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Experimental Study of Thermal Conductivity of Solid and Liquid Phases at the Phase Transition[1]

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An experimental method for the determination of the thermal conductivity of a pure material at its freezing melting point has been developed. In the present investigation, this method is discussed further by studying the effective thermal conductivity of the frozen as well as the thawed state of a wet porous material, and of solid and liquid benzene at the interface. The method involves the study of the transient propagation of the freezing or melting zone through the specimen as well as the steady state of the freezing/melting process. The method makes use of the heat of transition as the heat flow, and it enables the interface to act as a heat transfer surface, thus incorporating realistic features of the phase change process. Compared with data from the literature, the experimental results for benzene agree within 2% for the solid phase and within 3% for the liquid phase, when some precautions are made to avoid free convection. The experimental effective thermal conductivity of the packed bed is compared with data from a numerical analysis; the results agree within 4%, indicating that the method is applicable also for measurements on heterogeneous materials.

KEY WORDS: benzene; freezing; melting; packed bed; thermal conductivity.

1. INTRODUCTION

Natural and technical processes involve frequent melting and solidification of a material. The study of these processes creates a need for data on several physical properties of the solid as well as the liquid phase at the transition temperature. These are the heat of transition, thermal expansion,

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specific heat, and thermal conductivity, each of which should be determined by the most suitable method. A new method for the determination of thermal conductivity at the freezing/melting point of a pure material has been developed [1] as a supplement to existing methods [2]. These, however, may not be satisfactory in handling the special situation at the phase transition temperature. They are applicable to specimens of a single phase. The main problem of the experimental methods is to determine consistent data for the rate of heat flow and for the temperature gradient. By the present method this is solved by confining the specimen to an interface under simple conditions and studying the conduction of the heat of transition at the interface. The present method enables, further, the interface to be effective as the heat transfer surface at which the thermal conductivities are determined. In this way, features of the interface are incorporated in the experiment giving realistic data for the simulation of the freezing/melting process. The purpose of this study is to confirm the usefulness of the method by the determination of the thermal conductivity of different substances—benzene and a porous material made up of a packed bed of glass spheres with the voids filled with water. The results for benzene are compared with the data reported in the literature [3–5]; for the porous bed they are compared with the results from a numerical analysis.

2. METHOD

A theoretical treatment of the heat transfer during a phase change by melting/freezing of a material was first made by Neumann [6]. Relevant problems are discussed quite extensively in the literature [7–9]. Neumann formulated the heat transfer in a semi-infinite body of a homogeneous liquid initially at a temperature above the melting point. At a certain time, the boundary temperature was assumed to drop to a steady value below the freezing point. The melt starts to solidify at the surface, and then a solidification front propagates unidirectionally into the melt. Applied to a porous material, the phase transition takes place only in the void fraction, expressed by the porosity. Then, from Neumann's theory, the thermal condition at the interface can generally be formulated mathematically as

$$-k_s \frac{\partial T_s}{\partial x} + k_l \frac{\partial T_l}{\partial x} + \varphi \rho h \frac{d(s(t))}{dt} = 0 \qquad (1)$$

where k is the effective thermal conductivity, T is the temperature, x is the length coordinate perpendicular to the interface, $s(t)$ is the location of the interface relative to a fixed point, ρ is the density of the phase undergoing a transition, h is the heat of solidification referred to unit mass, t is the time, φ is the porosity, and the indices s and l indicate the solid and liquid states, respectively. For a nonporous sample, $\varphi = 1$, and the equation takes the original form by Neumann.

