solenoid valve in the liquid nitrogen line. In this way it was possible to control the temperature within the coil to ± 0.02° C at −50° C. This thermal variation was sufficiently attenuated in the system to give a negligible effect at the thermocouples.

A small platinum resistance heater maintained the top of the system at a constant time-average temperature. The platinum coil was covered with a thin layer of silicone-rubber cement which electrically isolated the heater from the ice/water. With the styrofoam insulation in place, temperature drifts for a constant power input never exceeded 0.01° C over a 24 h period. The

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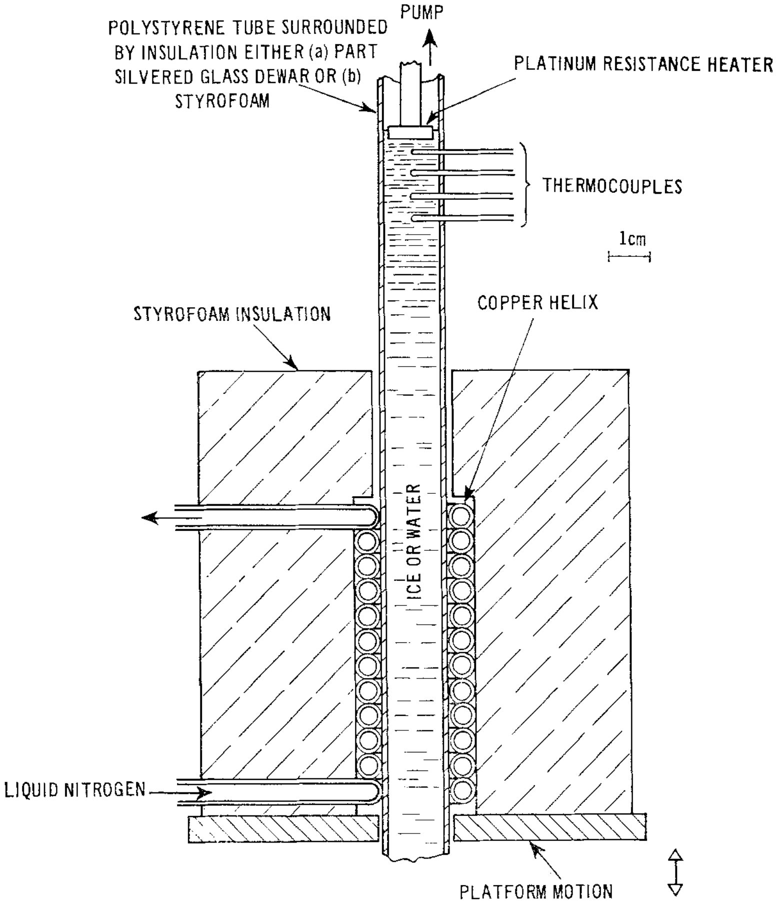

Figure 1 Apparatus for measuring thermal diffusivities of ice and water by a thermal wave method.

ambient temperature was controlled to ±0.1° C. The thermal wave was superimposed on the static gradient using the same platinum resistance heater. The voltage to the heater was supplied by a motorised cam attached to the shaft of a Variac having a stabilised input voltage. It was possible to vary the frequency, ω, and amplitude of the generated thermal wave over a wide range of values. The dc component of the power gave rise to a steady temperature gradient, and the ac component produced a modulation of ~1° C at the heater, corresponding to a peak-to-peak power variation of 1 W. The effect of the 60 cycle/sec carrier wave was averaged out because of the thermal inertia of the heater. The thermal wave measured at a point 0.5 mm below the heater deviated from a perfect sine wave by less than ±1 % of the amplitude, for all ωt where:

$$\theta = \theta_{\max} \sin \omega t \tag{3}$$

and t is time.

