

# Theoretical and Practical Aspects of the Thermal Conductivity of Soils and Similar Granular Systems

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The thermal conductivity of soils and allied phenomena play a major role in several engineering fields. A few examples are the frost problem in highway engineering, the dissipation of the Joule heat from buried electric cables, and the thermal exchange in heat pump systems.

It is not too difficult to measure actual heat conductivities of particular soils at specific moisture, density, and structural conditions. However, the values obtained can be used for purposes of prediction with regard to the normal weather – and seasonally conditioned changes in soil properties only by means of adequate hypotheses and theories. The more closely the theoretical concepts depict the actual mechanisms of heat transmission in soils, the fewer heat conductivity measurements must be made and the more useful to the engineer are those that are made.

Soils normally consist of solid, liquid and gaseous phases, and the mechanism of heat transmission differs for these different states. Therefore, the paper discusses thermal transmission in solid, liquid and gaseous phases before treating the more complex soil systems. The various theoretical and empirical equations available for the simple and complex systems are analyzed and results obtained with them are compared with actual experimental data.

The inadequacy of the present theories concerning thermal conductivity in soils is pointed out and ways toward correcting some of the deficiencies are indicated.

●SOILS ARE composed of solid, liquid and gaseous matter. In an undisturbed condition the solid particles and the liquid and gaseous phases in a grown soil are arranged in a definite structure or fabric, while in a completely disturbed condition distribution of particles and phases is random. The actual condition of most soils that are of interest to the engineer lies between these two extremes.

The thermal conductivity of a soil depends on the thermal conductivities of its solid, liquid and gaseous components, their volume proportions and their arrangement or structure. The structure itself is influenced by the size, shape and gradation of the components. Generally, solids conduct heat better than liquids, and liquids better than gases. It is important, therefore, whether in a soil structure the well conducting solid particles are in intimate contact with each other or whether and to what extent they are separated from each other by intervening liquid and gaseous phases.

In dispersed systems that are constituted of solid, liquid and gaseous phases, the transition from one phase to another is usually not abrupt. Rather, a transition zone is formed. This is especially important for the solid-liquid interfaces, in our case: the interface between soil particles and surrounding water films. The thickness and structure of this interaction zone are functions of the polar character of both, the solid surface and the surrounding liquid, and also of the temperature. This temperature dependence is the main cause for the transport of liquid in porous hydrophilic systems subjected to temperature gradients. In addition, diffusion and distillation may occur through the gaseous phase from locations of higher to those of lower temperatures. Hence, application of a thermal gradient to moist soils causes not only a heat transfer

through the different phases but also a mass transfer of the liquid in either or both, film and gaseous phases. Partial or complete removal of the liquid by these processes at a particular location in a soil lowers the thermal conductivity and also the heat capacity per unit volume of the soil at this location.

Considering the great complexity of heat transfer in natural soils one could be tempted to despair of the possibility of any significant practical results to be gotten from fundamental theoretical considerations. A theory covering all phenomena involved would be too cumbersome to handle, while one simple enough to be handled mathematically could not be expressive of the events actually taking place in a soil subjected to a temperature gradient. Such reasoning misses the most important point. It is better to have partial knowledge than none at all, as long as one realizes that it is partial. Also, all theory, even the best founded and simplest, proceeds by successive approximation, by starting with a simple picture and refining it when and as needed, employing physical parameters whenever it is easier to measure than to calculate them from basic assumptions. Even if we should never be able to do without actual determination of certain physical parameters, such as measured thermal resistivities, the mental discipline acquired and the creative imagination developed in pushing the theory as far as possible may pay a thousandfold by indicating ways and means to achieve desired practical ends. These ends are not only to predict thermal resistivities of soils from their composition and constitution, but also, and more importantly, to develop economical methods for maintaining the thermal behavior of soils at a level that is optimal for the intended purpose.

For the reasons given, the present report on the theory of heat transmission in soils and similar porous systems has been prepared. The treatment proceeds from the simpler to the more difficult aspects of the general problem.

### THE NATURE OF HEAT

Heat is a form of energy. As in the case of other forms of energy a definite amount of heat can be expressed as the product of a capacity factor and an intensity factor. The former is the heat capacity, the latter the absolute temperature. The heat capacity per gram of a material is called its specific heat, that for the atomic weight in grams of an element is the atomic heat, and that for a gram mol of a compound is the mol heat. The total heat content  $U$  of a system possessing the heat capacity  $C$  and being at an absolute temperature  $T$  is expressed by

$$U = \int_0^T C dT$$

$C$  itself is a function of the temperature.

The concept of heat as a form of motion of the ultimate particulate components of matter dates back to the ancients. Scientific proof of the essential validity of this concept was furnished by Rumford (Phil. Trans. 1798) and Davy (1799). This, however, was just a beginning. Only after Laplace, Dalton, Gay-Lussac, Dulong and many others had made their important contributions to the knowledge of the properties of gases, was it possible for Joule, Waterstone, Krönig and Clausius to found the kinetic theory of heat which was brought to maturity by Maxwell and Boltzmann.

The basic assumptions of this theory are amazingly simple. The experimentally found relationships between temperature, pressure and volume of normal gases led to the concept of the "ideal gas." The properties of the ideal gas are approached by many actual gases at normal temperature. The corresponding relationships can be expressed by the equation:

$$PV = nRT, \text{ in which}$$

$P$  = pressure  
 $V$  = volume  
 $n$  = number of moles of gas  
 $T$  = absolute temperature  
 $R$  = gas constant.

Both sides of the equation have the dimensions of energy or work, while  $R$  has the dimension of a specific heat or heat divided by temperature.

Numerical values for the specific heats and the mole heats of gases depend on whether they are determined at constant volume or at constant pressure. If determined at constant pressure, the volume will be increased and work will be done against the outside pressure. This work uses up heat energy. The difference between the mole heat at constant pressure  $C_p$  and that at constant volume  $C_v$  equals  $R = 1.985$  calories. The ratio  $C_p/C_v$  for mono-atomic gases is  $5/3$  or  $1.667$ ; the more complex the gas molecules become, the larger becomes  $C_v$  and the smaller becomes  $C_p/C_v$ . Also, the heat capacities of mono-atomic gases are relatively independent of temperature.

These gases have mole heats approximating  $\frac{3R}{2}$  or 3 calories while gases having molecules composed of two and more atoms have temperature coefficients that increase with increasing complexity of the molecules. Between  $0^\circ$  and  $1,000^\circ$  C, the mol heats of  $N_2$ ,  $O_2$ ,  $CO$  and  $HCl$  increase from about 5 calories to 6.2, while those of  $H_2O$ ,  $CO_2$  and  $SO_2$  start with about 6.7 and almost double in the given temperature range. From this type of evidence the theory concludes as follows:

The mole heat at constant volume, i. e., the amount of heat required to raise the temperature of one mole by one degree absolute, depends upon the number of different mechanical movements the individual molecules can make, or on the number of motion mechanisms in which they can invest energy. For each type of movement the energy  $\frac{R}{2}$  is assigned per mole. Thus a mono-atomic gas, the atoms of which have no other possibilities than moving in the 3 dimensions of space, has a mole heat of  $3\frac{R}{2}$  or about 3 calories. Diatomic molecules add to these 3 possible translatory movements rotations around two axes which results in mole heats of  $5\frac{R}{2}$ , while molecules with even more atoms have possible rotations about 3 axes with resulting mole heats of  $6\frac{R}{2}$  or about 6 calories. This assignment of  $\frac{R}{2}$  for each possible type of mechanical movement is called the equipartition theorem. In addition to the described types of movement there is the possibility especially at elevated temperatures for the various atoms in di- tri- and polyatomic molecules to oscillate with respect to each other. This again increases the mol heats.

The amazing thing about the kinetic gas theory is not that it has its definite limitations but rather how much can be done with a few simple assumptions, based, of course, on experimental results, and their logical mathematical development. The mechanical heat theory holds well for ideal gases and dilute solutions, but it becomes increasingly and often forbiddingly complex in the case of solids and liquids. Aside, however, from the unwieldy complexity for many material systems, the purely mechanistic heat theory has its definite theoretical limitations. These become apparent when the thermal kinetic movements have grown sufficiently intensive to affect the electric constituents of the atoms and molecules in a way to result in electromagnetic phenomena and in the emission of electro-magnetic waves. Heat as a form of energy is, of course, also subject to Planck's quantum theory.

The modern theory of the specific heat of gases which takes the electromagnetic phenomena into account is largely due to Albert Einstein while that for the specific heat of solids has been developed mainly by Debye. The greatest difficulties to theoretical treatment are still offered by the liquids.

So far, main consideration has been given to the capacity factor of heat energy while the intensity factor, temperature, has been neglected. According to the kinetic theory of gases the absolute temperature is directly proportional to the kinetic translatory

energy present in the gaseous system under consideration. It is also a measure of the intensity of the total molecular movement in a gas. According to the kinetic theory of the specific heat the total translatory energy of one mole of a gas at an absolute temperature  $T$  equals  $\frac{3R}{2} T$ . Recalling the ideal gas law  $PV = RT$  and the fact that  $PV$  also derives from the translational kinetic energy of a mol of gas at temperature  $T$ , one wonders why the proportionality constant on the right side of the equation is  $R$  and not  $\frac{3R}{2}$ . This can be explained in the following manner:

The pressure on the walls of a gas container is assumed to be the result of perfectly elastic recoil of the molecules hitting the walls at a particular moment. The molecules fly off the wall with the same speeds they had before the collision; that means they still possess their previous kinetic energies although the direction of movement has been reversed. However, there was an exchange of momentum with the wall which has received twice the momentum of the colliding particles. The pressure is, therefore, a function of twice the kinetic energy of the hitting particles or for one mol equal to  $f(3RT)$ . Assuming that only one-third of the molecules in a mol hit the walls of the containing vessels at a particular moment the function becomes  $f(RT)$  or, as Boltzmann has shown in an exact presentation, the proportionality constant becomes equal to  $R$ . This is in agreement with the experimentally found gas law. According to the latter there exists no energy at absolute zero ( $T = 0$ ); this means that all motion has stopped at this point.

In his derivation of the law of heat radiation from ideal black bodies Max Planck assumed that the walls of the hollow sphere representing the ideal black body consisted of oscillators. In order to accommodate the available experimental data Planck postulated that the oscillators involved could not take up energy continuously in arbitrary small increments but only in fixed units, called quanta. The magnitude of the quantum of energy  $\epsilon$  depends on the oscillator frequency  $\nu$  according to

$$\epsilon = h \nu \quad (2)$$

where  $h$  = Planck's constant (dimensions = Energy x time).

The average energy  $\bar{\epsilon}$  of an oscillator is derived to be:

$$\bar{\epsilon} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{1}{2} h\nu \quad (3)$$

where  $e$  = the base of natural logarithms  
 $k$  = the Boltzmann constant =  $\frac{R}{N}$

$R$  = universal gas constant  
 $N$  = Avogadro's number  
 $T$  = absolute temperature

This equation shows that even at the absolute zero temperature ( $T = 0$ ) the oscillator possesses a residual energy of

$$\bar{\epsilon}_0 = \frac{1}{2} h\nu \quad (4)$$

Equation (3) yields the classical value of  $\bar{\epsilon} = kT$  when  $h\nu$  becomes much smaller than  $kT$ . At the present time, the quantum theory is accepted not only for radiant energy but also for all other forms of energy.

## HEAT TRANSMISSION

The second law of thermodynamics is concerned with the degeneration of energy and the increase of the entropy. In accordance with this law, energy tends to go from a higher to a lower level of intensity. In the case of heat energy, this means that heat will flow from locations of higher to those of lower temperature. To achieve this end,

heat, as any other energy, will employ all ways and means at its disposition, though to different extent at different energy levels and depending on the composition and structure of the systems involved. Normally, there are available for heat transfer the following mechanism: radiation, conduction and convection.

### Radiation

In heat emission by radiation the absolute temperature of the radiating body is the most important single factor. Radiation is the transportation of heat through empty spaces or transparent media. Total radiation follows the relation found by Stefan and Boltzmann for radiation of a perfectly black surface, viz:

$$q = \sigma AT^4$$

where

$q$  = time rate of energy flow

$A$  = the area through which the energy flows

$T$  = absolute temperature

$\sigma$  = a natural constant known as the constant of black body radiation.

For imperfect black bodies  $\sigma$  is replaced by another factor. The commonly used value for  $\sigma$  in the above equation is  $4.96 \times 10^{-8}$  in the c. g. s. system (43).

### Conduction

Generally, heat conduction means the exchange of heat between continuous bodies or parts of a body. According to the kinetic theory, heat conduction is due to elastic impacts of molecules in gases, to longitudinal oscillations in solids which do not conduct electricity and oscillations plus movement of electrons in metals. The basic law for heat conduction in one dimension, also called Fourier's equation, is given by:

$$q = k \frac{A}{L} \Delta T,$$

where

$q$  = energy flowing through area  $A$  per unit time when a temperature drop  $\Delta T$  exists over a length  $L$

$k$  = coefficient of thermal conductivity, also called internal heat conductivity or just thermal conductivity.

### Convection

Heat convection is the transportation and exchange of heat by mixing or interflow of multimolecular masses of liquids and gases that are at different temperatures. It is controlled by the laws of fluid dynamics as well as by those of heat conduction.

Newton in 1701 recommended the equation

$$q = h A \Delta T$$

to describe the transfer of heat  $q$  per unit time between a surface and a contacting fluid for a contact area  $A$  and a temperature difference  $\Delta T$ ;  $h$  is called the surface coefficient, film coefficient or coefficient of heat transfer. However, this equation is not exact and is more a definition of  $h$  than a law (43).

## HEAT TRANSFER

Heat is propagated through space or different media in various manners depending on the type, composition and structure of the propagating substance.

(a) Heat transfer through a vacuum: the only way that heat can be propagated through a vacuum is by radiation. Radiation of heat being the same as light radiation, follows the laws of optics, both with regard to its geometry and dynamics, in addition to the previously mentioned energy radiation laws.

(b) Heat transfer through gases: the heat may be transported by radiation (if the gas is colorless), convection or conduction.

(c) Heat transfer through liquids: as in the case of gases, heat may be transferred by radiation (transparent liquid), convection and conduction.

(d) Heat transfer through solids: in dense transparent solids, radiation may contribute to the heat transfer. But, the most important mechanism at low temperatures is heat conduction. In porous or granular solids convection of gases or liquids in the pores contribute to the heat transfer. At very high temperatures, there will be internal heat propagation by means of radiation from pore wall to pore wall, which increases the apparent heat conductivity.

## HEAT CONDUCTION IN HOMOGENEOUS SUBSTANCES

### Conduction in Gases

According to the kinetic theory, the pressure of a gas is due to the force of the impacts of the gas molecules on the container wall. The temperature is proportional to the average translational kinetic energy of the molecules. The kinetic energy and its various manifestations such as pressure, temperature, specific heat, compressibility and others, will therefore be the dominating factors with respect to mass and heat transfer in gases.

The ideal gas is pictured as consisting of molecules, whose volume is no small as to be negligible in comparison with the total volume occupied by the gas. The molecules are conceived as elastic spheres with no attraction or repulsion forces between them. The ideal gas law and the corresponding thermodynamical treatments can be applied to this situation. If the actual volumes of the molecules and the interaction between them cannot be neglected changes in the ideal gas laws become necessary. The modifications by Van der Waals, Berthelot, Kammerlingh-Onnes and Beattie and Bridgeman are especially valuable.

It has been found that the coefficients of viscosity  $\mu$ , thermal conductivity  $k$ , and diffusion  $D$  are proportional to one another. Within the normal range of pressures viscosity, thermal conductivity and diffusion are independent of the pressure. This is in agreement with the kinetic gas theory.

Consider two layers of gas molecules a distance  $\delta$  apart where  $\delta$  is the mean free path of a molecule. If the velocity gradient in the gas is given by  $\frac{du}{dx}$ , one layer of molecules will be moving relative to the other layer with a velocity  $\delta \frac{du}{dx}$ . Because of the thermal motion of the molecules in both layers, some molecules will be passing from the faster moving layer to the slower one, and vice versa. The molecules in the faster moving layer have a higher kinetic energy and those that pass over to the slower layer will transmit their excess energy to the new companion molecules of the slower layer, thereby increasing the kinetic energy of the slower layer. The reverse will happen when molecules from the slower layer pass over to the faster moving layer. The slow molecules increase their kinetic energy while the average kinetic energy of the faster layer is decreased. The over-all effect is a tendency to equalize the velocities of the two layers; the resulting physical phenomenon is that of viscosity.

A molecule of mass  $m$  in traveling from a faster layer to a slower layer will transport the momentum  $m\delta \frac{du}{dx}$ . If there are  $n$  molecules per cc and their average speed

is  $\bar{c}$ , the total momentum transported per second is  $\frac{1}{3} nm\bar{c}\delta \frac{du}{dx}$ . Newton's law of viscous flow gives:

$$\text{Momentum change} = \text{Frictional force} = \mu \frac{du}{dx}$$

$$\mu \frac{du}{dx} = \frac{1}{3} nm\bar{c}\delta \frac{du}{dx}$$

$$\mu = \frac{1}{3} nm\bar{c}\delta$$

$$\mu = \frac{1}{3} \rho \bar{c}\delta$$

where

$\rho = nm$ , the density of gas.

The factor  $\frac{1}{3}$  derives from the assumption that about one-third of the molecules is moving from one layer to the other. The value of  $\frac{1}{3}$  (0.35 according to Boltzmann) is too low and a value of  $\frac{2}{3}$  should be used.

When the value of  $\delta$ , the mean free path, is substituted in the equation the coefficient of viscosity becomes:

$$\mu = \frac{m\bar{c}}{3\sqrt{2}\sigma^2\pi}$$

where

$\sigma$  is the molecular diameter.

The last equation is independent of the pressure. This situation is only true for perfect gases. In the case of imperfect gases the equation fails and the viscosity increases with the density of the gas.

