t = correction to geometric mean combination rule
T = absolute temperature
u = intermolecular potential energy
u^* = energy parameter in pair potential
U_x = potential energy of mixture
V' = configurational volume; same as V^L
V^E = excess volume
V^L = liquid molar volume
V_f, V_h, etc. = partial derivatives of V'
W_a = size and shape factor for molecule a
x = liquid mole fraction
y = vapor mole fraction

Greek Letters

α = thermal expansion coefficient
β = isothermal compressibility
γ = activity coefficient
μ = coefficient of attractive term in intermolecular potential function
ν = coefficient of repulsive term in intermolecular potential function
ϕ = universal function of distance r_{ij}
$\overline{\phi}_{i,p}$ = fugacity coefficient of species i in a gas mixture at T and p
$\phi_{i,p*}$ = fugacity coefficient of pure species i at T and its vapor pressure

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Peak-Time Method for Measuring Thermal Diffusivity of Small Solid Specimens

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A simple test method is developed for determining the thermal diffusivity of solids and granular materials by measuring the time at which the peak on a temperature-time record occurs. It allows the use of small easily prepared specimens and specimens of irregular shape (for example, stones). The tests can be performed at room temperature as well as at high temperatures, and can be repeated in short time intervals.

The principal difficulties of measuring the thermal diffusivity of solids are associated with specimen preparation. Very often a specimen has to be machined or ground to a certain shape, and for solids of considerable hardness this operation may be extremely time-consuming and costly. The difficulties are further increased by the fact that it is often next to impossible to find a piece of the solid sufficiently large to serve as a specimen.

This latter problem is especially acute with some concrete aggregates that are often unavailable in sizes larger than about 1½ in. As the thermal conductivity of aggregates is known to be the primary factor in the conductivity of concrete (*1*, *2*), inability to determine this property seriously hinders the design of concrete mixtures in applications where thermal characteristics are of principal importance.

The method to be described for measuring thermal diffusivity of solids is notable for its simplicity with regard to both specimen preparation and the performance of the test. It is especially suitable for nonmetallic materials, and can be carried out on very small specimens.

THEORY

It will be shown that a method developed earlier (*3*) for the measurement of thermal diffusivity, using idealized semi-infinite solids, can be extended to include the use of solids of more convenient geometry, such as cube, sphere, and even to solids of irregular shape.

If heat is supplied for a short period to the surface of a solid body, initially in equilibrium with its surroundings, the temperature at any point inside the solid will exhibit a maximum at some time following cessation of the heat supply. The thermal diffusivity of the solid can be determined by measuring the time at which the maximum temperature occurs. (For this reason it seems appropriate to refer to this method as peak-time method.)

By generalization of the results in reference *3*, one can assume that, at least approximately, the following relation is applicable to the peak

$$\frac{\kappa t_m}{\ell^2} = A\varphi_1\left(\frac{\tau}{t_m}\right)\varphi_2\left(\frac{h\ell}{k}\right) \tag{1}$$

where the coefficient A depends on the geometry of the solid body and on the location of the point of interest inside the body. As the φ_1 and φ_2 functions are such that

$$\varphi_1(\tau/t_m) \longrightarrow 1 \quad \text{as} \quad \tau/t_m \longrightarrow 0 \tag{2}$$

$$\varphi_2(h\ell/k) \longrightarrow 1 \quad \text{as} \quad h\ell/k \longrightarrow \infty \tag{3}$$

the two functions are actually correction terms applicable when the $\tau/t_m \longrightarrow 0$ and $h\ell/k \longrightarrow \infty$ conditions cannot be approximated closely enough in the experiment. (Approximate expressions for φ_1 and φ_2 will be presented later.)

