CALCULATION OF THE THERMAL CONDUCTIVITY OF POROUS MEDIA

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CALCULATION OF THE THERMAL CONDUCTIVITY OF POROUS MEDIA

WILLIAM WOODSIDE

ABSTRACT

The problem of determining the effective thermal conductivities of porous and other composite materials from the conductivities and volume fractions of their constituents is examined. An approximate equation is derived for the case of a cubic lattice of identical spherical particles in a medium having properties different from those of the particles. This equation is applied to the calculation of the thermal conductivity of snow at different densities in the range 0.10 to 0.48 gm/cc. The effect of water vapor diffusion in snow under a temperature gradient is taken into account by adding a latent heat term to the conductivity value for dry air. Conductivity values for snow, calculated in this manner, are found to agree satisfactorily with experimental data. An equation due to Russell is also shown to give conductivity values for several cellular thermal insulating materials which are in good agreement with experimental values.

INTRODUCTION

Although gases are the poorest heat conductors, by themselves they do not constitute the best heat insulators. If the linear dimensions of a gas-filled space exceed approximately 1 cm, convection makes a large contribution to the total heat transfer across the space. At high temperatures radiation also becomes important. The best heat insulators are therefore solids which contain a high percentage of gas (usually air) in such a way that the individual gas spaces are small enough that convective heat transfer across them is negligible. These include powders and porous and fibrous materials, e.g. silica aerogel, expanded cork, and mineral wool.

It would be advantageous if, in the design and manufacture of thermal insulating materials, the effective thermal conductivity of such composite gas–solid materials could be calculated from the properties and volume fractions of the component substances. Unfortunately the conductivity of a composite material of known composition cannot be arrived at by any simple law of addition of the conductivities of its components.

In the present paper, an equation due to Russell (1935) is applied to several dry cellular insulating materials. A further equation is developed for the thermal conductivity of a medium consisting of a gas in which uniform solid spherical particles are distributed. This is applied to the calculation of the conductivity of snow at different densities, taking into account the heat transfer through snow by vapor diffusion.

PREVIOUS WORK

Gemant (1950) derived a formula for the thermal conductivity of moist soils in terms of moisture content, thermal conductivity of water, and the...
solid particles composing the soil. He considered a spherical grain of soil in contact with six neighbors, i.e. a cubic lattice of uniform spheres. This lattice leads to a porosity value of 47.6%. The closest possible packing arrangement for uniform spheres gives a porosity value of 26%. Porosity values for sandy soils lie between these two extremes, averaging approximately 37%. Gemant assumed the moisture to occupy wedge-shaped rings around the contact points between the spheres, the volume of these rings varying with the moisture content. He then calculated the resistance to heat flow of a unit cube surrounding the soil grain, water rings, and air spaces, assuming parallel heat flow and neglecting the thermal resistance of the air spaces. The resulting thermal conductivities of several soils with moisture contents ranging from 5 to 25% by volume showed surprisingly good agreement with experimental values taken from the literature. Recently Webb (1956) has criticized the neglect of the air-phase resistance and de Vries (1956) has criticized the assumption of parallel heat flow in Gemant's development. Both criticisms are of course valid, yet the close agreement between calculated and experimental conductivities encourages the application of similar approximate methods to other materials.

Russell (1935), in connection with the thermal conductivity of refractory brick, has derived the effective thermal conductivity of a dry porous material from the properties of its component gas and solid for a distribution of uniform pores of cubical shape arranged in a simple cubic lattice. He assumed parallel heat flow and neglected convection across the pores. Russell's equation is

$$\frac{k_s}{k} = 1 - P^{1/3} + \frac{P^{1/3}}{(k_g/k_s)^{2/3} + 1 - P^{2/3}}$$

where the porosity $P = (\rho_s - \rho)/(\rho_s - \rho_g)$ and $0 \leq P \leq 1$. $k$, $k_g$, and $k_s$ are the thermal conductivities of the composite, gas, and solid respectively, and $\rho$, $\rho_s$, and $\rho_g$ are the densities of the composite, gas, and solid respectively.