Because the temperature  $T$  is proportional to the kinetic energy and, therefore, to the square of the average speed ( $\bar{c}^2$ ) of the molecules, it follows from the last equation that the viscosity  $\mu$  increases linearly with  $\sqrt{T}$ . However, real molecules are not solid hard spheres but must be regarded as surrounded by force fields. The higher the speed of the molecules (higher temperatures), the further they penetrate the force fields of the molecules which they encounter. A correction for the effective cross-section has been applied by Sutherland (93) which has the following form:

$$\sigma^2 = \sigma_\infty^2 \left(1 + \frac{C}{T}\right)$$

where  $\sigma_\infty$  and  $C$  are constants,  $\sigma_\infty$  is the value of  $\sigma$  as  $T$  approaches  $\infty$ , or the diameter of the hard core of the molecules,  $C$  the Sutherland constant, and  $T$  the absolute temperature. Numerical values for the dynamic viscosity of a few gases are given in Table 1. Bromley and Wilke (11) showed how the viscosities of various gases may be

TABLE 1

NUMERICAL VALUES OF THE DYNAMIC VISCOSITY OF SOME CASES AT  
ATMOSPHERIC OR LOWER PRESSURES

Gas	Chemical Formula	Dynamic Viscosity in Poise $\times 10^{-8}$					
		-200°C	-100 °C	0 °C	100 °C	200 °C	300 °C
Hydrogen	H <sub>2</sub>	33	61	85	103	120	138
Nitrogen	N <sub>2</sub>		114	165	208	246	
Air	-		120	171	218	259	296
Oxygen	O <sub>2</sub>		132.5	193	247	295	
Carbon Dioxide	CO <sub>2</sub>			139	188		

computed at various temperatures making use of tables of collision integrals published by Hirschfelder, Bird and Spotz (41). These collision integrals are based on an improved kinetic theory developed by Chapman and Cowling (16). An assumption is made for the energy of interaction potential between molecules, and it is possible to calculate accurately the viscosity for non-polar smooth spherical molecules.

The effect of pressure and temperature on the viscosities of gases has been investigated by Uyehara and Watson (96) on the basis of the law of corresponding states. They presented values of reduced viscosity against reduced temperatures for constant reduced pressure lines. Grunberg and Nissan (39) assumed that in a highly compressed fluid transfer of momentum may occur by two mechanisms, a translational type as in gases and a "vibrational" type as in liquids. The viscosity is correlated with reduced temperature and reduced density. It is claimed that the accuracy is in the order of 10 percent and that the method is applicable to highly compressed gases and to liquids

near the critical point. Comings and Egly (18) described a graphical method based also on the concept of corresponding states, to determine the viscosity of pure gases and of vapors at high pressure from known critical temperature and pressure data and viscosity values at atmospheric pressure. Othmer and Josefowitz (69) showed that at constant temperature the viscosity of a gas plotted against the kinematic pressure and divided by the density gives straight lines on an arithmetic plot.

Viscous flow involves the transfer of momentum across a momentum gradient, thermal conductivity the transfer of kinetic energy across a kinetic energy gradient and diffusion the transportation of mass across a concentration gradient. The concept employed for explaining viscous behavior of gases can also be applied to their thermal conductivities. The picture is that of molecules with higher kinetic energies moving to regions of lower kinetic energy (and vice versa) and exchanging energy by collisions. The basic relationship between the coefficient of thermal conductivity  $k$  and that of the viscosity  $\mu$  is given by:

$$k = \epsilon c_v \mu,$$

in which:

$$\begin{aligned} \epsilon &= \text{factor with values between 2.5 and 1.0} \\ c_v &= \text{specific heat of the gas at constant volume} \end{aligned}$$

According to the equipartition theorem the same fraction of the specific heat is contributed by each degree of freedom. The respective theoretical mol heats are:

$$\begin{aligned} \text{For monatomic gases} & \quad c_v = \frac{3}{2} R \\ \text{Diatomic gases} & \quad c_v = \frac{5}{2} R \\ \text{Tri- and more- atomic gases} & \quad c_v = \frac{7}{2} R, \end{aligned}$$

$R$  being the universal gas constant. The factor  $\epsilon$  may be considered as a measure of the effectiveness with which a molecule carries and disposes of its energy load by collision. According to Eucken (29) molecules possessing higher energies transfer energy faster than molecules possessing smaller energies. It has also been considered whether energies of rotation and oscillation will be reduced on impact in the same proportion as the translational energies. Chapman (15) calculated a value of  $\epsilon = 2.5$  for monatomic, spherical molecules with no central forces between them. For molecules possessing more than one atom, Eucken (27) obtained the following equation by considering energies of rotation and oscillation independent of the energy of translation.

$$\epsilon = \frac{4.47}{c_v} + 1$$

Incorporating the expressions for the viscosity and the Sutherland formula it follows (43) that:

$$k = \epsilon c_v \frac{B \sqrt{T}}{1 + \frac{C}{T}};$$

or:

$$k = \frac{BF(1 + GT) \sqrt{T}}{1 + \frac{C}{T}}$$

since within practical ranges:

$$\epsilon c_v = F(1 + GT).$$

With appropriate values for  $B$ ,  $F$ ,  $G$ ,  $C$ , this equation gives thermal conductivity coefficients with an accuracy of 0 to 6 percent in the range - 180 deg C to 200 deg C. Table 2 gives some measured thermal conductivities of the most common gases.

It was pointed out previously that diffusion, viscous flow and heat flow of gases follow the same mechanism according to the kinetic theory. The previous considerations were for conditions of pure gases. It is obviously desirable to be able to predict



physical properties such as diffusion constants, coefficient of viscosity and thermal conductivity for gas mixture when the composition and properties of the pure substances are known. For the diffusion coefficient  $D'_A$  of gas A with respect to a mix-

TABLE 2  
THERMAL CONDUCTIVITY OF SOME GASES

Gas	Molecular Weight		Thermal Conductivity in $\frac{\text{watt}}{(\text{sq cm}) (^\circ\text{C per cm})} \times 10^{-4}$				
			-200°C	-100°C	0°C	100°C	200°C
Hydrogen	H <sub>2</sub>	2	5.0	11.6	17.1	21.4	-
Nitrogen	N <sub>2</sub>	28	.71	1.62	2.44	3.03	
Air	-	29	-	1.62	2.44	3.08	
Oxygen	O <sub>2</sub>	32	.62	1.62	2.44	3.13	
Carbon Dioxide	CO <sub>2</sub>	44			1.40	2.09	2.68

ture of gases, Wilke (99) derived an expression based on theories of Maxwell and Stefan. The expression is:

$$D'_A = \frac{1 - y_A}{\frac{y_B}{D_{AB}} + \frac{y_C}{D_{AC}} + \frac{y_D}{D_{AD}} + \dots}$$

where  $y_A, y_B, \dots$  are the mole fractions of components A, B, C - - in the mixture and  $D_{AB}, D_{AC}, \dots$  are the diffusion coefficient of component A with respect to the pure components in the mixture. This relationship was verified experimentally by Fairbanks and Wilke (33).

For the viscosity of a mixture of two gases Sutherland (92) and later Thiesen (95) proposed the formula for  $\mu$  the viscosity of the mixture

$$\mu_n = \frac{\mu_1}{1 + \frac{x_2}{x_1} A} + \frac{\mu_2}{1 + \frac{x_1}{x_2} B}$$

where  $\mu_1, \mu_2$  are the viscosities of the pure components of the mixture and  $x_1$  and  $x_2$  their respective mole fractions.

A and B are dimensionless constants.

A simplification as shown by Schudel (82) results in

$$\frac{A \rho_1}{\mu_1} = \frac{B \rho_2}{\mu_2} = C$$

where  $\rho_1$  and  $\rho_2$  are the respective densities of the two components in the mixture, and C = Constant.

Buddenberg and Wilke (13) developed empirically the constant C in the formula of Schudel. Their expression is:

$$\mu_n = \frac{\mu_1}{1 + \frac{x_2}{x_1} \frac{1.385 \mu_1}{D_{12} \rho_1}} + \frac{\mu_2}{1 + \frac{x_1}{x_2} \frac{1.385 \mu_2}{D_{12} \rho_2}}$$

$D_{12}$  being the diffusion coefficient of gas 1 with respect to gas 2.

This equation was generalized to include multicomponent systems, resulting in:

$$\mu_m = \sum_{i=1}^n \frac{\mu_i}{1 + \frac{1.385 \mu_i}{x_i p_1} \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{D_{ij}}}$$

In a later article Bromley and Wilke (11) gave this expression as:

$$\mu_n = \sum_{i=1}^n \frac{\mu_i}{1 + \frac{1}{x_i} \sum_{\substack{j=1 \\ j \neq i}}^n x_j \phi_{ij}}$$

where

$$\phi_{ij} = \frac{\left[ 1 + \left( \frac{\mu_1}{\mu_j} \right)^{1/2} \left( \frac{M_j}{M_1} \right)^{1/4} \right]^2}{\sqrt{2} \left[ 1 + \frac{M_1}{M_j} \right]^{1/2}}$$

$M_i$ ,  $M_j$  being the molecular weights of components 1 and j respectively.

This treatment resulted from an extension by Wilke (100) of the treatment presented by Buddenberg and Wilke.

Analogous to the expressions for the viscosity and diffusion coefficients of gas mixtures as given by the Sutherland expression, Wassiljewa (98) proposed an equation for the thermal conductivity of a mixture of gases given by

$$k_m = \frac{k_1}{1 + A_{12} \frac{x_2}{x_1}} + \frac{k_2}{1 + A_{21} \frac{x_1}{x_2}}$$

where k represents the heat conductivity with subscripts to indicate the components.

$x_1$  and  $x_2$  are the mole fractions of components 1 and 2 respectively.

$A_{12}$  and  $A_{21}$  are dimensionless constants.

In a paper on the thermal conductivity of gas mixtures, Lindsay and Bromley (54) developed the following general equation from simple kinetic theory and using Sutherland's model:

$$k_m = \sum_{i=1}^n \frac{k_i}{1 + \frac{1}{x_i} \sum_{\substack{j=1 \\ j \neq i}}^n A_{ij} x_j}$$

and

$$A_{ij} = \frac{1}{4} \left\{ 1 + \left[ \frac{\mu_i}{\mu_j} \left( \frac{M_j}{M_i} \right)^{3/4} \frac{\left( 1 + \frac{S_i}{T} \right)}{\left( 1 + \frac{S_j}{T} \right)} \right]^{1/2} \right\}^2 \frac{\left( 1 + \frac{S_{ij}}{T} \right)}{\left( 1 + \frac{S_i}{T} \right)} ;$$

$S_i$  and  $S_j$  are the Sutherland constants for the gases  $i$  and  $j$  respectively and  $S_{ij}$  is taken as the geometric mean of the two Sutherland constants

$$S_{ij} = \sqrt{S_i S_j} ;$$

$M_i$  and  $M_j$  are the molecular weights.

This equation was verified for a two-component gas mixture and is claimed to be accurate within an average deviation of 1.9 percent. An approximate value for the Sutherland constant was taken as  $S = 1.5 T_B$  where  $T_B$  is the boiling point at 1 atmosphere pressure. For gases where molecules have a strong dipole:

$$S_{ij} = 0.733 \sqrt{S_i S_j} .$$

Comprehensive reviews of literature on the molecular transport properties of fluids have been compiled by Johnson (46) during the past few years. Improvement of variable significance may be found in the literature listed. These reviews treat the viscosity, diffusion, thermal conduction and thermal diffusivity properties of gases and liquids.

### Conduction in Liquids

In ideal gases the dispersive forces prevail and any interaction between individual molecules is negligible. The total energy of a gas is the sum of the kinetic energies of all the molecules. In liquids, the attraction forces between the molecules are sufficiently strong to lead to a condensed system but not strong enough to prevent considerable translation and rotation of the individual molecules. Liquids fall thus between gases which, at high temperatures at least, are characterized by complete disorder or randomness of the molecules, and crystals that hold atoms and molecules in nature's most orderly arrangement.

As a combination of the first and second law of thermodynamics we have the equation:

$$\left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

where  $\left( \frac{\partial E}{\partial V} \right)_T$  = change in internal energy  $E$  with volume change  $\partial V$  at constant temperature  $T$ ;

$\left( \frac{\partial P}{\partial T} \right)_V$  = change of pressure  $\partial P$  with change in temperature at constant volume  $V$ .

In words the equation means:

Internal pressure = thermal pressure - external pressure.

The thermal pressure is a measure of the tendency of a substance to expand as the result of the thermal kinetic motion of its molecules. For an ideal gas:

$$\left( \frac{\partial E}{\partial V} \right)_T = 0,$$

which means that there is no intermolecular attraction. For a typical liquid the internal pressure is of the order of magnitude of 3,000 atmospheres; for water the internal pressure is about 20,000 atmospheres according to J. H. Hildebrand (40).

Another picture of the relation between vapors and liquids is that vapors may be considered as void space in which a few molecules are moving at random, while in the liquid state a number of holes are moving at random through the fluid substances. Increase in temperature of a liquid increases the concentration of molecules in its vapor and also the concentration of holes in the liquid. At the critical point the vapor density is the same as the liquid density. This behavior, pointed out by Cailletet and Mathias (1886) is called the law of rectilinear diameters.

The kinetic-molecular mechanisms of viscosity are different for gases and liquids. The viscosity of a gas increases with temperature and is practically independent of pressure. In the case of a liquid, the viscosity increases with increasing pressure and decreases exponentially with increasing temperature. The viscosity coefficient  $\mu$  of a liquid is given by DeGusman (21) as:

$$\mu = Ae^{\frac{\Delta E(\text{vis})}{RT}}, \text{ where}$$

$\Delta E(\text{vis})$  is a measure of the energy barrier to be overcome before viscous flow occurs or according to Eyring (38) the energy required to make holes of molecular size into which the moving molecules can slip.

This equation was developed from the Arrhenius equation for chemical reaction rates (1):

$$\ln k = \ln A - \frac{E}{RT}$$

or

$$k = Ae^{-\frac{E}{RT}}$$

in which

$k$  is the reaction rate

$A$  and  $E$  are constants,  $E$  being called the heat of activation.

The equation of Arrhenius has become generally accepted as the expression of the temperature dependence of the specific rates of reaction. The form of equation also proved to be valid in expressing physical phenomena which require time for their occurrence and take place with a unique velocity under definite conditions. This was shown by Glasstone, Laidler and Eyring (38) for processes such as viscosity, diffusion, dipole orientation in an electric field, electrolytic conductance and electrode phenomena.

From the free energy of activation  $\Delta F^\ddagger$ , Powell, Roseveare and Eyring (75) gave an expression for the fluidity

$$\phi \left( \phi = \frac{1}{\mu} \right), \text{ viz. :}$$

$$\phi = \frac{V}{Nh} e^{-\frac{\Delta F^\ddagger}{RT}}$$

where:

$V$  = molal volume

$N$  = Avogadro's number

$h$  = Planck's constant

As shown by these authors, there exists a close correlation between  $\Delta F^\ddagger$  the free energy of activation for viscous flow and  $\Delta E_{\text{vap}}$  the energy change of vaporization. From this was derived the equation:

$$\mu = \frac{Nh}{V} e^{\frac{\Delta E_{\text{vap}}}{2 \cdot 45 RT}}$$

For many liquids the ratio  $\frac{\Delta F^\ddagger}{\Delta E_{\text{vap}}}$  lies between  $\frac{1}{3}$  to  $\frac{1}{4}$ ; but for liquid metals the range is from  $\frac{1}{6}$  to  $\frac{1}{20}$ . This leads to the conclusion that the units of flow in liquid metals are ions that are surrounded by an electron gas. At vaporization, the whole metal atom has to be expelled leaving a hole of corresponding size. The success of this theory to explain viscosity can be seen in the way it takes into account the effect of compositions. The corresponding equation for solutions is:

$$\mu = \frac{Nh}{V} e^{\frac{(N_1 \Delta F_1^\ddagger + N_2 \Delta F_2^\ddagger) - \frac{\Delta FE}{2.45}}{RT}}$$

This reduces to the best known empirical mixture law for not too imperfect solutions:

$$\log \mu = n_1 \log \mu_1 + N_2 \log \mu_2, \text{ in which}$$

$N_1$  and  $N_2$  are mole fractions of substance 1 and 2 respectively.

$\Delta FE$  is the free energy change of mixing (in excess of ideal). Similar molecular models are used for treating diffusion coefficients and ionic conductances.

From the Clausius Clapeyron equation

$$\frac{d \ln P}{dT} = \frac{L}{RT^2}$$

and the deGuzman treatment of fluidity  $\phi$ , we obtain

$$\frac{d \ln \phi}{dT} = \frac{E}{RT^2} \quad \text{in which}$$

$P$  is the vapor pressure,  $T$  the absolute temperature,  $L$  the latent heat of vaporization,  $R$  the universal gas constant and  $E$  the activation energy for viscous flow; Othmer and Conwell (68) correlated viscosity, vapor pressure and latent heats of liquids. Their equation for viscosity  $\mu$  is given as:

$$\log \mu = -\left(\frac{E}{L}\right) \log P^1 + C$$

where  $C$  is a constant. The authors maintain that the use of critical constants gives even better plots. Another attempt to relate viscosity and vapor pressure in a two-constant equation was made by Mitra and Chakravarty (62, 63). A simple two-constant equation of Mukherjee (65) combines the logarithms of viscosity, temperature and vapor pressure based on the assumption of free volume in liquids. Molecular refraction was used by Lagemann (52) to construct a nomograph for the determination of liquid viscosities. In a flow constant equation by Baum (7) the logarithm of viscosity is given as a function of absolute temperature. This expresses the fact that vapor pressure and viscosity of ten times plot as straight lines on log-log paper.

Cornelissen and Waterman (19) presented the following equation for the kinematic viscosity:

$$\nu = e^{\left(B + \frac{A}{T^x}\right)} \quad \text{to correlate the variation of the kinematic viscosity } \nu \text{ with the absolute temperature } T; \text{ the other symbols represent constants.}$$

While heat conduction in liquids is just as in gases due to movement of atoms and molecules, its mechanism is quite different from that in gases. The most promising theory assumes that heat is transferred by longitudinal vibrations, similar to the propagation of sound in a medium.

Bridgman (10) derived an equation for the thermal conductivity of a liquid on the above assumption. If  $R$  is the universal gas constant and  $N$  Avogadro's number, then  $\frac{R}{N} \Delta T$  is the kinetic energy taken up by an atom of a monoatomic substance upon increase in temperature by  $\Delta T$ . The energy increase per atom or molecule in

the solid state when heated by  $1^\circ\text{C}$  will be  $\frac{3R}{N} \times 1^\circ$ , one-half of which is kinetic, the other half potential energy. Because the specific heat  $c_v$  does not change much in the transition from the solid to the liquid state, the expression for  $C_v$  previously derived for the solid state and the equipartition between potential and kinetic energy may be considered true for liquids also.