Equation (1) describes the heat balance on the interface for a one-dimensional geometry. By a proper setting of initial and boundary thermal conditions, with x varying from 0 to H, Eq. (1) can be separated into three equations, expressing three alternative situations, serving as the basis for three different experiments. Further, if the experiments can be made in a way that the temperature field is linear in x, and that x and s have the same coordinate system, then the differentials can be replaced by differences. In this way we obtain the following equations, Eqs. (2), (4), and (6), and working expressions, Eqs. (3), (5), and (7), for the respective experiments:

(a) Freezing:

$$-k_s \frac{\partial T_s}{\partial x} + \varphi \rho h \frac{dx}{dt} = 0 \tag{2}$$

$$k_s = -\varphi \rho h \frac{\Delta x_s}{\Delta t} \bigg/ \frac{\Delta T_s}{\Delta x_s} \tag{3}$$

with the following initial and boundary conditions:

$$t < 0, \qquad 0 < x \leqslant H: \qquad T_{s,x} = T_0$$

$$t \geqslant 0, \qquad x = 0: \qquad T_{s,0} = T_0 - \Delta T_s$$

where T_0 is the freezing/melting temperature and ΔT_s is the temperature drop through the solid.

(b) Melting:

$$-k_l \frac{\partial T_l}{\partial x} + \varphi \rho h \frac{dx}{dt} = 0 \tag{4}$$

$$k_l = \varphi \rho h \frac{\Delta x_l}{\Delta t} \bigg/ \frac{\Delta T_l}{\Delta x_l} \tag{5}$$

with the following initial and boundary conditions:

$$t < 0, \qquad 0 < x \leqslant H: \qquad T_{l,x} = T_0$$

$$t \geqslant 0, \qquad x = H: \qquad T_{l,H} = T_0 + \Delta T_l$$

where ΔT_l is the temperature drop through the liquid.

(c) Thermal equilibrium across the interface:

$$-k_s \frac{\partial T_s}{\partial x} + k_l \frac{\partial T_l}{\partial x} = 0 \tag{6}$$

$$k_r = \frac{k_s}{k_l} = \frac{\Delta T_l}{\Delta x_l} \Big/ \frac{\Delta T_s}{\Delta x_s} \tag{7}$$

with the boundary conditions

$$\begin{array}{lll} t \geqslant 0, & x = 0: & T_{s,0} = \text{const} < T_0 \\ t \geqslant 0, & x = H: & T_{l,H} = \text{const} > T_0 \end{array}$$

From the working expressions, Eqs. (3), (5), and (7), the effective thermal conductivity can be evaluated. The quantities ΔT, Δx, and Δt are to be determined from measurements.

The temperature gradients at the interface must be known as a solution of Eq. (1). For the case of thermal equilibrium, Eq. (7), the temperature field is linear, assuming constant thermal conductivity. For the transient cases, Eqs. (3) and (5), the temperature field follows an exponential function of time and distance. The gradients at the interface might be determined as an iterative numerical solution to fit the temperature at the boundary. For engineering considerations, however, we refer to Grigull and Sandner [8], where an approximate solution of Eq. (1) is given, together with the condition for which the temperature field can be assumed to be linear through the layer. The condition is dependent on the phase transition number, the Stefan number, here defined as

$$\text{Ph} = \varphi h (C \Delta T)^{-1} \tag{8}$$

where C is mean specific heat and ΔT is the temperature difference across the layer of the melt or the solid. When $\text{Ph} > 10$, for example, the approximate solution of Eq. (1) deviates less than 2% from the exact solution. By this assumption the temperature gradient can be determined from the temperature at the interface, the freezing/melting point, and the measured temperature at the boundary. In the present experiments $\text{Ph} > 20$.

An interesting feature of the transient experiments by this method can be derived from Eqs. (3) and (5), namely that the Stefan number at the interface equals the Fourier number Fo [10]:

$$\text{Ph} = \varphi h (C \Delta T)^{-1} = \text{Fo} = k \, \Delta t (\rho C)^{-1} (\Delta x)^{-2} \tag{9}$$

This means that the Fourier number is constant during the experiments, and the thermal conductivity can, in principle, be determined from a short measuring period, and thereby be sensitive to variation of physical phenomena in the process. Further, the experiment is simplified by the heat capacity of the layer being insignificant compared with the heat of transition at the interface. These are the essential features of the method.