Maxwell (1873) and Rayleigh (1892) derived by rigorous analysis a formula for the electrical conductivity of a two-phase medium consisting of uniform spheres of one material arranged in cubic array in the second material. This has been extended by Burger (1915) to the case of ellipsoidal particles, and generalized by Eucken (1932) for the case of a multiple medium. De Vries (1952) has successfully applied this theory to the thermal conductivity of wet soils, i.e., three phases: air, water, and solid.

For the case of pores distributed in a solid the original formula of Maxwell and Rayleigh reads

$$\frac{k}{k_s} = \frac{1 - (1 - bk_g/k_s)P}{1 + (b - 1)P}$$

where $b = 3k_g/(2k_s + k_g)$, and porosity $P = (\rho_s - \rho)/(\rho_s - \rho_g)$. Eucken assumes that this equation is valid for values of $P$ as high as 0.5 with good approximation. This equation has also been derived by Kerner (1956).

ANALYSIS

To determine the thermal conductivity of a medium consisting of a cubic
lattice of uniform solid spherical particles in a gas, the following assumptions
are made: (i) the gas spaces are small enough that heat transfer by convection
may be neglected; and (ii) the isotherms are planes perpendicular to the direc-
tion of heat flow.

The second assumption is only valid when \( k_s = k_g \). The larger the value of
the ratio \( k_s/k_g \) the greater will be the errors introduced by this assumption.
Thus the equation developed should give best results for materials whose
values of \( k_s/k_g \) are close to unity.

Fig. 1 is a diagram of a unit cube containing one-eighth of a sphere. The
general case is considered in that the spheres are not assumed to be in contact.
For heat conduction purposes, this is a representative “atom” of a material
consisting of uniform solid spheres distributed in a cubic lattice in a gas. Thus
the thermal resistance of this cube to heat conduction in the direction shown
equals the thermal resistivity of the composite material.

![Representative “atom” of a material consisting of uniform solid spheres distributed
in a cubic lattice in a gas, used for calculation of thermal conductivity.](image)

Let \( R \) denote the radius of the solid sphere. \( R \) will be an equivalent radius in
the case of materials composed of nonuniform and/or nonspherical particles,
e.g. snow. If \( S \) represents the ratio of volume of solid to total volume, then

\[
S = 1 - P = \frac{\pi R^3}{6}
\]

where \( 0 \leq R \leq 1 \), and therefore

\[
R = \left(\frac{6S}{\pi}\right)^{1/3}
\]

where \( P \) is the porosity. The maximum value of \( R \) is unity, and hence the
equation to be developed will only be applicable to granular materials having
porosities greater than or equal to 47.6%. The value of \( S \) may be calculated
from \( \rho, \rho_s, \) and \( \rho_g \) since

\[
S = \frac{(\rho - \rho_g)}{(\rho_s - \rho_g)}.
\]

In Fig. 1 the thermal resistance of the shaded layer composed wholly of gas
is \((1 - R)/k_g\). The thermal resistance of the composite gas–solid layer of thickness \( dx \) is, by the second assumption,
The total thermal resistance of the cube is therefore

$$\frac{dx}{k_z \pi r^2/4 + k_g (1 - \pi r^2/4)}.$$  

The total thermal resistance of the cube is therefore

$$\frac{1}{k} = \frac{1 - R}{k_g} + \int_0^R \frac{dx}{k_z \pi r^2/4 + k_g (1 - \pi r^2/4)}.$$  

Since $r^2 = R^2 - x^2$ and $R = (6S/\pi)^{1/3}$, this results in

$$\frac{k_z}{k} = 1 - \left(\frac{6S}{\pi}\right)^{1/3} \left[ 1 - \left(\frac{a^2 - 1}{a}\right) \ln\left(\frac{a+1}{a-1}\right) \right]$$

where

$$a = \left[ 1 + \frac{4}{\pi (k_z/k_g - 1)(6S/\pi)^{2/3}} \right]^{1/2}, \quad S = \frac{\rho - \rho_g}{\rho_s - \rho_g}, \quad 0 \leq S \leq 0.5236.$$  

It may be shown that when $\rho = \rho_s$, i.e. when $S = 1$, $k = k_z$, and also that when $\rho = \rho_g$, i.e. when $S = 0$, $k = k_g$. Thus the thermal conductivity $k$ of a material of known density may be calculated if the densities and conductivities of its components are known and if it may be approximated by the above model. This formula may also be used to calculate the dielectric constant, electrical conductivity, and magnetic permeability of composite media.