The coefficient A can be determined by examining the solution of the following heat conduction problem:

$$\left.\begin{array}{ll} \dfrac{\partial^2 T}{\partial x^2}+\dfrac{\partial^2 T}{\partial y^2}+\dfrac{\partial^2 T}{\partial z^2}=\dfrac{1}{\kappa}\dfrac{\partial T}{\partial t} & \text{when } t>0 \quad (4) \\ T(x,y,z) = T_0 & \text{when } t \le 0 \quad (5) \end{array}\right\} x, y, z \text{ in } V$$

$$\left.\begin{array}{ll} T(x,y,z) = T_p & \text{when } 0 < t < \tau \quad (6) \\ T(x,y,z) = T_0 & \text{when } t > \tau \quad (7) \end{array}\right\} x, y, z \text{ on } S$$

on the condition that $\tau \longrightarrow 0$.

If $\overline{T}(x/\ell,\ y/\ell,\ z/\ell,\ \kappa t/\ell^2)$ represents the solution obtained when the above boundary conditions [Equations (6) and (7)] are replaced by

$$T(x,y,z) = T_0 + 1 \quad \text{when} \quad t > 0,\ x, y, z \text{ on } S \tag{8}$$

then the solution to the problem stated by Equations (4) to (7) is obtained as (*4*)

$$\begin{aligned} T = (T_p - T_0)\,[\overline{T}(x/\ell,\ y/\ell,\ z/\ell,\ \kappa t/\ell^2) \\ - \overline{T}(x/\ell,\ y/\ell,\ z/\ell,\ \kappa(t-\tau)/\ell^2)] \end{aligned} \tag{9}$$

or, in the limit as $\tau \longrightarrow 0$, as

$$T = \tau(T_p - T_0)\,\frac{\partial}{\partial t}\,\overline{T}(x/\ell,\ y/\ell,\ z/\ell,\ \kappa t/\ell^2) \tag{10}$$

Because at the maximum $\partial T/\partial t = 0$, the time coordinate of the maximum temperature (in the limit as $\tau \longrightarrow 0$) can be expressed from the equation

$$\frac{\partial^2}{\partial t^2}\,\overline{T}(x/\ell,\ y/\ell,\ z/\ell,\ \kappa t_M/\ell^2) = 0 \tag{11}$$

and the resulting expression is of the form

$$\frac{\kappa t_M}{\ell^2} = A(x/\ell,\ y/\ell,\ z/\ell) \tag{12}$$

It is logical to select the most important point of the solid, its center of gravity, as the point at which the temperature variation is to be observed. With this choice A becomes a unique function of the shape of the body.

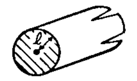
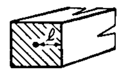
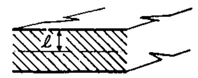
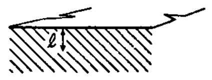
Solid Body		A
Sphere		0.0918
Infinite Circular Cylinder		0.1170
Cube		0.1261
Infinite Square Prism		0.1399
Infinite Slab		0.1666
Semi-infinite Solid		0.1667

Fig. 1. Values of the coefficient *A* (referred to center of gravity locations) for different solid bodies.

In Figure 1 the values of A (referred-to center of gravity locations) are listed for a number of body shapes that may be considered in thermal diffusivity studies. These values were calculated by using in Equation (11) the expressions of $\overline{T}$ developed by Carslaw and Jaeger (*4*) for these shapes. The interpretation of the characteristic dimension is also illustrated in the figure.

The coefficient A for a semi-infinite solid, the value of which was derived earlier (*3*), is also included in Figure 1. By comparing the last two items one may conclude that $A = 1/6$ holds good for any point inside a slab; or in other words that it is not affected by the other surface so long as the characteristic length is taken as the distance between the point and the nearest surface.

As pointed out in connection with Equation (1), φ_1 is a correction term applicable whenever the $\tau/t_m \longrightarrow 0$ condition is not fulfilled closely enough in the experiment.

An expression derived earlier (*3*) for φ_1 for a semi-infinite solid can be approximated as follows:

$$\varphi_1 \approx 1 + \frac{1}{2}\,\frac{\tau}{t_m} \tag{13}$$

which is sufficiently accurate to about $\tau/t_m = 0.15$. In Appendix *A* it will be proved that Equation (13) is applicable to solids of any geometry.