The chromel-constantan thermocouples, having time constants less than 0.25 sec, were supplied by Baldwin-Lima-Hamilton, Waltham, Massachusetts. They consisted of well-annealed 0.001 in. (1.0 in. = 2.5 cm) diameter wires separated from a stainless steel sheath (0.014 in. diameter) by magnesia tubes. Thus, the thermocouples were electrically insulated from each other and from the surrounding media. Four thermocouples were sealed into the polystyrene tube wall at 5 mm intervals. The signals were biased and amplified. A Leeds and Northrup "Speedomax" Chart Recorder recorded the amplified voltage as a function of time. The response time of the equipment was less than 2 sec to 98 % of the input signal. This was quite adequate to record the wave function of shortest period ($\tau = 2\pi/\omega \sim 100$ sec). The longest period was ~300 sec.

The single crystals of pure ice were grown according to the process described in [1]. The growing crystal was viewed through two unsilvered slits in a cylindrical glass dewar vessel that could be slipped around the polystyrene tube. The orientation in which the *c*-axis of the ice was parallel to the axis of the tube was readily recognised by the invariance of the colours revealed by polarised light as the tube was rotated about its axis [4]. Indeed, it was difficult to grow a crystal having a *c*-axis that deviated by more than a few degrees from the tube axis.

The part-silvered glass dewar vessel enabled the system to be observed during a simulated experiment. In this way it was possible to check for any convection currents by introducing several minute pieces of lint into the liquid. These pieces of microscopic debris were observed to be suspended, motionless, in the liquid during the normal time limit of an experiment.

The interface planarity appeared unchanged as the interface froze or melted past a thermocouple. Thus it was concluded that the thermocouples conducted a negligible amount of heat into the system. Furthermore, a good thermal contact between the thermocouples and the ice was assured.

Experiments were carried out with triply-distilled, deionised water, under a partial pressure of air of about 3 torr.

4. Results

The values obtained for the thermal diffusivities of ice and water are plotted against temperature in fig. 2. If a least-mean-squares analysis is applied to the data, the following equations describe the results for ice and water respectively:

$$\alpha_S = (8.43 - 0.101\,T)\,10^{-3}\mathrm{cm}^2/\mathrm{sec} \qquad (\sigma_S = \pm 4.0\%) \quad (4)$$

$$\alpha_L = (1.35 + 0.002\,T)\,10^{-3}\mathrm{cm}^2/\mathrm{sec} \qquad (\sigma_L = \pm 5.3\%) \quad (5)$$

where T is the temperature in ° C, and σ is the standard deviation of measured values of α from the least-mean-squares values.

The hθ term in equation 1 involves the assumption that the heat-loss from the specimen surface is proportional to, and in phase with, the temperature of the surface. In the present case, the specimen could not be maintained in a vacuum; consequently, the container was made of (thin-wall) polystyrene tubing surrounded by styrofoam insulation. Furthermore, the axial distance between the thermocouples was short compared with the length of the heat path from the thermocouple to thermocouple via the tube wall. This minimises the out-of-phase component of heat loss. Errors introduced in this way were estimated to be less than 1%. The distance