If $R = (6S/\pi)^{1/3} = 1$ is substituted into equation (3), the resulting equation is identical with the one derived and used by Webb (1956) for the calculation of the conductivity of dry soil. If the subscripts $s$ and $g$ are interchanged in equation (3) and the equation rearranged, it becomes the equation for the conductivity of a material consisting of uniform spherical pores distributed in a cubic lattice in a solid.

There are therefore three equations for the calculation of the thermal conductivity of a contingent medium (gas or solid) in which uniform particles (solid or gas) are distributed.

**APPLICATION TO CELLULAR MATERIALS**

Of the above equations, only equation (1) permits the porosity $P$ to have any value between zero and unity. Equation (3) when applied to cellular materials (subscripts $s$ and $g$ interchanged) limits $P$ to the range $0 \leq P \leq 0.52$, and equation (2) to the range $0 \leq P \leq 0.50$. Hence only equation (1) may be applied to the prediction of $k$ for cellular materials since most cellular materials have porosities higher than 0.52. The conductivities of six materials calculated from equation (1) are compared with the experimental values, in Table I. Pratt and Ball (1956) measured the thermal conductivity of a steel shot aggregate concrete and compared the measured value (13.8 B.t.u. in./hr ft² °F) with the theoretical estimate given by Maxwell’s formula (equation (2)) above. The value of $P$, i.e. the fraction of the total volume occupied by the steel shot, was given as 0.56 and the calculated value of $k$ was 11.8 B.t.u. in./hr ft² °F. The conductivity of this concrete may also be calculated from Russell’s equation (1) where $k_g$ now represents the conductivity of steel. This results in a value for $k$ of 13.85 B.t.u. in./hr ft² °F in agreement with the experimental value. The value of $k_s/k_g$ for this material is 0.0082.
TABLE I

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (lb/cu. ft)</th>
<th>Porosity (P)</th>
<th>(k_s/k_g)</th>
<th>Calc. cond. (k) (B.t.u. in./hr ft(^2) °F)</th>
<th>Measured cond. (B.t.u. in./hr ft(^2)°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellular glass</td>
<td>9.0</td>
<td>0.944</td>
<td>34.7</td>
<td>0.402</td>
<td>0.402</td>
</tr>
<tr>
<td>Cellular rubber</td>
<td>4.9</td>
<td>0.946</td>
<td>12.3</td>
<td>0.260</td>
<td>0.28</td>
</tr>
<tr>
<td>Expanded ebonite</td>
<td>6.0</td>
<td>0.897</td>
<td>5.8</td>
<td>0.237</td>
<td>0.23</td>
</tr>
<tr>
<td>Expanded polystyrene*</td>
<td>2.0</td>
<td>0.971</td>
<td>5.4</td>
<td>0.191</td>
<td>0.220</td>
</tr>
<tr>
<td>Cellular cellulose acetate*</td>
<td>5.5</td>
<td>0.933</td>
<td>9.7</td>
<td>0.204</td>
<td>0.305</td>
</tr>
<tr>
<td>Cellular polyvinyl chloride*</td>
<td>3.5</td>
<td>0.931</td>
<td>6.5</td>
<td>0.206</td>
<td>0.23</td>
</tr>
</tbody>
</table>


Thus Russell's equation results in calculated values for the thermal conductivity of certain composite materials which are in fair agreement with the measured values. Contrary to expectation the agreement does not appear to bear any simple relationship to the value of \(k_s/k_g\).