The explicit form of the other correction term, function φ_2, for semi-infinite solids can be evaluated from the graph in Figure 7 of reference *3*, which was arrived at theoretically. (In this plot the product of $\kappa t_m/\ell^2$ and $h\ell/k$ was used as the independent variable instead of the group $h\ell/k$.) This graph indicates that for finite values of $h\ell/k$, $\varphi_2 > 1$. For $h\ell/k > 10$ the following empirical equation seems to be applicable:

$$\varphi_2 \approx 1 + 2/(h\ell/k) \tag{14}$$

The results of many computer calculations indicate that this equation is also applicable to solids of other geometries,* at least when $h\ell/k > 10$. In thermal diffusivity

---

*According to Equation (14) $\varphi_2 \longrightarrow \infty$ as $h\ell/k \longrightarrow 0$. For points at center of gravity locations in simple bodies having three planes of symmetry, this is the expected behavior of φ_2, since $t_m \longrightarrow \infty$ as $h \longrightarrow 0$. For points in a semi-infinite solid, on the other hand, $\varphi_2 \longrightarrow 3$ as $h\ell/k \longrightarrow 0$. This may be seen from Figure 7 of reference *3*.

measurements, one should nevertheless endeavor to make the group $h\ell/k$ as high as possible—at least higher than 30. Methods of achieving this will be discussed.

EXPERIMENT

The cube is undoubtedly the most convenient shape for use as a specimen (see Figure 1). Figure 2*a* illustrates a cubic specimen prepared for thermal diffusivity test. To ensure high output and reduce heat conduction along the wires, very light gauge (say B and S gauge 36) chromel-alumel thermocouples are recommended. The twin-hole porcelain tube of $\frac{1}{8}$-in. O.D. provides reliable electrical insulation for the wires, both inside and outside the specimen, and a strong handle for manipulation. Extreme care should be exercised to ensure that the thermocouple junction is at the center of the specimen and that it is in good contact with the specimen material.

Thirty seconds seems to be a convenient order of magnitude for t_m. The characteristic specimen dimensions corresponding to this value have been calculated for several groups of materials and are listed in Table 1. Smaller specimens can also be used if the laboratory possesses facilities (for example, oscillograph) for recording rapid temperature changes. (It should be remembered that t_m is proportional to the square of the characteristic dimension.)

TABLE 1. CHARACTERISTIC DIMENSIONS OF CUBIC SPECIMENS

(corresponding to $t_m = 30$ sec.)

Group No.	Material group	ℓ, cm.
1	Insulating materials, wood, soils	0.5– 1.0
2	Most building materials	0.9– 2.0
3	Rocks	1.3– 2.8
4	Most ceramics	1.2– 5.2
5	Iron, lead, brass	5.3– 9.0
6	Aluminum, copper, silver	14.0–20.0

Because of the large specimen sizes required, the present method is not particularly well suited for measuring the thermal diffusivity of most metals. Although fast-response recording devices permit the selection of considerably smaller specimens, with the reduction of ℓ the group $h\ell/k$ also diminishes and t_m may become increasingly dependent on the function φ_2 [see Equation (1)], the exact nature of which is not yet known for lower values of $h\ell/k$.

To keep the group $h\ell/k$ at a conveniently high level, it is recommended that the specimen be submerged in a liquid metal bath (primary bath) during the pretesting period (that is, for $t < 0$, when the specimen acquires uniform temperature at the desired level, T_0) and after the application of the temperature pulse (that is, for $t > \tau$). It is immaterial whether the temperature pulse is a heat pulse or a cold pulse, that is, whether $T_p > T_0$ or $T_p < T_0$. In fact, it is very convenient to start the pulse by submerging the specimen (for $0 < t < \tau$) in a bath of the same liquid metal, referred to as the secondary bath, at some lower temperature level, $T_p \ll T_0$. In addition to providing high heat transfer coefficients, liquid metals also offer the advantage that they do not penetrate the pores of the specimen owing to their high contact angles.