For a temperature gradient  $\frac{dT}{dx}$  in a liquid with a molecular energy of  $\frac{3R}{N} T$ , the difference of energy between adjacent molecules in the direction of the temperature gradient is  $\frac{3R}{N} \cdot \frac{dT}{dx} \cdot D$ , where  $D$  is the mean distance of the centers of neighboring molecules when a simple cubical array is assumed. The difference in energy is assumed to be handed down a row of molecules with the velocity of sound  $v$ . The total energy passing a fixed point of any row of molecules per unit time is:

$$\frac{3R}{N} \cdot \frac{dT}{dx} D \cdot \frac{v}{D}$$

Dividing this expression by the cross-section  $D^2$ , we obtain a total energy transfer per unit cross-section of:

$$\frac{3R}{N} \cdot \frac{dT}{dx} D^{-2} v$$

By definition the transfer per unit cross-section equals  $k \frac{dT}{dx}$ ,  $k$  being the coefficient of thermal conductivity. Combining the last two expressions, we obtain:

$$k = \frac{3R}{N} v D^{-2}$$

This equation, despite its simplicity, renders data that are in good agreement with actual measurements, although considerable discrepancies are found for several liquids. A good agreement exists for the experimentally determined and the calculated thermal conductivity of water which is  $2\frac{1}{2}$  to 5 times that of organic liquids. Bridgman reasoned that this high conductivity of water is due to its low compressibility. The formula gives the right sign for the temperature coefficient of thermal conductivity at atmospheric pressure, both for organic liquids and for water. Table 3 shows the agreement between the measured conductivities of some liquids and the values calculated by means of the formulas of Bridgman and Kardos. Kardos (48) considered each molecule as a unit possessing a certain energy with the drop in energy  $\Delta Q$  and in temperature  $dt$  restricted to the distances between molecules. For a cubical array the distance between the surfaces of adjacent molecules is taken as  $L$ . By multiplying by  $\frac{L}{D}$ ,

the energy gradient is reduced to that of a quasi-homogeneous body. If, as before, the heat is assumed to be transmitted with sound velocity  $v$ , the heat flow per unit cross-section is:

$$q = -Lv \left( \frac{1}{D^3} \cdot \frac{dQ}{dt} \cdot \frac{L}{D} \right) \left( \frac{dt}{dx} \right)_L$$

From the basic equation of heat flow:

$$q = -k \left( \frac{dt}{dx} \right)_D = -k \frac{L}{D} \left( \frac{dt}{dx} \right)_L$$

The subscripts  $D$  and  $L$  denote over which range the derivatives are taken. For a cubical packing we obtain:

$$\frac{1}{D^3} \cdot \frac{dQ}{dt} = \rho c_p$$

TABLE 3

COEFFICIENTS OF THERMAL CONDUCTIVITY OF LIQUIDS FROM EXPERIMENT  
AND CALCULATION ACCORDING TO THE EQUATIONS OF BRIDGMAN AND  
KARDOS, AT 30 °C

Liquid		v	D	k, watt/(sq cm) (°C per cm) x 10 <sup>-3</sup>		
		cm/sec x 10 <sup>-3</sup>	cm x 10 <sup>-9</sup>	Bridgman	Kardos	Exper.
Water	H <sub>2</sub> O	145 <sup>a</sup>	31.0 <sup>a</sup>	6.21 <sup>a</sup>		
		150 <sup>c</sup>	31.0 <sup>c</sup>	6.41 <sup>c</sup>	5.96 <sup>c</sup>	6.10 <sup>c</sup>
Methyl alcohol	CH <sub>4</sub> O	112 <sup>a</sup>	40.2 <sup>a</sup>	2.84 <sup>a</sup>		
		113 <sup>c</sup>	40.8 <sup>c</sup>	2.79 <sup>c</sup>	2.02 <sup>c</sup>	2.11 <sup>c</sup>
Ethyl alcohol	C <sub>2</sub> H <sub>5</sub> O	104 <sup>a</sup>	45.9 <sup>a</sup>	2.04 <sup>a</sup>		
		114 <sup>c</sup>	46.0 <sup>c</sup>	2.22 <sup>c</sup>	1.98 <sup>c</sup>	1.82 <sup>c</sup>
Isoamyl alcohol	C <sub>5</sub> H <sub>12</sub> O	124 <sup>c</sup>	56.5 <sup>c</sup>	1.60 <sup>c</sup>	2.21 <sup>c</sup>	1.48 <sup>c</sup>
Glycerine	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	191 <sup>a</sup>	49.5 <sup>a</sup>	3.20 <sup>a</sup>	5.75 <sup>c</sup>	2.81 <sup>c</sup>
Carbon bisulfide	CS <sub>2</sub>	96 <sup>a</sup>	46.0 <sup>a</sup>	1.87 <sup>a</sup>		
		106 <sup>b</sup>		2.06 <sup>b</sup>		
		118 <sup>c</sup>	46.6 <sup>c</sup>	2.23 <sup>c</sup>	1.47 <sup>c</sup>	1.59 <sup>c</sup>
Acetone	C <sub>3</sub> H <sub>6</sub> O	108 <sup>a</sup>	49.5 <sup>a</sup>	1.81 <sup>a</sup>		
		114 <sup>c</sup>	50.0 <sup>c</sup>	1.88 <sup>c</sup>	1.82 <sup>c</sup>	1.79 <sup>c</sup>
Ether	C <sub>4</sub> H <sub>10</sub> O	92 <sup>a</sup>	55.0 <sup>a</sup>	1.25 <sup>a</sup>		
		92 <sup>c</sup>	55.9 <sup>c</sup>	1.21 <sup>c</sup>	1.40 <sup>c</sup>	1.37 <sup>c</sup>
Ethyl bromide	C <sub>2</sub> H <sub>5</sub> Br	90 <sup>c</sup>	50.2 <sup>c</sup>	1.48 <sup>c</sup>	1.13 <sup>c</sup>	1.20 <sup>c</sup>
Ethyl iodide	C <sub>2</sub> H <sub>5</sub> I	78 <sup>c</sup>	51.2 <sup>c</sup>	1.23 <sup>c</sup>	1.03 <sup>c</sup>	1.11 <sup>c</sup>

<sup>a</sup>Data for calculating coefficients were taken from (a) Chemical Engineer's Handbook. John H. Perry, McGraw-Hill, 1934; (b) Handbook of Chemistry and Physics. Chemical Rubber Publishing Co., 1946.

<sup>b</sup>Values of speed of sound  $v$  taken from Smithsonian Physical Tables.

<sup>c</sup>Other values taken from Heat Transfer (43).

where  $\rho$  is the density of the liquid and  $c_p$  the specific heat of the liquid at constant pressure. The equation for the coefficient of heat conductivity  $k$  is then:

$$k = \rho c_p vL$$

Kardos gives a value of  $L = 9.5 (10)^{-9}$  cm considering the theory of van der Waal's forces, molecular weights, density and compressibility. However, the calculation of  $L$  must be considered to be only semi-empirical. For some liquids the Kardos equation gives better values than that of Bridgman, but falls down in the case of glycerine.

The model for the conduction of sound or heat according to Powell, Roseveare and Euring (75) follows that of Kardos. It assumes the signal to be transmitted between molecules by the speed of sound, and across the molecules almost immediately:

$$\frac{U(\text{liquid})}{U(\text{gas})} = \left( \frac{V}{V_f} \right)^{1/3},$$

where

$V$  = molecular volume

$V_f$  = molecular free volume (or volume between molecules)

$U$  (liquid),  $U$  (gas) are velocity of sound in liquid or in gas respectively.

From the equation for the heat conductivity of gases (25) as interpreted by the authors:

$$K(\text{gas}) = \frac{1}{3} \left[ \frac{1}{4} \left( \frac{C_p}{C_v} - 5 \right) \right] \frac{N}{V} \bar{U} L C_v,$$

where

$C_p$  and  $C_v$  = the specific heat at constant pressure and volume respectively for one molecule

$\bar{U}$  = average kinetic theory velocity

$L$  = mean free path

$\frac{N}{V}$  = number of molecules per cc,

one obtains by multiplying the average velocity  $\bar{U}$  by  $\left( \frac{V}{V_f} \right)^{\frac{1}{3}}$ ,

replacing the  $L$  by  $\left( \frac{V}{N} \right)^{\frac{1}{3}}$  and taking a value of  $3k$  ( $k$  is the Boltzman constant) for  $C_v$ :

$$k(\text{liquid}) = 0.931 \left( \frac{C_v}{C_p} \right)^{\frac{1}{2}} 3k \left( \frac{N}{V} \right)^{\frac{2}{3}} \bar{U}.$$

This equation has the same form as that of Bridgman.

In an attempt to explain the abnormally high thermal conductivities of glycols and alcohols with respect to other "normal" liquids, Palmer (70) took into account the effect of the hydrogen bonding in these liquids. The "normal" liquids were classified as those which can be fitted with empirical equations. It is assumed that heat may be transported by two types of mechanisms – the transfer by collision between molecules and for hydroxyl groups by making and breaking of hydrogen bonds. More hydrogen bonds are broken where the heat intensity is higher, thereby absorbing heat, and more formed where the temperature is lower, thus releasing heat – a concept similar to that of von Grothaus for the electrical conductance of hydrogen ions in water. Further assumptions are that the effects of the two mechanisms are additive and that the normal entropy of vaporization (Trouton's constant) divided by the experimental value provides the parameter expressing the effect of hydrogen bonding.

A rather simple empirical equation by Weber:

$$k = 0.0043 \rho C_p \left( \frac{\rho}{M} \right)^{\frac{1}{3}}$$

in which

$k$  = thermal conductivity

$\rho$  = density

$C_p$  = the specific heat, and

$M$  = molecular weight,

was shown by Smith (85) to check experimental values to within an average error of 14.8 percent. By modifying this equation as discussed above, Palmer was able to reduce the average error to 8.8 percent. His equation is given as:

$$k = 0.0947 \frac{\rho C_p}{L_v} \left( \frac{\rho}{M} \right)^{\frac{1}{3}} \frac{1}{T}$$



where

$L_v$  = latent heat of vaporization and

$T$  = absolute temperature;

Trouton's constant - an average for all liquids - was assumed to be equal to 21.

Various authors have attempted to correlate the thermal conductivity of liquids with other measurable properties. Sakiadis and Coates (80) proposed a revised correlation based on Kardos which fits the observed values better. They also based a correlation on the theorem of corresponding states from which the thermal conductivity of liquids may be calculated. Johnson and Huang (46, 45) presented charts for calculating thermal conductivities from viscosity and specific heat data. Riedel (46, 79) correlated thermal conductivity with compressibility and surface tension from consideration of corresponding states.

In addition to the above more-or-less theoretical approaches, other investigators have attempted to derive pure empirical formulas. Smith (85) presented two empirical equations with one and five constants respectively. This is to a certain extent an adaptation of the equation by Weber. Bates (5, 4, 3) from determination of the thermal conductivity of water-glycerol, water-methyl alcohol and water-ethyl alcohol mixtures presented tables, graphs and empirical equations for the calculation of the thermal conductivity of the above mentioned mixtures. Bates (6) also determined experimentally the coefficient of thermal conductivity for nine liquid silicones. He also derived an empirical equation relating the thermal conductivity of a series of polymers with viscosity and temperature.

### Conduction in Solids

The ideal solid is the crystal. Between the solid and liquid state there exists a variety of intermediate forms represented by rubbers, resins, glasses, liquid crystals, fibers and protoplasm. Understanding of the thermal conductivity in solids presupposes an understanding of crystal structures.

**Crystal Structure.** The first law of crystallography specifies that the corresponding interfacial angles (in different crystals) are constant and in no way dependent on the development of the respective faces. In 1784 the Abbé René Just Haüy proposed that the regular external form of a crystal results from an internal regularity in the arrangement of the primary building stones. This concept was later verified by the work of Max von Laue with x-ray diffraction.

The faces of crystals and the planes within crystals can be specified by a set of three non-coplanar axes. It has been found that there always exists a set of axes on which the reciprocal intercepts of crystal faces are small, whole numbers. These

TABLE 4  
THE SEVEN CRYSTAL SYSTEMS

System	Axes	Angles	
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Rock salt
Tetragonal	$a = b; c$	$\alpha = \beta = \gamma = 90^\circ$	White tin
Orthorhombic	$a; b; c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombis sulfur
Monoclinic	$a; b; c$	$\alpha = \beta = 90^\circ \quad \gamma \neq 90^\circ$	Monoclinic sulfur
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite
Hexagonal	$a = b; c$	$\alpha = \beta = 90^\circ \quad \gamma = 120^\circ$	Graphite
Triclinic	$a; b; c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Potassium dichromate

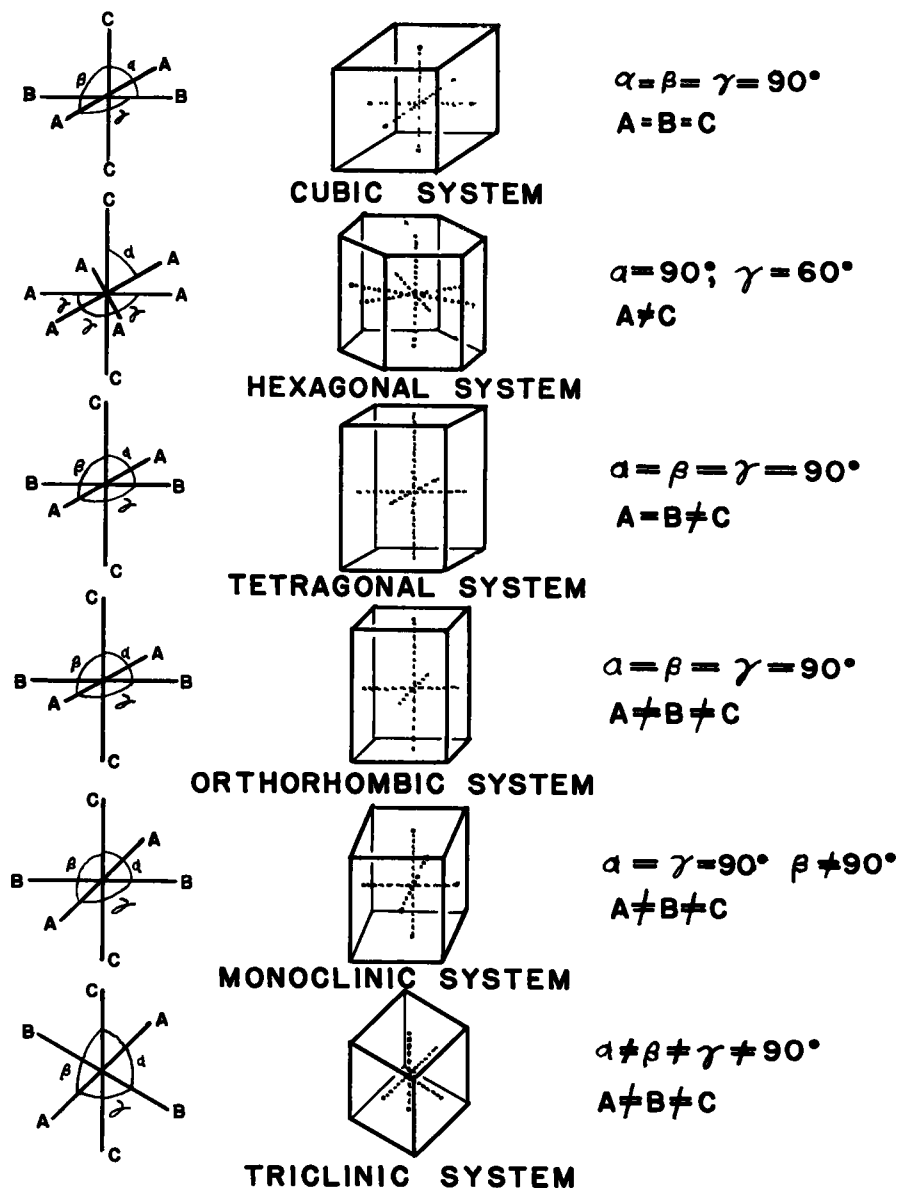


Figure 1. The six crystal systems.

reciprocal intercepts or Miller indices are used to define the crystal faces.

According to the set of axes used to define the crystal faces, the crystals may be divided into seven systems. If  $a$ ,  $b$  and  $c$  represent the three non-coplanar axes making angles of  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively, with each other, the seven systems can be represented (64) as given in Table 4 or Figure 1.

The atoms in a crystal are orderly arranged in small groups or unit cells in such a way that the whole crystal may be built out of these small cells. If we take a corresponding point in each of these cells, we will end up with a regular array of points in space which is called a lattice or a space lattice. The lattice points can be connected by a regular network of lines in various ways. Thereby the lattice is broken up into the unit cells. A. Bravais (1848) showed that all possible space lattices can be organized into 14 classes (see Fig. 2).