APPLICATION TO SNOW

Snow is a powdery substance composed of ice crystals and air, and hence the above equations may be used for the calculation of its thermal conductivity at any density since the properties of ice and air are known. However, in snow and other moist materials, there is an additional mechanism by which heat may be transmitted. When a temperature gradient is imposed upon a layer of snow, a corresponding vapor pressure gradient is also set up. Thus water vapor may evaporate from one layer of ice crystals and condense on another. In so doing the heat removed from the first layer as latent heat of sublimation is transferred to the second layer. The water vapor traverses the air space between the two layers by a process of diffusion. Since this process occurs only in the air spaces between ice crystals, this second heat transfer mechanism may be accounted for by using an equivalent thermal conductivity for the air which includes a term representing the contribution of water vapor diffusion.

Yosida (1955) proposed that for the air in snow

\[
(4) \quad k_{\text{eff.}} = k_{\text{air}} + aD_0L
\]

where

- \(k_{\text{eff.}}\) = effective conductivity of air in snow, taking account of water vapor diffusion, cal/cm sec °C,
- \(k_{\text{air}}\) = thermal conductivity of dry air, cal/cm sec °C,
- \(a\) = rate of increase of vapor density of ice with temperature, g/cc °C,
- \(D_0\) = diffusion coefficient of water vapor through air, cm\(^2\)/sec,
- \(L\) = latent heat of sublimation of ice, cal/g.

Yosida took the following values at 0° C, \(k_{\text{air}} = 5.3 \times 10^{-5}\), \(a = 0.39 \times 10^{-6}\), \(D_0 = 0.22\), and \(L = 676\) in the units given above, to give a value for \(aD_0L\)
of $5.8 \times 10^{-5}$ cal/cm sec °C. Yosida concluded that the air in snow has an effective thermal conductivity twice its normal value.

Krischer (1941) has shown that the effective thermal conductivity of the air in the pores of a material whose pore walls are wetted, may be expressed by

$$k_{\text{eff.}} = k_{\text{air}} + \frac{D}{R_s T} \left( \frac{P}{P - P_s} \right) \frac{dP_s}{dT} \cdot L \text{ cal/cm sec °C}$$

where

$$D = \text{diffusion coefficient of water vapor through air, cm}^2/\text{sec},$$
$$R_s = \text{gas constant of the water vapor, g-cm/g},$$
$$T = \text{absolute temperature, °K},$$
$$P = \text{air pressure, g/cm}^2,$$
$$L = \text{latent heat of evaporation, cal/g},$$
$$P_s = \text{partial pressure of water vapor, g/cm}^2.$$

Krischer experimentally studied the diffusion between the wetted walls of a greatly enlarged model of a pore, under the influence of temperature gradients. From his experiments the following value for the diffusion coefficient resulted,

$$D = \frac{230}{P} \left( \frac{T}{273} \right)^{2.5}.$$

Equation (5), when applied to the case of the air in snow, at 0° C gives

$$k_{\text{eff.}} = k_{\text{air}} + 6.24 \times 10^{-5} \text{ cal/cm sec °C}.$$ Taking the latest value for $k_{\text{air}}$ at 0° C as $5.77 \times 10^{-3}$,

$$k_{\text{eff.}} = 12.01 \times 10^{-3} \text{ cal/cm sec °C} = 0.029 \text{ B.t.u./hr ft °F}.$$

The thermal conductivity of snow at 0° C and at various densities may now be calculated with the aid of equations (1), (2), and (3). The results are shown in Table II.

**TABLE II**

**Comparison of Calculated and Experimental Conductivities of Snow**

<table>
<thead>
<tr>
<th>Density of snow, g/cc</th>
<th>Thermal conductivity at 0° C, cal/cm sec °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean of exp. values</td>
</tr>
<tr>
<td>0.10</td>
<td>$0.155 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.20</td>
<td>$0.330 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.30</td>
<td>$0.505 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.40</td>
<td>$1.04 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

In Table II. In the calculations the following values were taken for $\rho_s$, $\rho_a$, $k_s$, and $k_a$ at 0° C:

$$\rho_s = \rho_{\text{sw}} = 0.917 \text{ g/cc},$$
$$\rho_a = \rho_{\text{air}} = 0.0013 \text{ g/cc},$$
$$k_s = k_{\text{sw}} = 5.33 \times 10^{-3} \text{ cal/cm sec °C (Jakob 1949)},$$
$$k_a = k_{\text{air}} = 1.20 \times 10^{-1} \text{ cal/cm sec °C}.$$
The experimental values for the thermal conductivity of snow, which were averaged to give the values shown in the second column of Table II, are those of Kondrat'eva, Yosida, Abel's, Jansson, and Devaux. The experimental methods and results of these investigations are fully described by Yosida (1955) and Kondrat'eva (1954).