3. EXPERIMENTS

3.1. Apparatus

The equipment used in this investigation is illustrated in Fig. 1. Its main component is the cell C1 made up of two circular plates P1 and P2 with a cylindrical ring R between them, and kept together with six screws. In this way a cylindrical cavity is formed, with diameter 60 mm and height 10–12 mm, for the test fluid. The plates have internal channels through which coolant can circulate. The circulating coolant was pumped from baths that were thermostated. Three baths were available, each for a given

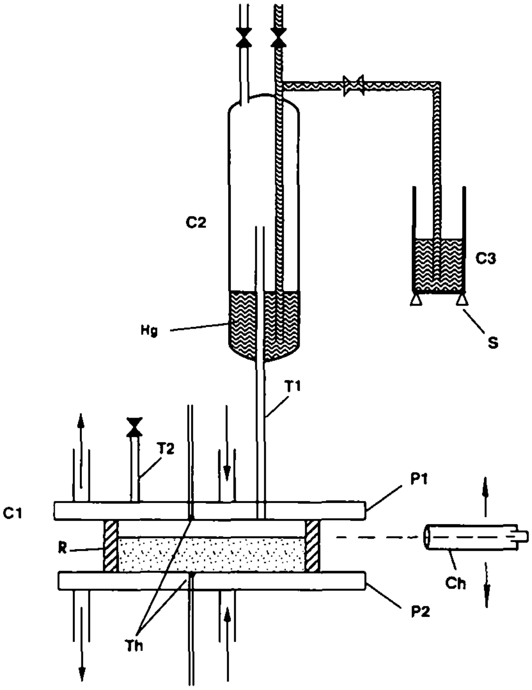

Fig. 1. Schematic drawing of the apparatus; for notations, see text.

temperature in the range of 0 ± 10°C. The surfaces exposed to the test fluid were made of copper, and their temperature was measured by thermocouples Th imbedded in the plates. For measurements on benzene the ring was of glass, thickness 2 mm, height 12 mm. For the porous bed the ring was acrylic, 5 mm thick, with height 10 mm. The cavity was accessed through the upper plate by two tubes T1 and T2 for filling the cell with liquid. Through one of them, T1, the liquid communicated with an external system, consisting of the bottle C2 filled with water and some mercury that in turn was connected to another bottle C3, resting on a scale S, as indicated in the figure. This arrangement was the basis for the determination of the position of the interface in the packed bed, namely by utilizing the fact that the specific volume of water is reduced during the freezing period. For measurement on benzene the position of the interface was determined by use of a cathetometer (Ch in Fig. 1). The ring was outside, isolated except for a window for visual access. The mass of the mercury was determined from the analog electric output of the scale. The electric signal from the scale together with the thermoelectric power from the thermocouples were registered by a Solartron 3530 ORION Data Logger, with a logging interval that could vary from 10 s to 1 min from one run to the other. The logger was linked to a microcomputer for further data processing.

3.2. Measurements

The cell was filled with specimen, either spheres of sodium glass immersed in distilled water, or benzene of 99.5% purity, with air bubbles removed by tilting the cell while liquid flowed through the cell. The cell was then mounted in a rig with the plates positioned horizontally. The experiment was started by circulating coolant of a temperature at the freezing point of the specimen through the upper and the lower plates until the isotherm condition was achieved. Then the coolant to the lower plate was quickly connected to the bath at a freezing temperature. A solid layer was formed on the bottom of the cavity, and a solidification front continued into the liquid as a plane surface parallel to the plates. Just before the front reached the top plate, the plates were again connected to coolant at the freezing point to allow the cell to acquire thermal equilibrium. Then the temperature of the upper plate was raised to some degrees above melting temperature and the interface moved downward. After the melting sequence the temperature of the lower plate was decreased below the freezing point and freezing from the bottom plate started again. The interface would then move upward, finally, after hours, to reach a stationary position, indicating a thermal equilibrium of the interface. Figure 2 illustrates