In the DBR/NRC laboratory mercury baths are used for room temperature tests. (The experimenter should consult reference *5* concerning the toxic characteristics of liquid metals.) The secondary bath is kept at the freezing point of mercury (−38.9°C.) by means of an alcohol jacket cooled by occasional addition of solid carbon dioxide.

With mercury the effective value of the heat transfer coefficient in the primary bath is of the order of 0.1 cal./(sq. cm.)(sec.)(°C.). This becomes several times higher when the specimen is gently shaken while submerged in the mercury. With $h = 0.1$ and with values of ℓ listed in Table 1, $h\ell/k$ is generally greater than 30 for the first two groups of materials. At such high values of the Nusselt number, φ_2 is sufficiently close to 1 and the effect on t_m of shaking the specimen in the primary bath is not detectable. For materials in the last three groups of Table 1 to achieve sufficiently high Nusselt numbers, mechanical agitation of the primary bath is necessary, even if full size specimens are used.

For measurements above 232°C. liquid tin baths seem to be most convenient. Within the 20° to 232°C. temperature range a low-melting alloy may be selected. (Without proper safety measures mercury must not be used at elevated temperatures.)

When using cubic specimens of sizes listed in Table 1 and mercury baths (primary at $T_0 = 20$°C., secondary at $T_p = -38.9$°C.), it is recommended that the thermocouple output be slightly amplified (say up to ×10) in order to have $\tau/t_m < 0.1$ and still obtain on a 1-mv. recorder a temperature-time record the maximum of which can be clearly determined. [As Equation (10) indicates, the thermocouple output is approximately proportional to the product $\tau(T_p - T_0)$.]

The tests can be repeated as soon as the temperature of the specimen in the primary bath (after the application of the pulse) ceases to show significant variation. This time is approximately eight to ten times t_m, so that if $t_m = 30$ sec. the test can be repeated in approximately 4 to 5 min. Easy repeatability is another advantage of the present method.

In Figure 3 the thermocouple output is shown for a test performed on a limestone rock specimen of cubic shape ($\ell = 1.27$ cm.). During this test the primary bath (mercury, $T_0 = 22$°C.) was agitated with an impeller stirrer. Submersion of the specimen in the secondary bath ($T_p = -38.9$°C.) lasted approximately 1 sec. From the output versus time record (Figure 3) $t_m = 18.4$ sec. Hence $\tau/t_m = 0.054$ and $\varphi_1 = 1.027$. Assuming temporarily that $\varphi_2 = 1.0$, the thermal diffusivity for this rock is obtained according to Equation (1), with $A = 0.1261$ (see Figure 1) as

$$\varkappa = \frac{0.1261 \times 1.027 \times 1.27^2}{18.4} = 0.0114 \text{ sq. cm./sec.}$$

It may be noted that with a different measurement technique (*3*) performed on a 20-cm. by 10-cm. by 10-cm. piece of the same rock, the thermal diffusivity was found to be 0.0115 sq. cm./sec.

The density of the rock is 2.65 g./cu. cm. Its specific heat is estimated at 0.2 cal./(g.)(°C.), so that its thermal conductivity is $k = 0.0114 \times 2.65 \times 0.2 = 0.0060$ cal./(cm.)(sec.)(°C.). Owing to the stirring of the primary bath, the heat transfer coefficient is