The values calculated from equation (3) agree with the experimental values much better than those calculated from equations (1) and (2) for the greater part of the above density range. Hence in the following, calculated values for the thermal conductivity of snow will refer to those calculated from equation (3).

The values of thermal conductivity shown in the fourth column of Table III are those calculated from equation (3) neglecting the contribution of water vapor diffusion to the heat transfer through snow, i.e. taking \( k_v = k_{at} = 0.577 \times 10^{-4} \text{ cal/cm sec } ^\circ\text{C} \). These values are thus the fictitious "pure" thermal conductivities which snow would possess at the densities shown, if there were no vapor diffusion mechanism. The last column of the table shows the percentage contribution to the thermal conductivity of snow made by this mechanism.

### Table III

<table>
<thead>
<tr>
<th>Density, g/cc</th>
<th>( S = 1 - P )</th>
<th>Thermal conductivity cal/cm sec (^\circ\text{C})</th>
<th>Conductivity neglecting water vapor transfer cal/cm sec (^\circ\text{C})</th>
<th>% contribution of vapor transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.1077</td>
<td>0.238 \times 10^{-3}</td>
<td>0.125 \times 10^{-3}</td>
<td>47.6</td>
</tr>
<tr>
<td>0.20</td>
<td>0.2171</td>
<td>0.355</td>
<td>0.192</td>
<td>45.9</td>
</tr>
<tr>
<td>0.30</td>
<td>0.3262</td>
<td>0.537</td>
<td>0.306</td>
<td>43.0</td>
</tr>
<tr>
<td>0.40</td>
<td>0.4355</td>
<td>0.901</td>
<td>0.576</td>
<td>36.0</td>
</tr>
<tr>
<td>0.45</td>
<td>0.4901</td>
<td>1.277</td>
<td>0.935</td>
<td>26.8</td>
</tr>
<tr>
<td>0.48</td>
<td>0.5228</td>
<td>1.666</td>
<td>1.445</td>
<td>13.2</td>
</tr>
</tbody>
</table>

The calculated thermal conductivity increases with density, the rate of increase being larger at the higher densities. The percentage contribution of vapor flow to the conductivity decreases as density increases. Both these results are caused by the fact that as density increases, the fraction of air present decreases.

At densities higher than 0.48 g/cc, i.e. at porosities lower than 47.7\%, equation (3) cannot be applied to calculate thermal conductivities, since at the corresponding value of \( S (= 1 - P) \), the value of \( R \) becomes unity, and the assumed solid spheres touch. The ice crystals in snow are not solid uniform spheres, but the agreement between the calculated and measured thermal conductivities indicates that they may be so represented for heat conduction purposes.

The above results are shown graphically in Fig. 2 where \( k \), the thermal conductivity of snow, is plotted against its density \( p \). The heavy full curve represents the variation of \( k \) with \( p \) calculated from equation (3), and the dashed curve the calculated variation omitting the vapor flow contribution.
The curves numbered 1 to 5 represent the experimental results of Kondrat'eva, Devaux, Jansson, Yosida, and Abel's. The results obtained by Abel's, expressed by the empirical relationship

\[ k = 6.8\rho^2 \times 10^{-3} \text{ in c.g.s. units}, \]

appear to be the commonly accepted values. Since the agreement between the experimental results is poor, the agreement between the calculated and experimental results may be considered satisfactory.

CONCLUSION

The application of equation (3) to the calculation of the thermal conductivity of snow, taking into account vapor diffusion, was straightforward, since the air in snow is at all times effectively saturated with water vapor, so that \( P \), in equation (5) is the saturation water vapor pressure over ice. The application to moist porous materials would be more complicated since the vapor pressure conditions in this case are less well-defined.

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