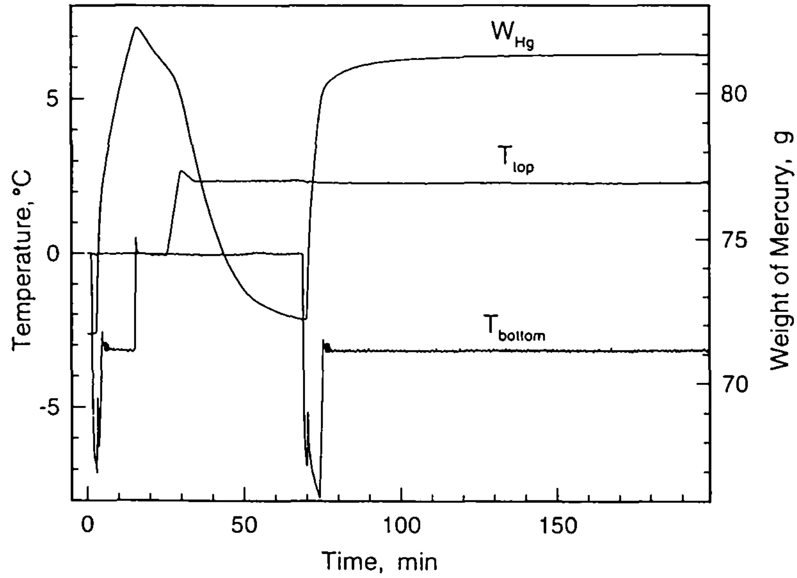

Fig. 2. Measured data from a run with the porous bed, indicating the sequence of freezing, melting, and the approach to thermal equilibrium of the interface of water.

the results from a typical experimental run with the packed bed, showing the scale reading of mercury and the temperature of the lower and upper plates as a function of time.

3.2.1. *Packed Bed*

During the freezing of the packed bed, water expanded into cell C2 and thereby displaced a certain amount of mercury from C2 into the bottle C3. During the melting process the volume in the cell contracted and mercury was sucked back from the bottle. From the weight of mercury on the scale the change of the fraction of ice in the cell was determined, and the thickness of the ice layer could be evaluated. The relation between the change of the thickness of ice and the change of the scale reading Δm can be expressed by

$$\frac{\varphi \, \Delta x_s}{\Delta m} = \frac{4}{\pi D^2} \frac{1}{\rho_m (1 - \rho_s/\rho_l)} \tag{10}$$

Uncertainty of x_s is estimated to be less than 3%. This measurement enables the thickness x_l to be evaluated as $H - x_s$, and the quotients $\Delta x/\Delta t$ and $\Delta x_s/\Delta x_l$ in Eqs. (3), (5), and (7) can be determined. The temperature gradients at the interface were evaluated from the difference of the temperature of the plate and the temperature of the interface, 0°C, divided by the thickness of the respective layers, assuming the linear temperature field.

The porosity of the packed bed was determined in a separate measurement. A freezing process was started and the interface was allowed to reach the top plate. In this way all the water in the voids was converted into ice. From the data on the specific volume of ice and water, the voids, i.e., the porosity, could be evaluated to give the value $\varphi = 0.47$.

3.2.2. *Benzene*

When benzene started to solidify from the lower plate, gas bubbles were released that created counteracting processes of shrinking of the benzene and of volume expansion by the released gas. The weighing technique described above was then useless, and the position of the interface was determined by the use of the cathetometer within an uncertainty of ± 0.03 mm. Benzene solidified in crystals apparently with vertical lines or cracks. Gas bubbles could arise along these lines, moving to the interface and partly to the upper plate to form greater bubbles. During the melting process the bubbles gradually vanished; occasionally they were drawn back into the cracks, presumably by capillary forces. The liquid phase turned out to be very clear and the interface gave a sharp line on the glass ring. The surface was smooth except for a few dark traces, evidently from impurities. The release of gas by the freezing of benzene is also reported in the literature [3–5], with the assumption that it was air. An attempt was made to degas the liquid before filling the cell. However, there was no influence on the processes in the cell.