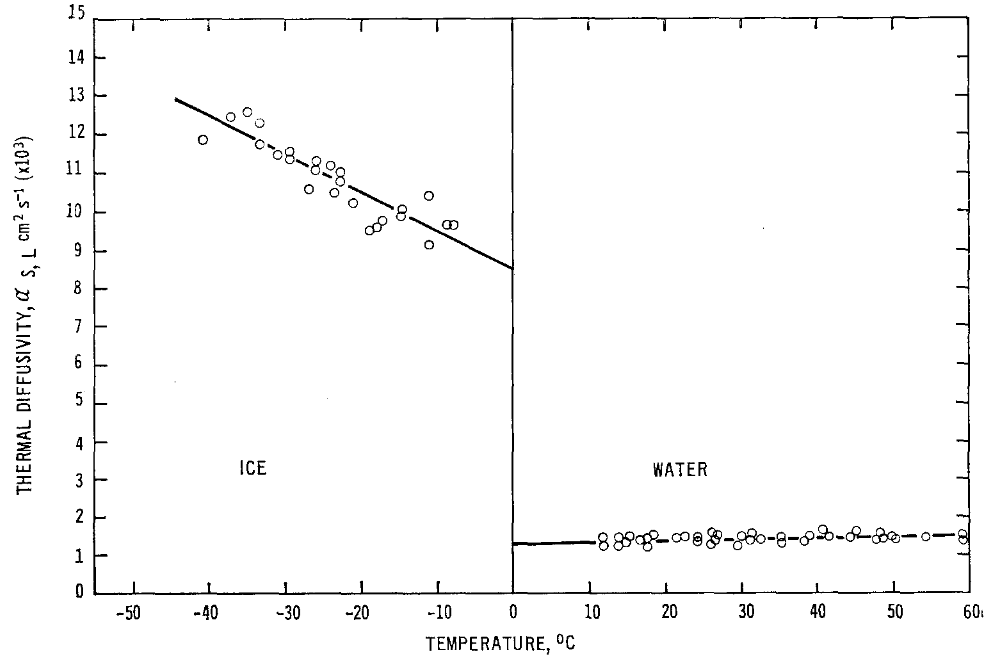

Figure 2 Thermal diffusivity of ice and water.

between thermocouples, L, is another source of error. This measurement was performed with an accuracy of $\pm 1\%$ using a filar eyepiece attachment to the microscope. The thermocouples were of a finite size, however, and the length of the thermal path between them might differ from the measured value of L. Errors in τ were considered to be negligible and errors in $\ln g$ were in all cases less than $\pm 3\%$.

5. Discussion

5.1. Ice

There appears to be only one previous determination [5] of the thermal diffusivity of ice. The investigation involved measurement of the attenuation of the annual thermal cycle in a massive, polycrystalline sample of Antarctic ice. The ice contained impurities and air bubbles. The effects of anharmonic components and absorbed solar radiation were not considered. An average value of $\alpha_s = (15.4 \pm 0.9) \times 10^{-3}$ cm^2/sec was quoted for an estimated temperature of $-20°$ C. This compares with $\alpha_s = (10.4 \pm 0.4) \times 10^{-3}$ cm^2/sec at $-20°$ C for the "c" direction of an ice single crystal obtained in the present investigation.

The thermal diffusivity coefficient is related to the thermal conductivity coefficient, K, by the relationship

$$K = \rho C_p \alpha \qquad (6)$$

where ρ is the density and C_p the specific heat of the material. Measurements of the thermal conductivity of ice were first reported during the nineteenth century. Since that time only one investigation has provided reliable data [6]. In this reference, Ratcliffe discusses shortcomings of earlier attempts. Ratcliffe's specimens were polycrystalline and contained entrapped air. There was also the possibility of poor thermal contacts between the heat sink and specimen causing distortion of heat flow in the ice. The present results are compared with those of Ratcliffe at 0 and $-40°$ C in table I.

5.2. Water

There are no previous measurements of the thermal diffusivity of water with which to compare the present data. There are, however, a large number of determinations of the thermal conductivity of water. These have been adequately reviewed by Powell [7]. Thermal conductivity is a property which does not lend itself to accurate measurement. The main difficulty is the avoidance of heat leakage to, or from, the specimen. This is a particularly serious problem for poor conductors such as water. With any liquid there is also the problem of thermal convection. This may be alleviated by reducing the thickness of the liquid layer, but then further errors arise in the measurement of this thin layer.

With the above considerations in mind, the present data can be compared with the "Proposed Values" of Powell, [7], table I. In fact, the data agree to within the limits of experimental error. The agreement is especially good at the lower temperatures. For the higher temperature range, published data for ρ and C_p become increasingly unreliable.

Acknowledgement

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TABLE I Comparison of published data with thermal conductivities calculated from present data.

Phase	Temp. (°C)	Thermal conductivity (watt/cm°C) Present value*	"Best value"	Ref.
Ice	0	$15.90 \pm 0.60 \times 10^{-3}$	$22.00 \pm 1.10 \times 10^{-3}$	6
	-40	$20.80 \pm 0.80 \times 10^{-3}$	$27.00 \pm 2.70 \times 10^{-3}$	6
Water	0	$5.70 \pm 0.28 \times 10^{-3}$	$5.60 \pm 0.06 \times 10^{-3}$	7
	$+60$	$6.18 \pm 0.31 \times 10^{-3}$	$6.53 \pm 0.07 \times 10^{-3}$	7

*Values of ρ and C_p taken from International Critical Tables.