By means of x-rays which are diffracted by the atoms in the crystal, the regular arrangement of the primary building stones was confirmed. The outstanding pioneering work in this connection was performed by Max von Laue (1912) and by W. H. Bragg

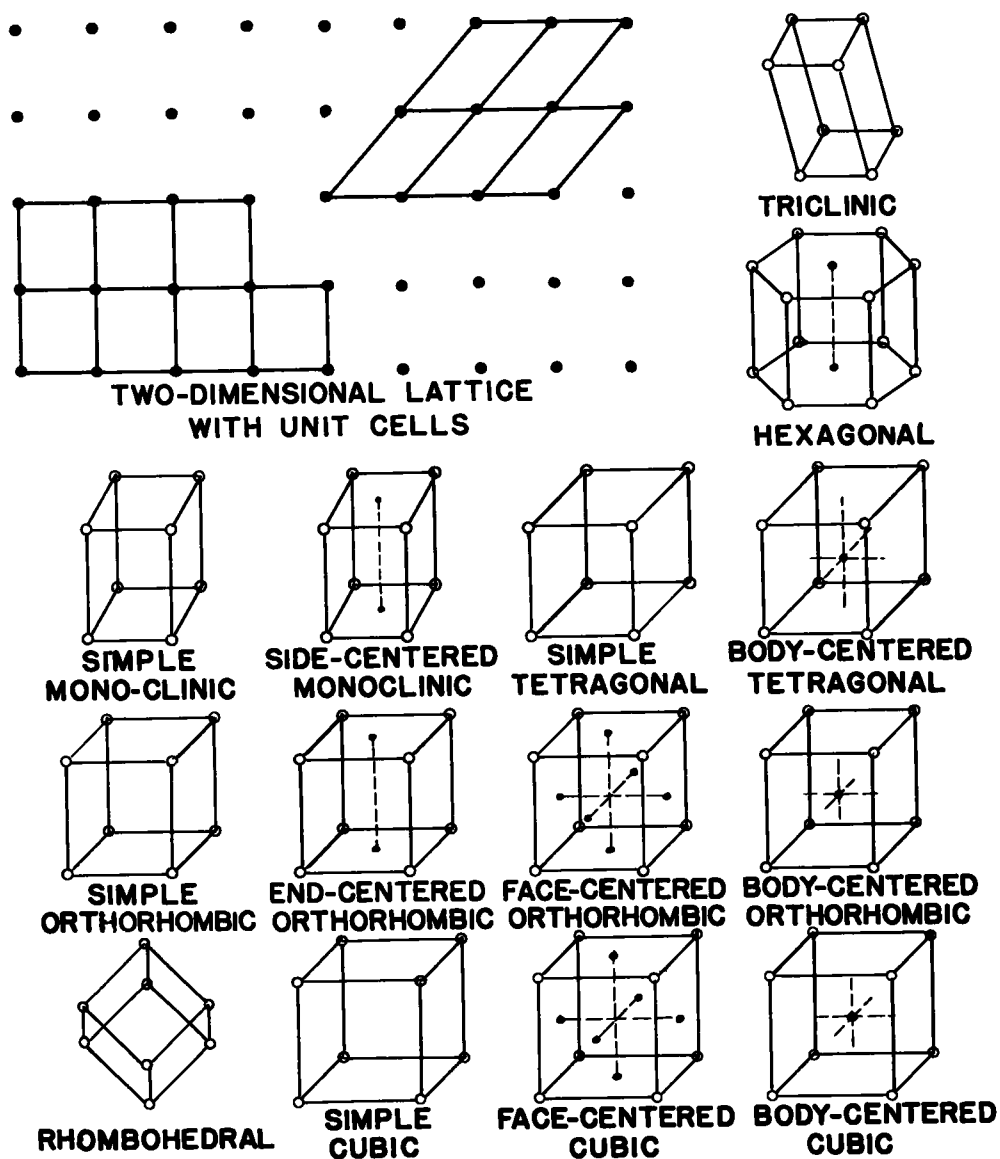


Figure 2. The fourteen Bravais crystal lattices.

and W. L. Bragg (9). Instead of using a single crystal with a definite orientation, P. Debye and P. Scherrer found that a mass of finely divided crystals with random orientations may be used.

Symmetry is described in terms of symmetry operations; application of such symmetry operations to one or more crystal faces reproduces the geometric form of the crystal. The symmetry of a crystal is evident not only in the face development but in all other physical properties such as electrical and thermal conductivity, density,

piezoelectric phenomena, and refractive index. The symmetry operations, rotation, reflexion, translation and their combinations follow from certain elements of symmetry such as rotation axes, mirror planes and centers of inversion. The total number of possible combinations of the symmetry elements found in crystals is 32. Hence, there exist 32 point-groups defining the 32 crystal classes. There are only seven crystal systems but each system contains several classes representing different degrees of symmetry.

The packing of the primary building stones is of the greatest importance in determining the crystal structure of a substance. Once the spatial requirements of the packing have been satisfied, the effect of cohesive forces or bonding must also be considered. There are two theoretical treatments with respect to bonding (64).

The crystal structure is pictured as a regular arrangement of atoms, each with electrons used to form bonds with surrounding atoms. The bonds may be:

(1) The Van der Waals-London bonds. These bonds are the result of second order forces between neutral atoms or molecules that are due to the polarization of one atom or molecule by the fluctuation of the charge distribution in a second, and vice versa.

(2) The ionic bonds. This is the type of bond that exists in the NaCl molecule. The ionic bond is spherically symmetric with no preferred direction. An ion will be surrounded by as many oppositely charged ions as is geometrically possible, provided that over-all electrical neutrality is satisfied.

(3) The covalent bonds. These bonds result from the sharing of electrons between atoms. They extend in three dimensions and may lead to a variety of crystal structures depending on the constituent atoms. The diamond crystal is an example of this type of bond.

(4) Intermediate type bonds. Bonds of this type arise from resonance between covalent and ionic bonds. Examples are the structures of the silver halides.

(5) The hydrogen bond. This type of bond is important in many crystal structures. Examples are certain inorganic and organic acids, salt hydrates and ice.

(6) The metallic bond. This is closely related to the covalent bond. There are more orbitals available for bond formation than electrons to fill them. The covalent bonds thus oscillate among the available positions. Another picture of the metallic structure is that of a lattice of separate metal ions surrounded by an electron gas. A ready flow of electrons will take place when an electric field is applied.

The band model theory assumes an arrangement of nuclei at their appropriate spacings. The total number of available electrons is poured into the resultant force field. The electrons will arrange themselves in bands of energy around the nuclei; each atomic orbital contributing one level to a band. In partially filled upper bands, the electrons may readily move from one level to an unfilled level within the band, giving rise to current flow when an electric field is applied. If the outermost bands of the nuclei overlap, the electrons can flow freely through the whole structure. For nuclei arranged at the points of a perfectly periodic lattice, there will be no resistance to the flow of an electric current. The perfect periodicity is disturbed by thermal vibrations of the lattice nuclei and also by introducing foreign atoms in the structure (alloys). This is the picture for conductors of electricity or metals.

Insulators have completely filled lower bands with a wide energy gap between the outermost filled band and the lowest empty band. Semiconductors have, in addition to the normal bands, also narrow impurity bands which are either unfilled levels closely above a filled band or filled levels below an empty band. The extra levels are a result of foreign atoms or departure from the ideal stoichiometric composition.

Conduction in Crystals. According to the Nernst theorem, the specific heats of elements and compounds becomes zero at or close to the absolute zero temperature. For solid elements, the atomic heats increase slowly from zero temperature to a temperature of 10 or 15 deg K, hence more rapidly; subsequently, they pass through a turning point and finally tend to reach asymptotically an end value of  $6 - 6.4$  cal

according to the rule of Dulong and Petit. This rule, however, is only approximate. The atomic heat of cobalt reaches a value of 12 calories at 1,000 deg C while those of elements possessing atomic weights of less than 30 show slower increase with temperature. Immediately above the absolute zero point, the atomic heats are proportional to the third power of the temperature. The mole heats of compounds can be calculated approximately from the atomic heats of the components in accordance with Kopp's rule. The specific-, atom-, and mole-heats are important with respect to thermal diffusivity or thermometric conduction in addition to their theoretical

TABLE 5  
VARIATION OF THERMAL CONDUCTIVITIES OF CRYSTALS  
with Absolute Temperature  $k$  in watt/square cm  $^{\circ}\text{C}$  per cm

Crystal	$^{\circ}\text{K}$ Temperature	$k$	Crystal	$^{\circ}\text{K}$ Temperature	$k$
Quartz	373	0.0902	Rock salt NaCl	373	0.0485
parallel to axis	273	0.1360		273	0.0698
	195	0.1960		195	0.1043
	88	0.4660		83	0.2666
	83	0.490	Potassium Chloride	373	0.0492
Perpendicular	373	0.0559	KCl	273	0.0698
to axis	273	0.0726		195	0.1041
	195	0.1010		83	0.2103
	83	0.246		23.1	0.478
	21	2.51		22	0.510
Calcite perpen-	374	0.0357		21	0.572
dicular to axis					
$\text{CaCO}_3$	273	0.0430	Corundum	273	0.104
	195	0.0577	$\text{Al}_2\text{O}_3$	373	0.0865
	83	0.1586		473	0.0692
Mullite	273	0.059		673	0.0588
$3 \text{ Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	373	0.052		873	0.0519
	673	0.0346		1,073	0.0466
	1,073	0.0294		1,273	0.0415

From Eucken (30) Eucken (28) Jakob (43)

importance.

According to the trend of the specific heat near the absolute zero temperature, atoms and molecules have very little thermal motion at very low temperatures. It is logical to expect that the coefficient of thermal conductivity also becomes zero at the absolute zero temperature. Theoretical treatment of heat transfer is based on the assumption that the flow of energy between neighboring locations is proportional to the gradient of the internal energy. The heat flow through a unit area in the  $x$ -direction can be written as (43):

$$q = -B \frac{du}{dx} = -B \frac{du}{dT} \cdot \frac{dT}{dx} = -B c_v \frac{dT}{dx}$$

where

$u$  = internal energy

$c_v$  = specific heat at constant volume

$B$  = constant

By definition:

$$q = -k \cdot \frac{dT}{dx}$$

It follows, therefore, that  $\frac{C_V}{k}$  should be a constant. This is very roughly the case for quartz glass but not for quartz crystals.

Another mechanism must, therefore, exist which opposes that of the specific heat and which prevails at low temperatures. Eucken (30) found that the thermal conductivity of crystals decreased with increase in temperature at a rate almost inversely proportional to the absolute temperature (see Table 5).

According to Debye (20) the heat transfer in solids from hot to cold regions is by means of thermo-elastic waves. Bragg visualized the crystalline structure as atoms linked together by springs. Vibrations caused by heat displace the atoms from their normal position and thereby propagate the heat energy. The waves are of two kinds, namely, compressional and distortional, propagated with different velocities. Many simultaneous wave trains exist which are unharmonic and, therefore, give rise to disturbances which greatly increase with temperature. The most important of the disturbances is the heat motion of the crystal lattice itself; this may control the dependence of heat conduction upon temperature. The disturbances cause a scattering of the waves analogous to that of light in an opaque medium. The mean free path  $\lambda_S$  is defined as that distance in which the energy waves have been scattered in a ratio  $\frac{1}{e}$  where  $e$  is the base of the natural logarithms. Debye derived the following equation for the thermal conductivity:  $k = \frac{1}{4} \lambda_S W_S \rho_S C_V$ , where  $W_S$  is the average propagation of the elastic waves, defined by:

$$W_S = \sqrt{\frac{M}{\rho_S}}$$

$$M = \frac{\Delta p}{\frac{\Delta V}{V}} = \text{bulk modulus}$$

$\rho_S$  = density, and

$C_V$  = specific heat of solid.

The evaluation of  $\lambda_S$ , the distance of comparatively free passage of the thermal waves, is rather difficult. Debye obtained  $\lambda_S$  numerically by expressing the mutual influence of the waves by the coefficients of thermal expansion and of mechanical compressibility. He showed that  $\lambda_S$  is almost proportional to  $\frac{1}{T}$  from the fact that

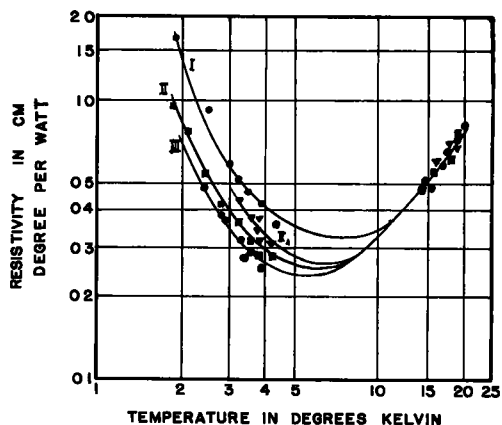
the thermal oscillations and, therefore, the wave disturbances decrease with decreasing temperature.

Meissner (60) pictured the crystal as a chain of many slightly damped oscillators, turned to the same frequency and coupled very loosely. These chain links have to be incited one after another and, because of the great number of elementary oscillators, it follows that they must be very loosely coupled and very slightly damped. These waves can exist only in crystals.

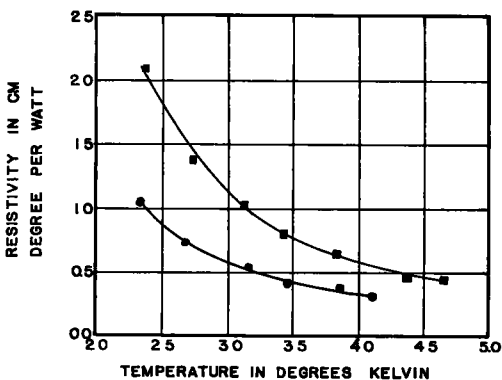
Experiments by de Haas and Biermasz (22) on quartz crystals, extending down to 2.77 deg K showed that the thermal conductivity of quartz reaches a maximum at about 10 deg K. The trend in the conductivity curve is towards zero at the absolute zero point. From measurements on KCl rods of different cross-sections and from different samples, de Haas and Biermasz (23, 22) concluded that the dimensions of the rods have an influence on the specific thermal resistance of a crystal. For thinner rods the resistance was more than for the thicker ones. The same was found in the case of quartz crystals. Table 6 and Figure 3, taken from de Haas and Biermasz's papers illustrate their conclusions. A discussion by Makinson (56) of the factors

determining the conductivity of real crystals may be used to explain the deviations from the theory of Debye. He considers that the scattering of the thermal waves is also produced by irregularities of atomic dimensions as would be caused by impurities and by large-scale interruptions of the lattice such as grain boundaries. A free path is defined for each of these sources of scattering. At high temperatures, the effective wave-lengths of the thermal waves are so short that the various lattice impurities have almost no influence upon the scattering, which is primarily due to lattice motion. The conductivity will then be approximately inversely proportional to the absolute temperature.

With decrease in temperature the effective wave-lengths increase, the effect of the lattice motion diminishes and conduction is limited first by small-scale irregularities and at very low temperatures by the size of the crystal itself. Figure 4, taken from Makinson's paper illustrates these points.



THERMAL RESISTIVITY OF KCl



THERMAL RESISTIVITY OF QUARTZ

Figure 3. Thermal resistivity at low temperature (after de Haas and Biermasz).

conductivity of metals increases with decreasing temperature (see Table 8).

At low temperatures, Eucken's equation can be applied:

$$\frac{k}{k_0} = \frac{T_0}{T}$$

where the subscript 0 relates to 0°C. By differentiation one obtains:

$$\frac{dk}{dT} = -\frac{k_0 T_0}{T^2}$$

At high temperatures, impurities in the metals may cause  $k$  to pass through a

At very low temperatures, the conductivity is limited by reflection of the thermal waves at the boundaries of the crystal grains. The smaller the grains, the higher is the temperature at which this condition becomes important. Scattering by irregularities or impurities of atomic dimensions reduces the conductivity below the value determined by lattice motion alone. The whole picture is still rather qualitative since it is not possible to fix precise temperatures and proportions of the curve for actual crystals. Furthermore, De Haas and Biermasz (23) have indicated that for a perfect crystal such as diamond the conductivity starts decreasing at a higher temperature than would have been believed from Makinson's concept. Measurements by Eucken (28) show results similar to those of De Haas and Biermasz; the conductivity of diamond is relatively temperature-independent or at least much less temperature conditioned than that of some other pure crystals. In Table 7 the average of three determinations by Eucken (28), De Haas and Biermasz (23) is presented; as a matter of interest, conductivity values for an Acheson graphite are also included (43).

**Conduction in Metals.** As in non-metallic crystalline substances, the thermal

TABLE 6

DE HAAS AND BIERMASZ' DATA SHOWING THE INFLUENCE OF THE ROD DIMENSIONS ON RESISTIVITY  
w in deg C cm/watt

KCl rods, square with side length d								Quartz SiO <sub>2</sub> perpendicular to axis			
d = 0.763 cm		d = 0.511 cm		d = 0.383 cm		d = 0.252 cm		Diameter 0.454 cm		Diameter 0.216 cm	
T(°k)	w	T(°k)	w	T(°k)	w	T(°k)	w	T(°k)	w	T(°k)	w
19.27	0.721	19.83	0.758	19.25	0.778	19.24	0.730	19.81	0.266	20.12	0.270
18.59	0.693	17.29	0.637	17.99	0.668	17.93	0.674	17.75	0.213	18.80	0.236
16.95	0.611	16.38	0.596	17.05	0.647	16.41	0.590	16.75	0.182	17.17	0.196
15.12	0.493	14.73	0.498	15.77	0.570	14.83	0.507	15.99	0.164	15.82	0.167
3.90	0.262	4.12	0.280	4.18	0.290	4.28	0.360	15.40	0.146	15.11	0.151
3.66	0.290	3.86	0.285	3.88	0.31	3.91	0.419	4.10	0.331	4.62	0.435
3.51	0.286	3.50	0.311	3.75	0.36	3.55	0.472	3.83	0.386	3.81	0.66
3.31	0.322	3.17	0.352	3.69	0.34	3.32	0.527	3.47	0.439	3.45	0.82
2.94	0.379	2.83	0.411	3.52	0.36	3.02	0.620	3.13	0.551	3.10	1.06
2.90	0.388	2.46	0.537	3.30	0.44	2.49	0.921	2.68	0.745	2.73	1.37
2.47	0.495	1.87	0.973			1.92	1.67	2.32	1.066	2.37	2.09
										2.20	2.56
										1.80	4.54
										1.67	5.85

TABLE 7

THE THERMAL CONDUCTIVITY k OF DIAMOND AND ACHESON GRAPHITE

Diamond				Graphite	
De Haas and Biermasz		Eucken		Jacob (43)	
Temp °K	k watt/cm°C	Temp (°K)	k watt/cm°C	Temp °K	k watt/cm°C
89.4	14.3	345	1.53	123	1.78
20.6	8.3	273	1.51	273	1.75
18.8	7.5	196	1.55	423	1.70
17.0	5.89	88	1.27	573	1.54
15.8	5.14	21	0.92	773	1.26
14.9	4.45	These values obviously are too low as indicated by the investigator.		973	0.93
14.0	3.33				
12.8	3.18				
11.5	2.86				
4.21	0.222				
3.59	0.154				
2.99	0.126				

minimum with increasing temperature. With some non-metallic solid bodies such as carborundum bricks, a maximum has been observed for the k-values as a function of temperature. Both kinds of behavior can be derived from the equation

$$k = \frac{1}{aT + b + \frac{c}{T}}$$

The constants a, b and c of the equation depend on the mixture of crystals and amorphous constituents and on the absolute values of their conductivities. These



constants may be found from measurements of  $k$  at three different temperatures. Impurities of metals must be considered as disturbances of the lattice structure.

Metallic single crystals have much higher conductivities than ordinary crystalline metals and a much steeper increase of  $k$  with decreasing temperature. A sudden drop occurs when the metal is melting, a behavior which corresponds with that of melting non-metallic crystalline substances.