4. NUMERICAL ANALYSIS

In order to verify the measurements of the porous bed specimen a simple numerical model was developed to simulate the phase transition. Assuming that the glass spheres in the cell C1 are packed in a cubic lattice with void fraction $\varphi = 0.476$, the computational domain is chosen as a unit cell in cylindrical coordinates. In the vertical direction of the cell the domain comprises three spheres. The radius of the domain equals the sum of the radius of the sphere and a layer of water (or ice) whose thickness is determined by the porosity of the specimen. The two-dimensional domain is subdivided into 48 and 14 control volumes in the axial and radial direction, respectively. At the freezing/melting temperature, within limits of ± 0.001°C, the specific heat is set equal to the heat of transition divided by the temperature limits. The computation was made with the following data for the spheres: specific heat $778\ \mathrm{J \cdot kg^{-1} \cdot {}^{\circ}C^{-1}}$, density $2700\ \mathrm{kg \cdot m^{-3}}$ and thermal conductivity 1.09 W · m^{-1} · °C^{-1} [11]; and with similar numbers for water (4186, 1000, and 0.56) and for ice (2040, 917, and 2.19) [12]. The results are compared with the results by Wakao and Kato [13]. The model has also been tested by calculating the phase transition of pure water and ice; the results are in good agreement with the theoretical solutions.

5. RESULTS

The results, together with data from the literature, are given in Table I. For the solid phase the thermal conductivity is obtained from measurements of the freezing process. For the liquid phase, the thermal conductivity is calculated from the value for the solid and the ratio between them.

For solid benzene, the thermal conductivity agrees with the data from Refs. 3 and 4 within the limits of the uncertainty of our measurements, 3% for solid and 6% for liquid. This good agreement indicates that in these cases the benzene has solidified in a similar crystalline structure. Chudnovskiy et al. [4] discusses the ratio k_r. They give a theoretical value of $k_{r\text{th}} = 2.0$, and their experiments give the ratio $k_{r\text{th}}/k_r = 1.25$. Our value $k_r = 1.7$ gives $k_{r\text{th}}/k_r = 1.18$. Ref. 5 gives experimental data for the thermal conductivity of solid benzene parallel to the principal axis of the crystal that are about twice our values. This may indicate that the solid benzene in our experiments was predominantly polycrystalline.

The agreement between experimental and numerical values for the thermal conductivity of the glass bed is better than 3% for the frozen bed and better than 6% for the thawed bed. Calculations from Ref. 13 give the same result.

Table I. Thermal Conductivity of the Specimen at the Melting Point: Experimental and Theoretical Results

			Thermal conductivity (W · m^{-1} · °C^{-1})					
Specimen	Phase	T_0 (°C)	Measured k_s	Numerical		Evaluated k_l*	Ratio k_r	Literature data (W · m^{-1} · °C^{-1})
Bed	Solid	0	1.60	1.56	1.56 [13]	—	—	—
Bed	Liquid	0	—	0.78	0.83 [13]	0.81	2.0	—
							1.9 [13]	—
C_6H_6	Solid	5.53	0.26	—	—	—	—	0.27 [3, 4]
								0.58 [5]
C_6H_6	Liquid	5.53	—	—	—	0.15	1.7	0.15 [4]
							1.6 [4]	—
							2.0 [4]$_{\text{theory}}$	0.58 [5]
H_2O		0	—	—	—	—	3.88 [10]	—

* $k_l = k_s \cdot k_r^{-1}$.

As shown in Fig. 2, when the freezing process is stopped, a melting process can be observed in the packed-bed specimen, despite the fact that the cell is maintained at the freezing point. This phenomenon appeared also in benzene. It may be caused partly by the volume change of the crystals, partly by convection in the liquid layer. For water, a positive density gradient in the liquid layer may create convective heat transfer; in benzene the evolution of the bubbles may cause a similar contribution. This effect seems, however, not to have had any significant influence on the results at thermal equilibrium.

Despite the reservations pointed out here, the present method seems to be valuable for studies of the thermal conduction at the freezing/melting point, as well as of other physical processes at the interface.

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