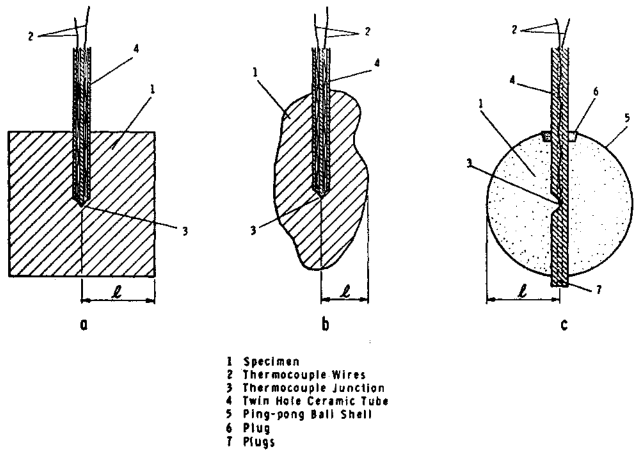


Fig. 2. Specimens for thermal diffusivity tests; (*a*) cubic specimen, (*b*) irregular shaped specimen, (*c*) specimen of some granular material.

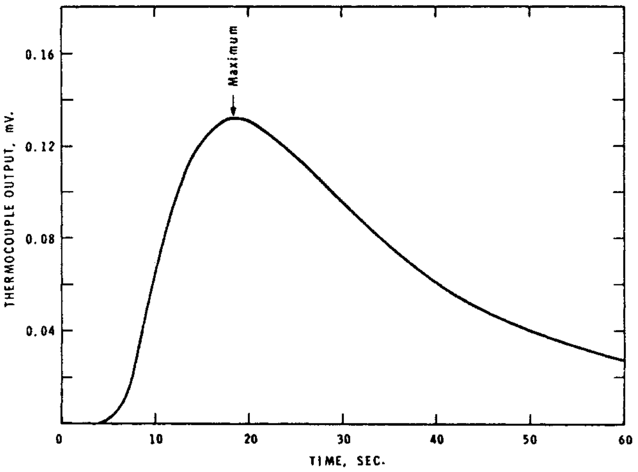


Fig. 3. Thermocouple output in a test performed on a limestone cube.

probably of the order of 1.0 cal./(sq. cm.)(sec.)(°C.); thus $h\ell/k = 1.0 \times 1.27/0.0060 = 212$, which is sufficiently high to validate the assumption that $\varphi_2 = 1.0$.

The accuracy of this peak-time method of measuring the thermal diffusivity of solids depends on several factors: the accuracy of evaluating t_m from the temperature-time record; the accuracy of locating the thermocouple junction in the center of the specimen; whether a good contact has been achieved between the junction and the specimen material; the amount of foreign material (ceramic tube, thermocouple wire) along some short heat flow path; the value of the group, $h\ell/k$, if it is lower than about 30.

Experience shows that t_m can be determined to an accuracy of about 3%. Errors associated with locating the thermocouple junction and achieving good thermocouple-to-specimen contact depend entirely on the care taken in the experiment, and are difficult to assess. (These errors may be reduced by radiographic inspection of the specimens.) Errors associated with the fourth and fifth factors depend, to some extent, on the size of the specimen. To reduce them, the largest available piece of the material should be selected for the specimen, preferably such that $\ell > 1.0$ cm.

For specimens of elongated shape (for example, cylindrical, prismatic, ellipsoidal), it is advisable to introduce the ceramic tube and the thermocouple wires along some long heat flow path. An example is shown in Figure 2*b*.

It is good practice to stir the primary bath well and to check the magnitude of the Nusselt number after the calculation of thermal diffusivity.

Experience gained in the DBR/NRC laboratory indicates that for materials listed in the first four groups of Table 2 an overall accuracy better than ±7% can be achieved if great care is exercised in preparing the specimen and in performing the test.

Whenever possible, the test specimen should be machined or ground to one of the regular shapes shown in Figure 1. If, however, the material is very hard or available only in small pieces, it is possible to test irregular shaped specimens (Figure 2*b*).

Figure 1 reveals that the range of variation of coefficient A is relatively narrow. It is possible, therefore, to estimate its value for shapes other than those listed if only an approximate value of the thermal diffusivity is of interest.