There exists a simple relation between the thermal and electrical conductivity of most pure metals. It is expressed in the Wiedemann-Franz-Lorenz equation:

$$L = \frac{k}{k_e T} = \text{constant}$$

where

- $k$  = thermal conductivity
- $k_e$  = electrical conductivity
- $T$  = absolute temperature
- $L$  = so-called Lorenz number

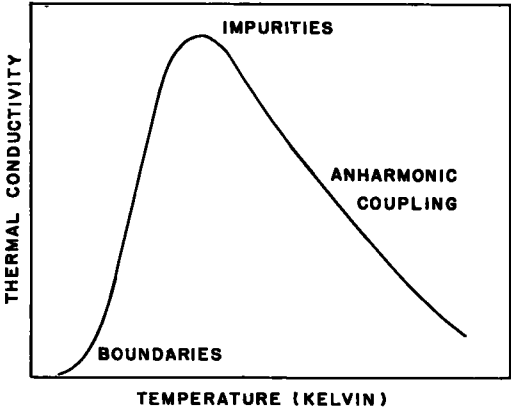


Figure 4. Variation of conductivity with temperature in dielectric crystals (after Makinson).

Drude (26) assumed that both the thermal and electrical conductances in metals are due to free electrons inside the metal which behave like gas molecules and move freely across the lattice of ions that form the skeleton of a metal. He derived an equation for the thermal conductivity of this electron gas analogous to that of a real gas. An expression for the electrical conductivity is known from the ordinary theory of electrons. The comparison leads to:

$$L = \frac{k}{k_e T} = 3 \frac{(\bar{k})^2}{(\epsilon)^2} = \text{constant}$$

where

- $\bar{k}$  = Boltzmann constant =  $\frac{R}{N}$
- $\epsilon$  = elementary charge of an electron

TABLE 8  
THERMAL CONDUCTIVITY OF METALS  
in watt/cm<sup>2</sup> °C per cm

Metal	Copper	Tin	Zinc	Nickel	Iron	Aluminum	Lead
Impurities	0.1	.03	0.2	0.1	0.1		.002
Temperature percent							
-200	5.36	0.845	1.21	1.16	1.002	2.60	0.444
-100	4.06	0.737	1.16		0.753	2.34	0.386
0	3.89	0.670	1.123	0.838	0.719	2.25	0.373
100	3.80	0.633	1.09	0.822	0.684	2.25	0.348
200	3.72	0.600	1.055	0.735	0.615	2.25	0.338
400	3.65	0.330 <sup>a</sup>	0.934	0.588	0.485	2.25	0.15 <sup>a</sup>
600	3.54		0.58 <sup>a</sup>	0.648	0.398		0.14 <sup>a</sup>

<sup>a</sup> Molten

Refinement of the theory leads to a factor 3.3 instead of 3.

The deviations of  $L$  for pure metals are not great but for alloys they are. The deviations are explained by the fact that in addition to the proper metallic thermal conductivity which may be proportional to the electrical conductivity, a non-metallic thermal conductivity of the lattice must also be considered, such as in electrical non-conductors. Its influence will be the greater, the smaller is the electrical conductivity of the material. Thus, for poor electrical conductors  $L$  should be very large. For

TABLE 9  
LORENZ NUMBER  $L$  FOR SOME METALS AND ALLOYS  
(taken from Jakob (43) )

Metal		Alloy	
	in $10^{-9}$ volt <sup>2</sup> /C <sup>2</sup>		in $10^{-9}$ volt <sup>2</sup> /C <sup>2</sup>
Al	22.3	92% Al + 8% Cu	16.5
Cu	22.3	77% Mg + 20% Cu + 3% Si	19.0
Ni	23.3	82% Cu + 18% Zn	26.5
Zn	24.1	Steel with 1% C	27.7
Pb	24.7	86% Al + 14% Mg	28.3
Pt	25.1	88% Mg + 12% Al	35.8
Solid Hg	28.0	70% Cu + 30% Mn	44.0

Note: C is degree Centigrade or Kelvin

TABLE 10  
RELATIVE VALUES OF  $a$ ,  $b$  AND  $c$  FOR VARIOUS MINERALS  
(from Thelen)

Isometric	All minerals	$c$	$a$	$b$	$D$
		1.00	1.00	1.00	
Tetragonal	Rutile	0.79	1.00	1.00	
	Zircon	0.90	1.00	1.00	
	Scapolite	0.85	1.00	1.00	
	Vesuvianite	0.95	1.00	1.00	
Hexagonal	Quartz	0.76	1.00	1.00	
	Specularite	1.10	1.00	1.00	
	Dolomite	1.05	1.00	1.00	
	Apatite	0.96	1.00	1.00	
	Tourmaline	1.15	1.00	1.00	
	Calcite	0.91	1.00	1.00	
Orthorhombic	Borite	1.00	1.06	1.03	
	Anhydrite	1.00	0.971	0.943	
	Staurolite	1.00	0.97	0.901	
Monoclinic	Tremolite	1.00	0.60	0.75	-5°
	Hornblende	1.00	0.71	0.80	
	Epidote	1.00	0.93	1.09	-14.5°
	Gypsum	1.00	0.80	0.65	+17°

L-values of some pure metals and alloys see Table 9.

The influence of temperature upon L is not great. Between 0° and 900°C, increments of 15, 12 and 26 percent have been observed with Swedish iron. The electrical superconductivity of metals at low temperatures has no thermal analogy.

Influence of Crystal Structure on Conductivity. The theories of the mechanism of heat transfer through solids presented this far, are applicable only to isotropic crystals or crystals in the regular (cubic) system. As was mentioned previously the thermal conductivity and other physical properties of the crystals vary along dissimilar crystal axes.

The anisotropism of crystals with respect to thermal conductivity was first extensively investigated by de Senarmont (24). His experimentations included quartz and a great number of other minerals. The wax-figure technique used by him was originated by Ingen-Houtz (42). Thin slices of crystal are covered with wax and perforated by a hole; through the latter a heated silver tube is passed. When the wire or tube is heated, the wax melts away from the hole at a rate proportional to the thermometric conductivity  $\alpha$  of the crystal in the direction under consideration:

$$\alpha = \frac{k}{\rho c_p}$$

where

$k$  = thermal conductivity coefficient

$\rho$  = density of the crystal

$c_p$  = specific heat of the crystal

De Senarmont found spherical heat conductivity wax figures for the isometric system. For the tetragonal and hexagonal systems oblate or prolate ellipsoids of revolution (the c-axis being axis of revolution) were obtained. The orthorhombic, monoclinic and triclinic systems gave triaxial ellipsoids in all cases. In the orthorhombic system the three axes were parallel to the crystallographic axes. In the monoclinic system one axis was parallel to the orthodiagonal and in the triclinic no axis corresponded to any of the crystallographic axes.

If we designate the lengths of the axes of the isothermal ellipsoids by  $a$ ,  $b$  and  $c$  (being in the same direction as the crystallographic axes in the orthorhombic system) we have:

$$a^2 = \alpha_{11} = \frac{k_{11}}{c_p}; \quad b^2 = \alpha_{22} = \frac{k_{22}}{c_p}; \quad c^2 = \alpha_{33} = \frac{k_{33}}{c_p}$$

The ratios of  $a$ ,  $b$  and  $c$  for minerals in the different systems are given in Table 10 taken from Thelen (94).

In the monoclinic system  $c$  signifies the length of the ellipsoidal axis parallel to the axis of elasticity which lies nearest to the crystallographic c-axis. The column headed  $D$  gives the position of the ellipsoidal c-axis with respect to the crystallographic c-axis. For a positive value of  $D$  the axis lies in the obtuse angle between the c-axis and the a-axis or clinodiagonal. The numbers show the magnitude of deviation from the c-axis. The third column indicates values parallel to the crystallographic b-axis. The second column indicates values along a line perpendicular to  $b$ ; and the direction of  $c$  is indicated in the first column.

The equation for heat conduction in one direction was given as:

$$Q_x = -k \frac{dt}{dx}$$

where  $Q_x$  is called the "heat flux," "density of heat," or "intensity of the heat current."

The general equation for heat flow in a crystal (83) (91) (97) (44) is derived later on. For homogeneous isotropic bodies the direction of the heat flow is perpendicular to the isothermal planes in the body. In a nonisotropic crystal, the direction of the heat flux coincides with  $n$ , the normal to the isothermal planes, only when  $n$  is an axis of symmetry of the crystal.

When temperature differences exist from point to point in the crystal we may choose X, Y, Z as fixed rectangular coordinates with  $Q_x$ ,  $Q_y$ ,  $Q_z$  and  $dt/dx$ ,  $dt/dy$ ,  $dt/dz$  the components of heat flux and temperature differences, respectively, in the chosen directions. The components of the heat flow will depend not only on the temperature differences in their respective directions but also on the temperature differences in the other two directions. From this the "fundamental law" of heat flow is derived.

$$-Q_x = k_{11} \frac{\partial t}{\partial x} + k_{12} \frac{\partial t}{\partial y} + k_{13} \frac{\partial t}{\partial z}$$

$$-Q_y = k_{21} \frac{\partial t}{\partial x} + k_{22} \frac{\partial t}{\partial y} + k_{23} \frac{\partial t}{\partial z}$$

$$-Q_z = k_{31} \frac{\partial t}{\partial x} + k_{32} \frac{\partial t}{\partial y} + k_{33} \frac{\partial t}{\partial z}$$

The nine constants  $k_{11}$  to  $k_{33}$  are called the internal heat conductivities. They depend on the nature of the substance and the orientation of the coordinates. With increasing symmetry of a crystal the number of constants required for complete description of the thermal flux decreases, becoming one in the cubic system. The number of parameters required for the different crystal systems is shown in the following:

(1) All crystals in the cubical system:

$$a = b = c, \quad \alpha = \beta = \gamma = 90^\circ$$

$$-Q_x = k \frac{\partial t}{\partial x}; \quad -Q_y = k \frac{\partial t}{\partial y}; \quad -Q_z = k \frac{\partial t}{\partial z}$$

(2) Anisotropic crystals with one isotropic axis and two-valued symmetry axes perpendicular to it.

$$a = b, \quad c, \quad \alpha = \beta = \gamma = 90^\circ$$

$$-Q_x = k_{11} \frac{\partial t}{\partial x}; \quad -Q_y = k_{11} \frac{\partial t}{\partial y}; \quad -Q_z = k_{33} \frac{\partial t}{\partial z}$$

(3) Anisotropic crystals with one isotropic axis but no other symmetry axis.

$$a = b, \quad c, \quad \alpha = \beta = 90^\circ \quad \gamma = 120^\circ$$

$$-Q_x = k_{11} \frac{\partial t}{\partial x} + k_{12} \frac{\partial t}{\partial y}; \quad -Q_y = k_{12} \frac{\partial t}{\partial x} + k_{11} \frac{\partial t}{\partial y}$$

$$-Q_z = k_{33} \frac{\partial t}{\partial z}$$

(4) All rhombic crystals. They have the coordinates in the direction of the crystallographic axes.

$$a, \quad b, \quad c, \quad \alpha = \beta = \gamma = 90^\circ$$

$$-Q_x = k_{11} \frac{\partial t}{\partial x}; \quad -Q_y = k_{22} \frac{\partial t}{\partial y}; \quad -Q_z = k_{33} \frac{\partial t}{\partial z}$$

(5) All monoclinic crystals. When the Y-axis coincides with the b-crystallographic symmetry axis.

$$a, \quad b, \quad c, \quad \alpha = \beta = 90^\circ; \quad \gamma = 90^\circ$$

$$-Q_x = k_{11} \frac{\partial t}{\partial x} + k_{13} \frac{\partial t}{\partial z}; \quad -Q_y = k_{22} \frac{\partial t}{\partial y}$$

$$-Q_z = k_{31} \frac{\partial t}{\partial x} + k_{33} \frac{\partial t}{\partial z}$$

## (6) All triclinic crystals.

$$a, b, c, \alpha \neq \beta \neq \gamma \neq 90^\circ$$

The general equation applies in this case.

If a heat source exists in a homogeneous crystal of infinite extent, the general equation will be applicable. Stokes (91) indicated that the stream lines for classes 3, 5 and 6 will not proceed in straight lines but in spatial spirals. Voigt (97) found from experiments on two apatites and dolomites that the differences  $k_{23} - k_{32}$ ,  $k_{13} - k_{31}$ ,  $k_{12} - k_{21}$  are almost zero or so small that their real value cannot be determined accurately.

As shown previously:  $Q_n = k_n \frac{\partial t}{\partial n}$ . In this equation  $k_n$  changes with the direction  $n$  as the reciprocal square of the radius vector of a fixed ellipsoid. If  $k_{23} = k_{32}$ ,  $k_{13} = k_{31}$ ,  $k_{12} = k_{21}$ , the equation of the ellipsoid will be:

$$k_{11}x^2 + k_{22}y^2 + k_{33}z^2 + 2k_{23}yz + 2k_{31}zx + 2k_{12}xy = 1.$$

If the coordinates  $x, y, z$  are the main axes of this ellipsoid, then the equation becomes:

$$k_{11}x^2 + k_{22}y^2 + k_{33}z^2 = 1;$$

and if the general equation is determined for the same coordinates, then:

$$-Q_x = k_{11} \frac{\partial t}{\partial x}; Q_y = k_{22} \frac{\partial t}{\partial y}; -Q_z = k_{33} \frac{\partial t}{\partial z}.$$

In the cubical system an infinite number of coordinate orientations exists which is independent of temperature. The heat conductivity is then expressed by one value of  $k$ .

For crystals in the hexagonal, rhombohedral and tetragonal systems the position of the main axes is fixed. This orientation is not temperature dependent. The heat conductivity is characterized by two values  $k_{11}$  and  $k_{33}$ . The axes coincide with the crystallographic axes.

The main axes in the rhombic system are also fixed and temperature independent;  $k_{11}$ ,  $k_{22}$  and  $k_{33}$  express the main heat conductivities. The main axes correspond with the three crystallographic axes.

In the monoclinic system only one main conductivity axis is independent of the temperature - this axis corresponds to the crystallographic  $b$ -axis. The other two axes are temperature dependent and their direction must be given by the angle which they make with the crystallographic  $c$ -axis. In addition, the heat conductivity values are given by  $k_{11}$ ,  $k_{22}$ ,  $k_{33}$  (the main heat conductivities).

The three main conductivity axes in the triclinic system are all temperature dependent. The heat conductivity is characterized by  $k_{11}$ ,  $k_{22}$ ,  $k_{33}$  and the positions of the three axes by their relation to the three crystallographic axes.

The equation for the isothermal ellipsoid in a crystal is given by (44):

$$\frac{x^2}{k_{11}} + \frac{y^2}{k_{22}} + \frac{z^2}{k_{33}} = 1,$$

where the axes of the ellipsoid will be  $\sqrt{k_{11}}$ ,  $\sqrt{k_{22}}$ , and  $\sqrt{k_{33}}$ , respectively. The isothermal ellipsoid is not to be confused with the heat conductivity ellipsoid as given previously.

If we consider the heat energy in an element ( $dx, dy, dz$ ) of the material during the time element  $d\tau$ , the requirements for equilibrium are:

$$\left. \begin{array}{l} \text{Total heat entering} \\ \text{the element} \\ + \\ \text{Heat energy} \\ \text{developed in} \\ \text{the element} \end{array} \right\} = \left\{ \begin{array}{l} \text{Total heat leaving} \\ \text{the element} \\ + \\ \text{Heat energy} \\ \text{stored in} \\ \text{the element} \end{array} \right.$$

This consideration leads to the equation:

$$\rho c_p \frac{\partial t}{\partial \tau} = (k_{11} \frac{\partial^2 t}{\partial x^2} + k_{22} \frac{\partial^2 t}{\partial y^2} + k_{33} \frac{\partial^2 t}{\partial z^2}) + q'$$

in which:

$\rho$  = density

$c_p$  = specific heat at constant pressure

$q'$  = heat developed per unit volume and in unit time.

The thermal conductivities  $k_{11}$ ,  $k_{22}$  and  $k_{33}$  are considered to be independent of temperature. If they are temperature dependent the equation becomes:

$$\rho c_p \frac{\partial t}{\partial \tau} = \frac{\partial}{\partial x} (k_{11} \frac{\partial t}{\partial x}) + \frac{\partial}{\partial y} (k_{22} \frac{\partial t}{\partial y}) + \frac{\partial}{\partial z} (k_{33} \frac{\partial t}{\partial z}) + q'$$

For the steady state with no heat evolution in the body and heat conductivities constant we obtain:

$$k_{11} \frac{\partial^2 t}{\partial x^2} + k_{22} \frac{\partial^2 t}{\partial y^2} + k_{33} \frac{\partial^2 t}{\partial z^2} = 0.$$

The mathematical treatment does not include the nature and extent of the influence various factors have on the absolute value of the thermal conductivity. Birch and Clarke (8) concluded that at relatively high temperatures a more correct statement of the experimental data is that the thermal resistivity tends to increase linearly with temperature and not directly proportional as was approximated by Eucken (30). From experiments on quartz crystals Birch and Clarke found that the conductivity does not decrease as rapidly as the theory would predict; indicating the possibility of some factor not included in the theory of Makinson. On some feldspar aggregates the conductivity increased with temperature - a phenomenon which is attributed to some crystalline imperfection and not completely to aggregation as was suggested by Eucken and Kuhn (32).

It is accepted that very fine imperfections may exist in crystals but the extent, degree of regularity and amount of disorientation in supposedly perfect crystals are not yet completely evaluated. It has been proposed that the mentioned factors are dependent upon the conditions of crystal growth and the mechanical and thermal history of the crystals. Evidence of the dependence of the conductivity even to high temperatures upon the fine-structure was presented by Powell and Griffiths (76). They found the thermal resistance of certain micas across the basal planes to decrease when the planes were pressed together as shown in Table 11. Wood (102) discovered, by means of x-rays, that the irreversible decrease of conductivity when mica is heated over 200 deg C (see Fig. 5) was due to the breaking up of the original mica structure into a group of small regions which were tilted from their original positions. Birch and Clarke obtained values of the conductivity of rocksalt at temperatures where impurities and imperfections should have very little effect. The resistivity was very closely a linear function of the temperature but the absolute values were much lower than those reported by Eucken and Kuhn from tests on crystals grown artificially from melts and solutions. Birch and Clarke concluded that the effect of fine-structure must persist to higher temperatures than was supposed previously.

Wooster (103) attempted to correlated the anisotropies in the thermal conductivity of crystals with their structure. For this purpose the crystals were divided into three groups:

(a) Crystals having bonds of about the same strength in the different directions. He assumes that the three principal conductivities  $k_1$ ,  $k_2$ ,  $k_3$  are given by  $\sum S \cos^2 \theta_1$ ,  $\sum S \cos^2 \theta_2$  and  $\sum S \cos^2 \theta_3$  respectively. The summation is taken over all the bonds in the unit cell;  $S$  is the number of equivalent bonds which makes angles  $\theta_1$ ,  $\theta_2$  and  $\theta_3$  with the principal axes.

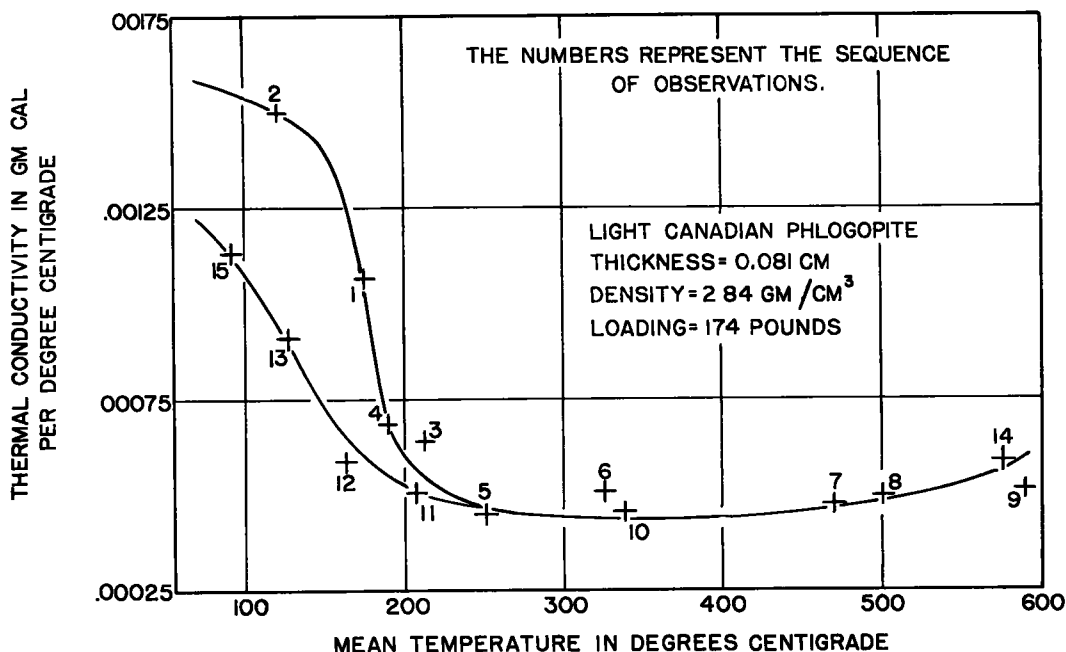


Figure 5. Temperature effect on a light Canadian phlogopite.

(b) Crystals having layered lattice structures; the conductivity in the plane of the layer is greater than that perpendicular to it.

(c) Crystals of the chain lattice type: the conductivity along the chains is greater than that perpendicular to it. The theory of Wooster was applied only to the first group but not to the second and third groups due to the inadequacy of the experimental data.

Thermal conductivity increases when magnesium (in dolomite) is substituted for calcium (limestone), which is explained according to the Debye theory as due to increase in density and sound velocity. The dense ultrabasic minerals having high elastic constants and high sound velocities give high conductivities as compared with the feldspars. Quartz, however, has a higher heat conductivity than either the ultrabasic silicates or the feldspars despite its lower density. To what extent this is due to the greater perfection of the quartz crystals is not known.

With increase in temperature the anisotropism in crystals with respect to thermal conductivity decreases as shown in Figure 6 taken from Birch and Clarke.

## HEAT CONDUCTION IN HETEROGENEOUS SUBSTANCES

### Conduction in Aggregates

The primary factors in the thermal conductivity of homogeneous aggregates are the conductivity of the single crystals and the thermal contact between them. However, to determine the average conductivity of a specimen containing a large number of crystals oriented at random it would be impracticable to attempt any rigorous computation. An average value for random orientation is obtained by averaging the conductivity value over-all direction for a single crystal. When the conductivity of a crystal does not vary greatly in different directions, then the average conductivity will not be very much different from the reciprocal of the average resistivity; for anisotropic crystals, however, they cannot be equal.

It was pointed out previously that the conductivity  $k_n$  in the direction  $n$  changes with the direction like the reciprocal square of the radius vector of a fixed ellipsoid. If for crystals having a principal axis the equation of the ellipsoid is expressed in

polar coordinates, then the thermal conductivity  $k_n$  is given according to Voigt (97) by:

$$k_n = k_{\perp} \sin^2 \beta + k_{\parallel} \cos^2 \beta$$

where  $\beta$  is the angle between the principal axis and the given direction,  $k_{\perp}$  and  $k_{\parallel}$  the thermal conductivities perpendicular and parallel, respectively to the principal axis.

By taking the averages of  $\sin^2 \beta$  and  $\cos^2 \beta$  over all directions an average value of  $k$  is obtained.

$$(\sin^2 \beta) \text{ av. } = \frac{2}{3} \text{ and } (\cos^2 \beta) \text{ av. } = \frac{1}{3} ; k_n = \frac{2}{3} k_{\perp} + \frac{1}{3} k_{\parallel} .$$

The equation gives the conductivity of a single layer of crystals oriented at random,

TABLE 11  
EFFECT OF PRESSURE ON THE THERMAL CONDUCTIVITY OF  
A MADAGASCAN DARK AMBER PHLOGOPITE  
(after Powell and Griffith)

Pressure lb/sq in.	Thickness cm	Density gm/cm <sup>3</sup>	Conductivity watt/cm <sup>2</sup> °C per cm		
			100°C	300°C	500°C
23	0.109	2.80	0.0046	0.0021	0.0021
48			0.00586	0.00252	0.00252
176	0.105	2.90	0.0067	0.00335	0.00377
330			0.00755	0.0046	0.00503

TABLE 12  
MEAN CONDUCTIVITY OF QUARTZ AND CALCITE CRYSTALS  
(in watt/sq cm °C per cm)

Temp., °C	Calcite				Quartz			
	$k_{\perp}$	$k_{\parallel}$	$k_{\text{mean}}$		$k_{\perp}$	$k_{\parallel}$	$k_{\text{mean}}$	
			$\sqrt[3]{k_{\perp}^2 k_{\parallel}}$	$\frac{1}{3}(k_{\parallel} + 2k_{\perp})$			$\sqrt[3]{k_{\perp}^2 k_{\parallel}}$	$\frac{1}{3}(k_{\parallel} + 2k_{\perp})$
-190	0.1845	0.3070	0.2182	0.2253	0.2455	0.490	0.309	0.327
0	0.0348	0.401	0.0365	0.0366	0.0684	0.1142	0.0811	0.0833
50	0.0301	0.0340	0.0313	0.0314	0.0565	0.0940	0.0670	0.0690
100	0.0272	0.0300	0.0281	0.0281	0.0495	0.0796	0.0580	0.0595
200	0.0238	0.0256	0.0244	0.0244	0.0407	0.0632	0.0471	0.0482

with heat flow perpendicular to the plane. On substituting the resistivity values for the various conductivities in the equation, the mean resistivity of a crystal can be calculated. The reciprocal of this mean resistivity is the conductivity of a filament of randomly oriented crystals placed on top of each other with the heat flowing along the filament. An aggregate may be considered to be composed of a great number of filaments or layers. Neither of these treatments is correct; for nearly isotropic minerals their results will approach each other but they will differ considerably in heterogeneous aggregates of minerals of greatly differing conductivities. The method is considered



chiefly because of its simplicity. Eucken and Kuhn (32) used the formula

$$k_{\text{mean}} = 3 \sqrt{k_{\perp}^2 k_{\parallel}}$$

to calculate the mean conductivity  $k_{\text{mean}}$  of calcite. It may not be applicable to other minerals.

From measurements on natural crystals, crystals grown from melts and solutions, and on aggregates either natural or artificially pressed from crystals powders, Eucken and Kuhn attempted to determine the effect of the grain size on the thermal conductivity. They found that the experimental data obeyed approximately the following empirical equation:

$$k = \frac{k_0}{nB + 1}$$

in which

$k$  = conductivity of the crystalline material

$k_0$  = conductivity of the compact crystal

$n$  = number of grains per cm, and

$$B = \frac{T_s}{T_0} = \frac{\text{Temperature difference between adjacent grain surfaces}}{\text{Temperature decrease per cm length}}$$

It was indicated that the quality  $\frac{BC_v}{k_0}$  is approximately temperature independent.

The formula does not apply for aggregates consisting of particles of one component crystallizing in the regular system.

According to data obtained by Birch and Clarke from tests on a marble, the value of  $B$ , the constant in Eucken and Kuhn's formula, varies proportionally with the size of the crystals. These authors (8) suggested that the reduced conductivity in the ag-

TABLE 13  
VALUES OF B ACCORDING TO EUCKEN AND KUHN'S FORMULA

Temp. k ideal		Marble						Limestone					
°C	Calcite	k	n	B	k	n	B	k	n	B	k	n	B
-190	0.218	0.0423	138	0.030	0.0563	103	0.028	Birch and Clarke's					
0	0.0478	0.0351	138	0.0026	0.0373	103	0.0027						
0	0.0366	Eucken and Kuhn's Data						0.0305	30	0.0067	0.0302	5,000	$4 \times 10^{-5}$
50	0.0314							0.0268	30	0.0057	0.0257	5,000	$4.4 \times 10^{-5}$
100	0.0281							0.0244	30	0.0050	0.0232	5,000	$4.2 \times 10^{-5}$
200	0.0244							0.0214	30	0.0047	0.0200	5,000	$4.4 \times 10^{-5}$

gregates is due to spaces of relatively low conductivity between some crystals. Sample calculations are shown in Tables 12 and 13.

Mixed Aggregates

The shortcomings of the theory regarding the thermal conductivity of pure crystals, even in the regular system, point out the difficulties to be overcome in the development of a theory for the thermal conductivity of aggregates consisting of more than one component.

Mixed aggregates still exhibit a negative temperature coefficient like the crystals of which they are composed. However as Eucken and Kuhn (32) have pointed out, mixed crystalline aggregates cause a marked decrease in the absolute value of the thermal conductivity and in the negative temperature coefficient of the constituents crystals. From mixed crystals of KCl with various percentages of KBr, they determined the deviation of the measured values from the calculated ones using the mixing formula:

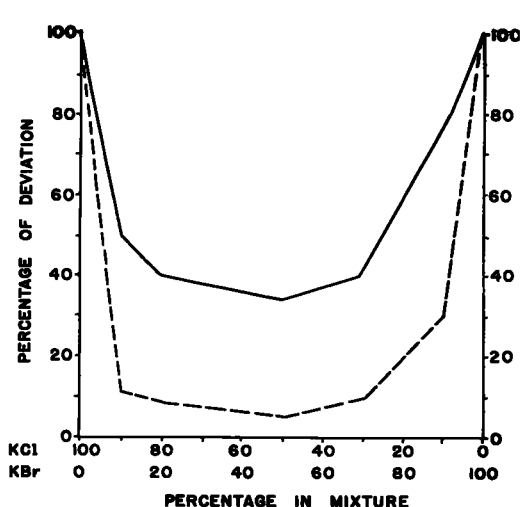


Figure 7. The deviation of the measured values from that calculated according to formula (after Eucken and Kuhn).

$$k_{\text{mix}} = \frac{n_{\text{KCl}} \cdot k_{\text{KCl}} + n_{\text{KBr}} \cdot k_{\text{KBr}}}{n_{\text{KCl}} + n_{\text{KBr}}}$$

where  $n$  represents the proportion of the respective component present in the mixture. The correlation between calculated and measured values is represented in Figure 7.

The authors maintain that Mathiesen's law for expressing the effect of impurities on the electrical conductivity may also be used to indicate the effect of impurities on the thermal conductivity, viz:

$$w_u = w_v + \Delta$$

where

$w_u$  = thermal resistivity of an impure aggregate

$w_v$  = thermal resistivity of a pure crystal =  $\frac{1}{K}$

$\Delta$  = "Increment" resistance which should be independent of temperature.

Birch and Clarke used the concept that the heat flows through piles in the aggregate; no heat was supposed to flow across the side walls of the piles. The piles were considered to be one crystal thick and to contain the constituents in the same proportion in which they occur in the whole mass, in random distribution and in orientation. When the thickness of the sample was too small with respect to the crystal size, the "series" treatment became inappropriate and a "parallel" consideration was employed.

Although the heat flow is much more complicated than the previous two treatments suggest, the "series" concept was found to agree with experimental data within 5 percent, except where the crystal thickness was small with respect to the crystal size. In that case the parallel treatment gave correct values. The authors concluded that the grain size should not be important unless an appreciable proportion of the resistance occurs at the intercrystalline contacts. This resistance is low for relatively fresh igneous rocks. They ascribed the permanent decrease in conductivity of the rocks when heated over 300 deg C in part to loss of moisture and development of imperfections.

De Vries (25) expressed the thermal conductivity of a granular material as a function of the thermal conductivities and the volume fractions of its constituents by making use of the analogy between heat conductivity, electric conductivity, dielectric constant, magnetic permeability and diffusion coefficient. Because of mathematical difficulties only an approximate solution can be given. Different authors used different approximations to find a solution for the case of a composite material consisting of a continuous medium in which particles of spherical or ellipsoidal shape are distributed at random. All these theories were developed mainly in analogy with the theory of the dielectric constant. This means that the phenomena specifically associated with heat conduction are not taken into account.

Before the various theories studied by De Vries are discussed in detail, it might be advantageous to consider some other effects.

In the calculation of the thermal conductivity of mixed crystals either the method

used by Birch and Clarke can be followed or the theory of Maxwell-Burger-Eucken. Table 14 gives the conductivities of mixed crystals as determined by Eucken and Kuhn from pressed crystal pastes. The value of the conductivities of the pure crystals were also obtained from Eucken and Kuhn's data. The values were calculated for 0 deg C.

Table 15 gives examples taken from the investigations of Birch and Clarke. The rocks tested were considered to consist of major constituents such as quartz ( $k_{av.} = .069$ ),

TABLE 14  
THERMAL CONDUCTIVITIES OF MIXED CRYSTALS  
in watt/sq cm °C per cm

Composition by Volume, Percent			Shape of Particle	Measured Conductivity	Calc. Conduct.	
Kcl	KBr	NaCl			Birch and Clarke	Burger and Eucken
100	--	--	--	0.0900	--	--
--	100	--	--	0.0365	--	--
--	--	100	--	0.088	--	--
8.7	91.3	--	Spherical	0.0290	0.0385	0.0397
22.3	77.7	--	Spherical	0.0196	0.0420	0.0452
46.4	53.6	--	Spherical	0.0237	0.0504	0.0562
72	28.0	--	Spherical	0.0336	0.0636	0.0704
88.6	11.4	--	Spherical	0.0484	0.0770	0.0815
58		42	Spherical	0.0694	0.0891	0.0892

plagioclase feldspar ( $k_{av.} = .019$ ), olivine ( $k_{av.} = .044$ ), pyroxene ( $k_{av.} = .0415$ ) and orthoclase feldspar ( $k = .0193$ ). The minor constituents were grouped with some of the major components, e.g.: hornblende and magnetite with olivine or pyroxene; sericite with feldspar; micropertite assumed to have a  $k$  value of 0.020; biotite assumed to have the same conductivity as pyroxene. The thermal conductivities were calculated for 50 deg C.

#### HEAT CONDUCTION IN GLASSES

It was observed that the thermal conductivity of quartz glass with the same chemical composition as that of a quartz crystal decreases with decrease in temperature. As was previously indicated  $\frac{c_v}{k}$  is approximately constant for quartz glass where  $c_v$  = specific heat and  $k$  = thermal conductivity of the glass. Eucken (31) approximated the thermal conductivity of glass by the formula:

$$\frac{1}{k_g} = C + \frac{D}{T}$$

in which:

$k_g$  = thermal conductivity of the glass

$T$  = absolute temperature

$C$  and  $D$  are constants

TABLE 15  
THERMAL CONDUCTIVITIES OF CERTAIN ROCKS  
in watt/ sq cm °C per cm

Rock	Composition <sup>a</sup>		Particle Size, mm	Measured Conduct.	Calc. Conductivity <sup>a</sup>	
	Mineral	Percent			Birch and Clarke	Eucken and Burger
Barre granite	Quartz Albite Orthoclase Biotite	26 37 25 12	1.2 x 0.8 medium 1.5 x 1 spheres	0.0264	0.0268	0.0309 (0.0280)
Quartz monzonite	Quartz Orthoclase Ab <sub>72</sub> An <sub>28</sub> Biotite Hornblende	34 27 33 5 1	1 x 0.8 1.0 dia. medium spheres	0.0294	0.0264	0.0320 (0.0296)
Tonalite	Quartz Ab <sub>88</sub> An <sub>12</sub> Biotite Hornblende	28 50 15 7	1 x 0.8 medium 1.2 x 0.9	0.0260	0.0268	0.0326 (0.0291)
Wisconsin gabbro	Ab <sub>40</sub> An <sub>60</sub> Pyroxene Olivine	73 15 12	medium spheres spheres	0.0197	0.0209	0.0223
Rockport granite	Quartz Microperthite Amphibole	30 64 6	1.5 x 1 medium spheres	0.0340	0.0268 (0.0348)	0.0299 (0.0334)

<sup>a</sup>Biotite grouped with feldspar instead of with pyroxene, gives the values in parentheses in the last column. Both calculated values for Rockport granite are far off. Following the suggestion by Birch and Clarke that a parallel treatment would be more appropriate in this case, the value in parentheses in the fifth column was obtained. The value in parentheses in the last column was obtained by considering the quartz as the continuous medium and the other components as dispersed in it.