For irregular shaped specimens half of the smallest diameter of the body should be taken as the characteristic dimension ℓ. Consequently, the thermocouple junction has to be located half way between these two governing surfaces (Figure 2*b*) and A should be assessed on the basis of their curvature and the nearness of the other surfaces, making use of the values listed in Figure 1.

To obtain an accurate value of the thermal diffusivity of irregular shaped specimens it is necessary first to determine the value of A for the particular shape and thermocouple location from a separate experiment. A copy of the specimen must be made (using some simple molding technique) from a convenient reference material (for example, beeswax) whose thermal diffusivity has previously been determined to a high degree of accuracy. Into this copy specimen the thermocouple junction is installed in the same way as in the original specimen. After determining t_m for this copy specimen (for $h\ell/k \longrightarrow \infty$), A can be expressed from Equation (1).

Figure 2c illustrates the application of the present method to the measurement of thermal diffusivity of granular materials. A ping-pong ball may be used to provide a spherical shell for the granules. Naturally, the test result is applicable only to a certain degree of compaction of the granular material. It should also be remembered that, in general, there is no simple relationship between the thermal diffusivity of a two-phase system, such as a granular material, and those of the constituent phases (*6* to *9*).

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NOTATION

A = coefficient, dimensionless
h = heat transfer coefficient (in the primary bath), cal./(sq. cm.)(sec.)(°C.)
k = thermal conductivity, cal./(cm.)(sec.)(°C.)
ℓ = characteristic dimension, cm.
S = surface of solid
t = time, sec.
T = temperature, °C.
$\overline{T}$ = unit step response temperature, dimensionless
V = volume bounded by surface S
$\left.\begin{matrix} x \\ y \\ z \end{matrix}\right\}$ = space coordinates, cm.

Greek Letters

κ = thermal diffusivity, sq. cm./sec.
τ = period of heat or cold pulse, sec.
φ = function

Subscripts

m = at the maximum of T
M = at the maximum of T when $\tau \longrightarrow 0$
o = at $t = 0$
p = of the medium starting the pulse

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APPENDIX A: VERIFICATION OF EQUATION (13)

The defining equation for the function φ_1 is obtained by dividing Equation (1) (with $\varphi_2 = 1$, that is, for $h \longrightarrow \infty$) by Equation (12):

$$\varphi_1 = t_m/t_M \tag{1a}$$

At t_m, $\partial T/\partial t = 0$; using Equation (9) one obtains

$$\frac{\partial}{\partial t}\overline{T}(t_m) - \frac{\partial}{\partial t}\overline{T}(t_m - \tau) = 0 \tag{2a}$$

The Taylor series expansion of $\overline{T}(t)$ in the neighborhood of t_M is

$$\overline{T}(t) = \overline{T}(t_M) + \frac{\partial}{\partial t}\overline{T}(t_M)(t - t_M) + \frac{1}{2}\frac{\partial^2}{\partial t^2}\overline{T}(t_M)(t - t_M)^2 + \frac{1}{6}\frac{\partial^3}{\partial t^3}\overline{T}(t_M)(t - t_M)^3 + \ldots \tag{3a}$$

where the third term on the right side of the equation is zero on account of Equation (11). By differentiating

$$\frac{\partial}{\partial t}\overline{T}(t) = \frac{\partial}{\partial t}\overline{T}(t_M) + \frac{1}{2}\frac{\partial^3}{\partial t^3}\overline{T}(t_M)(t - t_M)^2 + \ldots \tag{4a}$$

If this expression, with the retention of the above two terms only, is applied to $t = t_m$ and $t = t_m - \tau$, and the two expressions are substituted into Equation (2*a*), the following equation results:

$$(t_m - t_M)^2 - (t_m - \tau - t_M)^2 = 0 \tag{5a}$$

from which

$$\frac{t_m}{t_M} = 1 + \frac{1}{2}\frac{\tau}{t_M} \tag{6a}$$

By virtue of Equation (1*a*) and of the fact that $t_m \approx t_M$ for small values of τ/t_m, this equation provides proof for the general applicability of Equation (13).

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