TABLE 16  
THERMAL CONDUCTIVITY OF SOME GLASSES  
in watt/sq cm °C per cm

Glass	Temperature °C						
	-200	-100	0	100	200	300	400
Quartz Glass	0.00612	0.0110	0.0136	0.0148	0.0158	0.0170	0.0185
Pyrex Glass			0.0120	0.0132	0.0144	0.0155	0.0166
Heavy Optical Flint	0.00303	0.0058	0.0071	0.0075			
Obsidianite			0.0135	0.0146	0.0157	0.0157	0.0179
Soiled Quartz Glass	0.00467	0.00900	0.01122	0.0125	0.0131		0.0150

From the concept of glasses being liquids with high viscosities, it was proposed that the Bridgman formula, developed for liquids, be used for calculating the thermal conductivity of glasses. Some basic differences exist, however, as was pointed out by Birch and Clarke (8): The molecular weight of glass is not exactly defined and two types of waves exist in glasses instead of the one compressional wave in liquids.

If the formula is used to determine the average distance between the heat propagating units from known conductivity values, it is found that the distance comes out to be in the order of the distance between nearest silica atoms in silica glass (3.3 Å). For this (8) a mean velocity  $V = \frac{1}{3} (V_1 + 2V_t)$  was used in the equation:

$$k = \frac{3kV}{\delta^2}$$

TABLE 17  
CONDUCTIVITY,  $k$ , OF SOME FIREBRICKS  
in watt/sq cm  $^{\circ}\text{C}$  per cm (from Ref 17)

Brick							Temp. , °C	k
Type	Constituents, Percent					Density, lb/cu ft		
	MgO	Fe <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>			
Magnesite	86.8	6.3	3	2.6	--	158	204	0.0381
							650	0.0277
							1,200	0.0190
Alumina	--	--	--	--	82	170	500	0.0223
							800	0.0211
							1,100	0.0208
							500	0.0104
							800	0.0107
Silica	--	--	--	93	--	105	500	0.0132
							800	0.0147
							1,100	0.0161
							500	0.0147
							800	0.0163
Silicon carbide	--	--	--	--	--	129	600	0.1852
							800	0.1592
							1,000	0.1385
							1,200	0.1212
							1,400	0.109

where  $V_l$  and  $V_t$  are the velocities of the longitudinal (compressional) and distortional waves, respectively,  $k$  is the Boltzmann constant and  $\delta$  is the distance between the nearest silicon atoms in silica glass.

The Debye formula gives greater distances for the mean free path (8.5 Å for silica glass, 4.9 Å for diabase glass). This indicates an atom-to-atom heat exchange. The thermal waves are scattered in such short distances by the random assembly of the atoms that the wave concept becomes irrelevant. For the same reason, small amounts of impurities probably have little influence. Table 16 gives a few values for the thermal conductivities of glasses.

### CONDUCTION IN CRYSTALLINE-AMORPHOUS MATERIAL

Eucken (30) found from measurements on materials such as paraffin and ebonite that the thermal conductivity of these partly crystalline, partly amorphous materials is little temperature dependent. Jakob (43) discussed the variations encountered in the thermal conductivities of various sorts of magnesite bricks of about the same density and of moderately varying content in magnesium oxide (86 to 92 percent). He concluded that, in cases where small values of conductivity with positive temperature coefficients were observed, the bricks contained predominantly glassy substances. Where the conductivity was large and had a negative temperature coefficient, the materials consisted mainly of crystalline components. Analogous results were found by Birch and Clarke (8) on some feldspar aggregates.

Eucken (31) proposed the following approximate equations:

$$\text{for uniform crystals: } \frac{1}{k_{cu}} = AT$$

$$\text{for mixed crystals: } \frac{1}{k_{cm}} = AT + B$$

$$\text{for glasses: } \frac{1}{k_g} = C + \frac{D}{T}$$

in which  $k_c$  and  $k_g$  are the thermal conductivities of the crystals and glasses and A, B, C and D are constants. Assuming (43) that the material is an aggregate of heat resistors of crystalline and amorphous types connected in series, the following expression is obtained:

$$k = \frac{1}{\frac{a}{T} + b + \frac{C}{T}},$$

a, b, and c being constants.

The equation gives an increase of  $k$  with increasing temperature if  $T$  is small and a decrease of  $k$  with increasing temperature if  $T$  is high. This results from the three equations of Eucken. It will be noticed, too, that the form of the equation is related to the curve by Makinson.

The burning of a refractory material influences  $k$  considerably because of the chemical and crystallographic changes as well as the changes in density due to sintering. Sintering or cementation also reduce the surface area per unit volume thereby improving the interfacial conductivity. In fire bricks the chemical composition has an influence on the conductivity. Table 17 shows the influence of predominance of  $MgO$ ,  $Al_2O_3$  and  $SiO_2$  on the thermal conductivity of fire bricks.

### CONDUCTION IN GRANULAR MATERIALS

Granular materials are defined as systems composed of a solid phase or phases within a liquid or gaseous environment. In such systems, the surfaces between the

phases are of more importance than in the case of pure solid aggregates.

### Fine Powders

From considerations of the kinetic theory of gases, Kundt and Warburg (51) pointed out that for a gas flowing along a wall a discontinuity of velocity occurs. They also did experiments to verify their conclusion. Smoluchowski (89) applied this concept to thermal conduction and found, also from experiment, that a corresponding temperature discontinuity exists. The temperature discontinuity  $\theta$  if replaced by an assumed continuous change of gas temperature  $dT$  leads to the equation (43):

$$k \frac{dT}{dn} = h\theta \quad \text{or} \quad \theta = \xi \frac{dT}{dn}$$

in which

$k$  = thermal conductivity of the gas

$n$  = distance in direction normal to the wall

$h$  = coefficient of heat transfer between wall and medium, and

$\xi = \frac{k}{h}$  is a coefficient of discontinuity

An analogous  $\xi$  for the discontinuity  $\theta$  in the velocity  $v$  of a gas flowing along a wall is given as:

$$\theta = \xi \frac{dv}{dn}.$$

The quantity  $\xi$  measured in centimeters is dependent on the type of gas and the character of the wall. The coefficient of discontinuity is of the same order of magnitude as the free path of the molecules and proportional to the free path; it is, therefore, also inversely proportional to the absolute pressure of the gas.

From measurements by Smoluchowski (90), Gehrcke (34) and Lasareff (53),

$$\xi = A \times (10^{-6}) \frac{760}{p},$$

where

$p$  = gas pressure in millimeters of mercury, and

$\xi$  is measured in centimeters.

For air:  $A = 13.4$  to  $19.6$

For  $\text{CO}_2$ :  $A = 8.0$  to  $12.7$

For hydrogen:  $A = 105$  to  $145$

The rate of heat conduction for two parallel walls at distance  $L$  and temperature difference  $\Delta T$  will be

$$q = k \frac{A}{L} \Delta T.$$

When a perfectly conducting plate of thickness  $s$  is inserted, the total width of gas layer will be  $(L - s)$  but the effective length will be  $(L - 2 + 2\xi)$ . For  $n$  plates we obtain:

$$q = k \frac{A}{(L - ns + 2n\xi)} T.$$

With decrease in pressure  $2\xi$  will increase and will eventually become greater than  $s$ . The use of fine powders and reduction of pressure can lead to lower conductivity values than possessed by air.

While it is still widely believed that the lowest value of the thermal conductivity under atmospheric pressure is that of stationary air, it was shown by Kistler and Caldwell (50) on silica aerogel, by Johnstone, Jacobson and Prechshot (47) on zinc

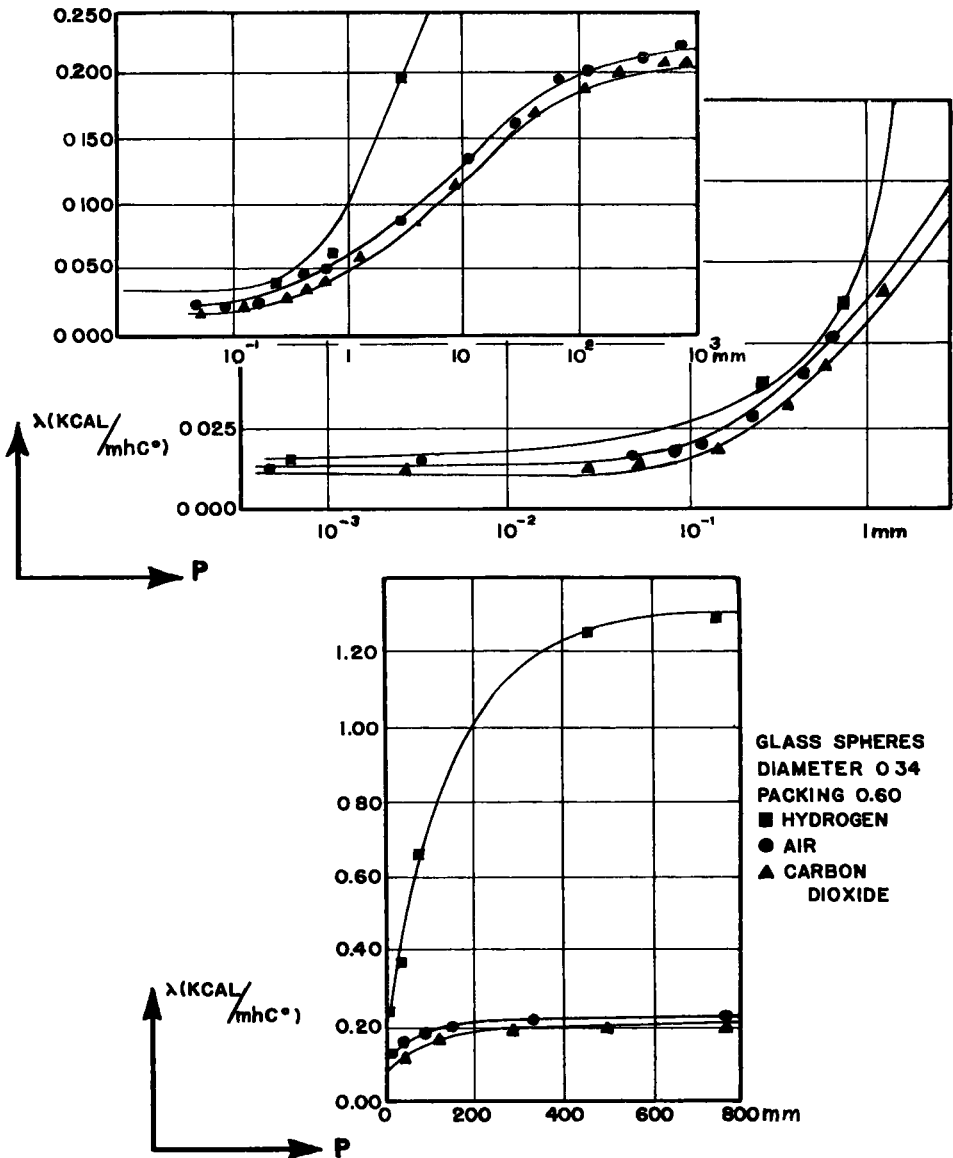


Figure 8. Heat conduction by a powder of glass spheres in different atmospheres at different pressures.

oxide, and by Smith and Wilkes (88) on carbon blacks, that still lower values can be reached when the above materials are used. An aerogel results when a gel is dehydrated without loss of the structure of the solid constituent. The silica aerogel (density 7.49 lb/cu ft) had good mechanical strength (30 pounds per square inch without crushing), a pore size of the order of 10<sup>-6</sup> cm in diameter and appeared optically empty under the ultra-microscope. Kistler and Caldwell also showed that the thermal conductivity of cork decreases when the pressure is lowered. The zinc oxide powder (density 1.78 lb/cu ft) gave conductivities about the same as air at atmospheric pressure. When the powder was compressed the conductivity increased. Reduction in gas pressure decreased the conductivity. Carbon blacks in the finely divided state have conductivities less than that of still air. For the commercial carbon black pellets (spheron) tested, Smith and Wilkes found a conductivity value close to that of



air. The density was 20.2 lb/cu ft.

From heat conduction measurement on powders in various gaseous atmospheres, Prins et al (77) found some residual conductivity at very low pressure (see Fig. 8). This conductivity was attributed to solid contact of the particles. Magnesium oxide being angular gave a lower residual value than glass spheres. The pressures ranged from 880 mm to  $4 \times 10^{-4}$  mm of mercury. Calculation of the contact radius based on a formula by Hertz gave the right order of magnitude.

De Vries (25) employed a simplified method to calculate theoretically the limits within which the thermal conductivity must lie, taking into account the touching of particles. In an assumed cubical array of spheres the lower limit is obtained when a pile of spheres is divided into concentric cylinders and the cylinders are combined in parallel. The upper limit is obtained when all planes perpendicular to the axis of the sphere pile are considered as isothermal planes - essentially a series treatment. As was observed by the investigator, the values obtained from the two treatments differ widely, thereby limiting its practical value. He believed that the correct value will be close to the lower limit considering test data by Prins and others.

### Porous and Loose Materials

In heat insulators use is made of substances composed of small particles with a high percentage of void space between them. The solid material may consist of porous particles (the solid phase being continuous), powders, grains, fibers, etc.

The use of fine powders for heat insulation has been discussed. Insulating materials of fibrous and porous material make use of the insulating value of the air in the material which is kept stationary by the presence of the solid phase. This eliminates convection currents of the air and thereby reduces the conductivity of the material. The fibers themselves may possess a low heat conductivity. However, it has been shown (58, 101) that material of high conductivity, like aluminum foil - plain or crumpled, may be used for insulation. The bright surface reflects the heat and reduces the transmission of heat by radiation. The value of aluminum foil insulation is therefore greater at high temperatures where radiation plays a predominant role in heat transport.

### Calculation of Thermal Conductivities

Eucken (31) proposed the following expression for the apparent conductivity  $k$  of a material consisting of a medium of conductivity  $k_s$  in which small particles of conductivity  $k_p$  are dispersed.

$$k = k_s \frac{1 - \left(1 - a \frac{k_p}{k_s}\right)b}{1 + (a - 1)b}$$

where

$$a = \frac{3k_s}{2k_s + k_p}$$

$$b = \frac{V_b}{V_s + V_b}$$

in which

$V_b$  = total volume of dispersed particles

$V_s$  = total volume of medium

The equation can be used only for values of  $b$  that are less than 0.5. When the particles in the medium consist of air then  $k_p$  will be small compared to  $k_s$ , resulting in the equation:

$$k = k_S \frac{1 - b}{1 + \frac{b}{2}}$$

For elliptic or tubular pores the equation becomes:

$$k = k_S \frac{1 - b}{1 + \frac{b}{3}}$$

For plane gaps with one-third of all fissures extending perpendicular to the direction of heat flow, Eucken derived the formula:

$$\frac{1}{k} = \frac{1}{k_S} + \frac{b}{3 k_p}$$

By considering a fissured body as a series of parallel solid plates and air layers of thickness  $L_{12}$  and  $L_{23}$  respectively, Nusselt (66) derived the following equation taking into account the effect of radiation. Referring to Figure 11(A):

$$k = \frac{L_{12} + L_{23}}{\frac{L_{12}}{k_S} + \frac{1}{\frac{k_p}{L_{23}} + 4 \sigma T^3}}$$

in which  $\sigma$  is the radiation constant and  $T$  the absolute temperature. For very high temperatures:  $4 \sigma T^3 \gg 1$ , one obtains:

$$k = \frac{L_{12} + L_{23}}{L_{12}} k_S$$

If radiation is neglected at low temperatures and  $k_p \ll k_S$ , then the lower limit of the heat conductivity will be:

$$k = \frac{L_{12} + L_{23}}{L_{23}} k_p$$

From the field of electricity and magnetism, De Vries (25) applied the theories of the behavior of granular media to the problem of thermal conductivity. He considered an isotropic medium with dielectric constant  $\epsilon_0$  in which there are grains of different types. All grains having the same dielectric constant and being of the same shape and size are grouped as one type of particle. The volume fraction of grains of the  $i$ -type is given as  $x_i$ , the volume of the medium is  $x_0$ . If there are  $N$  types of particles, then:

$$\sum_{i=0}^N x_i = 1$$

The mean apparent dielectric constant of the material is then:

$$\epsilon = \frac{\bar{D}}{\bar{E}} = \frac{\sum_{i=0}^N x_i \bar{E}_i}{\sum_{i=0}^N x_i \bar{E}_i} \quad (A)$$

where:

$\bar{D}$  = mean dielectric displacement,

$\bar{E}$  = mean electric field-strength

$\bar{E}_i = \frac{1}{V_i} \int E_i dV_i$  = mean electric field-strength within particle  $i$ , and

$V_i$  = volume of particle.

Because of mathematical difficulties equation (A) cannot be solved exactly. To calculate  $\bar{E}_i$ , it is assumed that all grains of the 1-type are surrounded by a homogeneous, isotropic medium with dielectric constant  $\epsilon^1$  in which a field-strength  $E^1$  exist at great distance from the particle under consideration.

By means of tensor analysis (74) it is possible to obtain a solution after values for  $\epsilon^1$  and  $E^1$  have been selected. The different theories treated by De Vries (25) differ mainly in the selection of  $\epsilon^1$  and  $E^1$ . The theories are as follows:

- (1) Theory of Maxwell (59), Burger (14), Eucken (31).

Assumption:  $\epsilon^1 = \epsilon_0$  and  $E^1 = \bar{E}_0$ ; that means, the interaction of the grains is neglected. Maxwell used it in the calculations for spherical grains; Burger extended it to ellipsoidal particles for the electrical conductivity, while Eucken first applied it to thermal conductivity.

- (2) Theory of Ollendorf (67)

Assumption:  $\epsilon^1 = \epsilon_0$ ,  $E^1 = \bar{E}_p$ , where  $\bar{E}_p$  is the field which will exist in the space of a removed ellipsoid. It is further assumed that the polarization remains unchanged in the rest of the ellipsoids. Ollendorf then derived a formula for  $\bar{E}_p$ , the magnetic permeability.

- (3) Dielectric constant, Theory of Polder and Van Santen (74)

Assumption:  $\epsilon^1 = \epsilon$ ;  $E^1 = \bar{E}$ .

- (4) Differential Theory of Bruggeman (12) which has been improved upon by De Vries (25).

Assumption:  $\epsilon^1 = \epsilon$ ;  $E^1 = \bar{E}$ , the same as the previous but in order to get the volume fraction of  $\Delta x_1$ , the grain of the first type is thought to be added in small quantities with volume fraction  $\Delta x_1$  approaching zero.

In the treatment of Rayleigh (78) the effect of the arrangement of the grains on the conductivity is taken into account. De Vries has shown how the theory could be extended to some other packings as was treated by Rayleigh.

De Vries then compares the various theories with each other and also with experimental data on grains of spherical shape. He concludes that for the ratio of particle conductivity  $k_1$  to the conductivity  $k_0$  of the medium  $\frac{k_1}{k_0} < 300$  the correct value

of the net conductivity  $k$  will lie between the theoretical values of Maxwell and

Bruggeman while for  $1000 < \frac{k_1}{k_0} < 2000$  the value of  $k$  will be within 10 percent of the

value given by Bruggeman's formula and will be greater. The volume fractions varied from 0.42 to 0.69. The deviation of experimental data obtained for soil from the Maxwell-Burger-Eucken theory is of the same order of magnitude as that for spherical particles. Because of the various assumptions it was pointed out that the treatment is of semi-empirical character.

At an earlier stage we introduced the method of Birch and Clarke for calculating the thermal resistivity of mixed aggregates. In this treatment, heat flow piles one crystal thick are made up of its components arranged in series; each constituent is present in the same proportion in which it occurs in the whole mass. Compare with Figure 9(A)

where

$k_g$  = conductivity of the gas;  $x_g$  its volume fraction,

$k_w$  = conductivity of the water;  $x_w$  its volume fraction  
 $k_s$  = conductivity of the solid;  $x_s$  its volume fraction.

For the series treatment the effective conductivity  $k$  can be calculated from:

$$\frac{1}{k} = \frac{x_g}{k_g} + \frac{x_w}{k_w} + \frac{x_s}{k_s} \tag{1}$$

The parallel treatment results in the equation:

$$k = k_g x_g + k_w x_w + k_s x_s \tag{2}$$

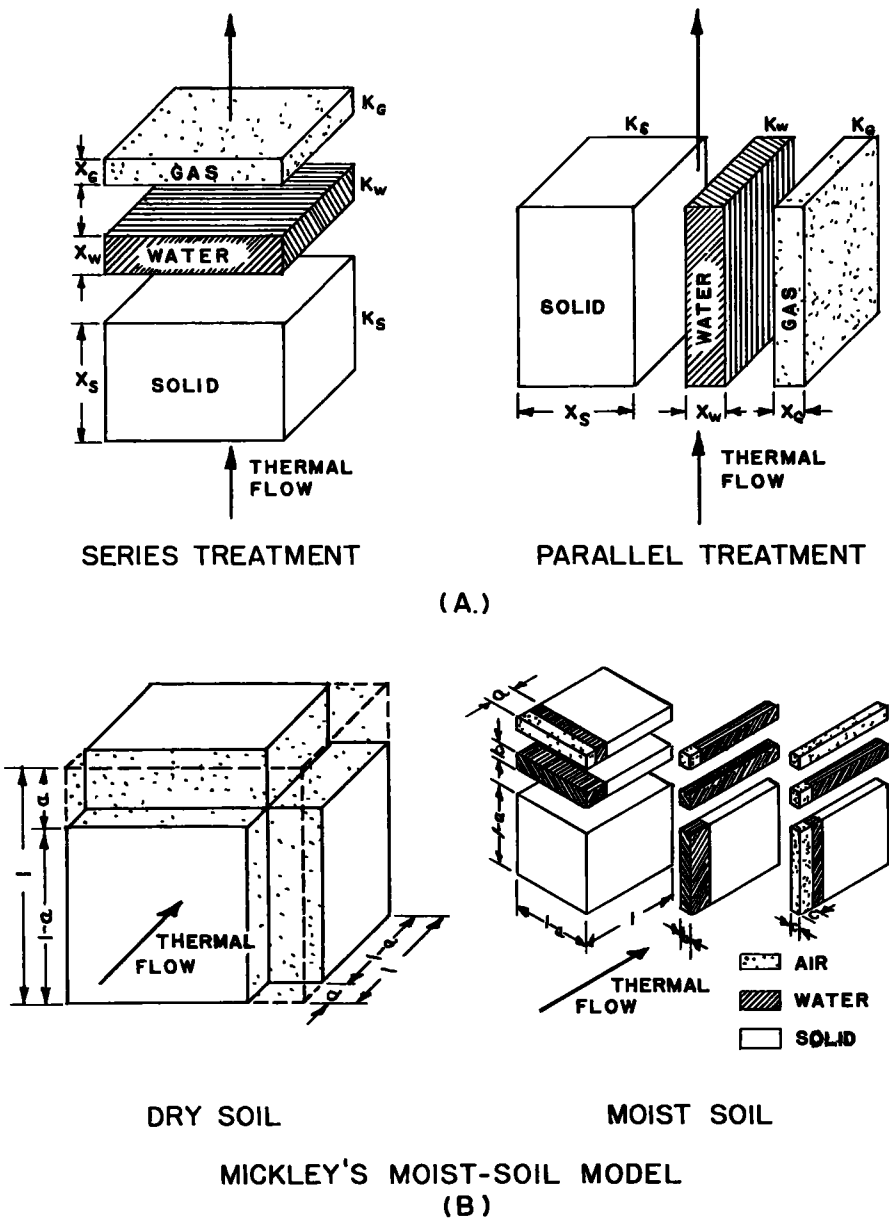


Figure 9.

It is obvious that actual values of  $k$  will lie somewhere between those given by (1) and (2). The first equation does not take into account intergranular contact while the second one assumes perfect intergranular contact.

Another method of approximating the thermal conductivity of a soil mass is that given by Mickley (61). His picture of the three-component system is as shown in Figure 9(B). The equations derived for the condition shown are as follows: (61)

$$\text{Completely Dry Soil: } k = k_g a^2 + k_s (1-a)^2 + \frac{k_s k_g (2a-2a^2)}{k_s(a) + k_g(1-a)}$$

$$\text{Completely Saturated Soil: } k = k_w a^2 + k_s (1-a)^2 + \frac{k_s k_w (2a-2a^2)}{k_s(a) + k_w(1-a)}$$

In these equations the volume fraction of the solid  $x_s = 1 - 3a^2 + 2a^3$  from which  $a$  can be calculated if  $x_s$  is known.

Moist Soil:

$$\begin{aligned} k = & k_g c^2 + k_s (1-a)^2 + k_w (a-c)^2 + \frac{2k_w k_g c (a-c)}{k_w c + k_g (1-c)} \\ & + \frac{2k_s k_w k_g c (1-a)}{k_w k_s c + k_s k_g (a-c) + k_g k_w (1-a)} \\ & + \frac{2k_w k_s (a-c) (1-a)}{k_s a + k_w (1-a)} \end{aligned} \quad (3)$$

Expressed in volume fractions  $x_s$ ,  $x_w$  and  $x_g$  it follows:

$$\begin{aligned} x_g + x_w &= 3a^2 - 2a^3 \text{ or } x_s = 1 - 3a^2 + 2a^3 \\ x_g &= 3c^2 - 2c^3. \end{aligned}$$

Equation (3) yields the complete dry or saturated soil condition when  $b = 0$  ( $c=a$ ) or  $b = a$  ( $c=0$ ), respectively. This equation is a means of averaging between equations (1) and (2). As was stated by Mickley, the equation (3) does not hold for dry or nearly dry soil because the contact between grains is not always a face contact. The equations (1), (2) and (3) do not take into account the size, shape and arrangement of the components of the soil.

W.O. Smith (87) took into account the possibility of structure in the soil. His derivation runs similar to that of Mickley for dry or saturated soil except that he assumes a different ratio of voids in series to voids in parallel with the solid and neglects intergranular contact. From Figure 10 the thermal conductivity follows to be:

$$k = k_g \frac{\sum A_a}{A} + \frac{\sum A_s}{A} \left( \frac{1}{\frac{d_s}{k_s d} + \frac{d_i}{k_g d}} \right)$$

where

$k_g$  = thermal conductivity of air

$k_s$  = thermal conductivity of the solid

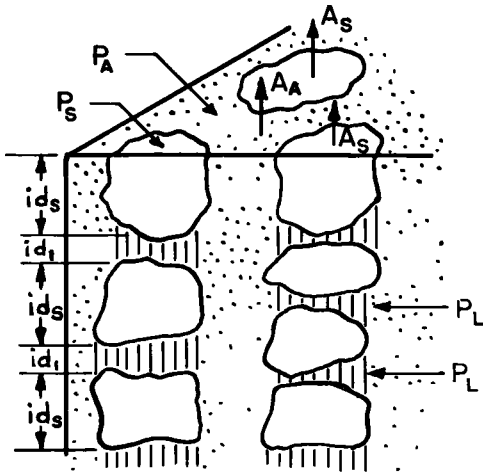
$A_a$  = area of the air column

$A_s$  = area of the grain pile column,

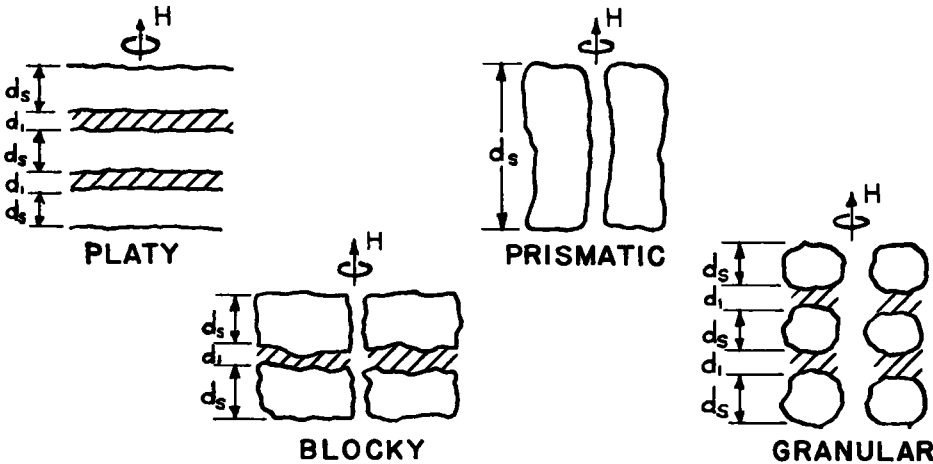
$d_s$  = total length of grains in column length  $d$ , and  
 $d_i$  = total length of air gaps between grains in grain column

Further, if

- $A$  = total area of the soil sample
- $P_a$  = partial volume of all the soil air
- $P_s$  = partial volume of the solid framework



GRAIN PILE FOR DEVELOPMENT OF  
HEAT FLOW EQUATION



VARIOUS SOIL STRUCTURAL FORMS

Figure 10. Heat conduction in structured soil (after W. O. Smith).

$P_1$  = partial volume of the material in the gaps between the grains in the grain column

$$k = k_g (P_a - P_1) + \frac{P_s + P_1}{\frac{1}{P_s + P_1} \left( \frac{P_s}{k_s} + \frac{P_1}{k_g} \right)}$$

If  $k_g P_1$  is neglected (being small) and  $\alpha = \frac{P_1}{P_s}$  then

$$k = k_g P_a + \frac{P_s (1 + \alpha)}{\frac{1}{k_s} + \left( \frac{1}{k_g} - \frac{1}{k_s} \right) \left( \frac{\alpha}{1 + \alpha} \right)}$$

This formula may be used for calculating the thermal conductivity of structured soil if a proper value of  $P_1$  is chosen.

- $P_a$  denotes the total porosity structural and textural;
- $P_1$  denotes the pore space effective in introducing resistance in series with the grains and will depend on the type of structure;
- $P_1$  can be obtained by calculating values of  $\alpha$  from observed data. The equation has the form:

$$k = k_g P_a + k_o P_s \quad \text{or} \quad k_o = \frac{k - k_g P_a}{P_s}$$

where

$$k_o = \frac{1 + \alpha}{\frac{1}{k_s} + \left( \frac{1}{k_g} - \frac{1}{k_s} \right) \left( \frac{\alpha}{1 + \alpha} \right)}$$

and is called the effective conductivity of the soil. From this equation  $\alpha$  is calculated if  $k_o$  is obtained from experiments on structured soil and from known values of  $k_a$  and  $k_s$ . A few values of  $k_o$  are indicated in Table 18.

Assuming the grains to be spherical and the water collected around the particle

TABLE 18  
THERMAL STRUCTURE FACTORS OF DRY SOIL  
 $k_o$  in  $10^{-3}$  watt/sq cm  $^{\circ}\text{C}$  per cm

Soil Structure	Approx. Dimensions cm	Structured		Finely Fragmented	
		$\alpha = \frac{P_1}{P_s} k_o$		$\alpha = \frac{P_1}{P_s} k_o$	
Coarse Blocky	1 to 3	0.036	5.65	0.063	3.80
		0.039	5.30	0.060	3.91
Medium Blocky	0.8 to 2	0.045	4.94	0.072	3.42
	1 to 2.5	0.044	5.00	0.075	3.30
	0.6 to 1.9	0.045	4.81	0.071	3.45
		0.046	4.63	0.071	3.47
	1.3 to 1.9	0.047	4.65	0.058	4.01
		0.059	3.95	0.060	3.92
Coarse Platy	1 to 2	0.041	5.15	0.063	3.80
		0.041	5.22	0.061	3.90
Medium Platy	0.2 to 0.4	0.051	4.45	0.066	3.68
		0.053	4.37	0.066	3.68
Fine Platy	0.1 to 0.2	0.054	3.96	0.056	4.11
Medium Granular	0.5 to 1.0	0.060	4.15	0.065	3.60
		0.069	3.72	0.074	3.35
Fine Granular	0.1 to 0.3	0.094	2.77	0.075	3.38

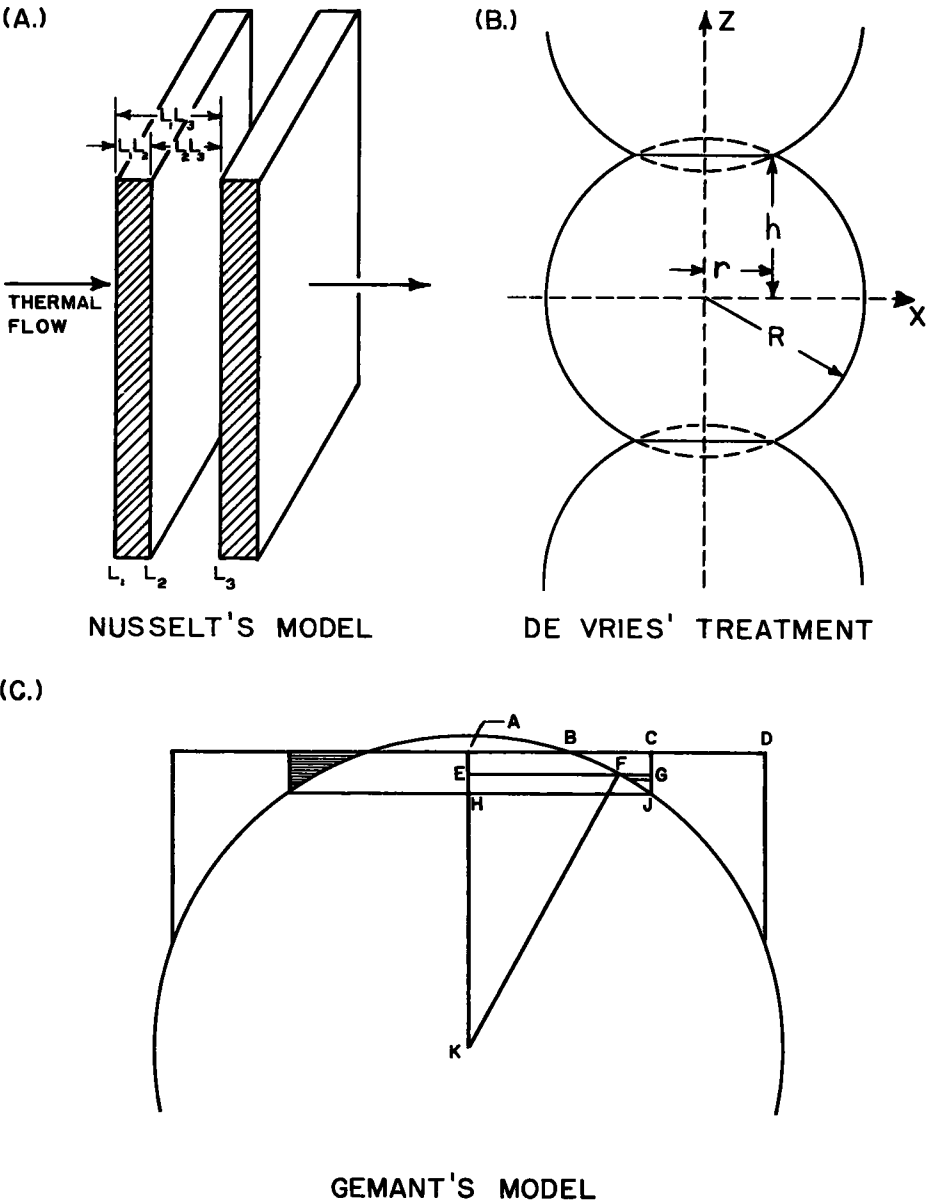


Figure 11.

contacts as shown in Figure 11(C), Gemant (37) derived an approximate formula for the thermal conductivity of moist soil. He neglected the conductivity of the air and the influence of the water rings around the middle four contacts of the grain. Strictly speaking, therefore, his formula only holds for moisture contents up to about 0.2 per-cent. In the figure:  $KH = y_0$ ;  $HJ = x_0$ ;  $AB = a$  = radius of the flat contact surface;  $KF = r$  = the radius of the spherical particle. If  $m$  is the moisture content and  $k_s$  and  $k_w$  the thermal conductivities of solid and water, respectively, we have:

$$(2y_0^3 - 3y_0^2 + 1) = 1.272 m$$
$$f^2 = (1 + a^2) k_s - y_0^2 k_w$$
$$g^2 = k_s - k_w$$



$$f'^2 = (1 + 2^2) k_S$$

$$g'^2 = k_S$$

The resistivity of the soil is then given as:

$$R = \frac{1}{k} = \frac{2}{\pi f g} \log \frac{(f+g)(f-gy_0)}{(f-g)(f+gy_0)} + \frac{2}{\pi f' g'} \log \frac{f' + g' y_0}{f' - g' y_0}$$

Gemant maintains that this equation gives good agreement with the experimental data above 5 percent moisture. Below 5 percent the experimental data are higher. Unfortunately the formula does not account for variation in densities or in grain sizes.

Making use of a cubical array of spheres, Figure 11(B), and following De Vries' (25) reasoning to calculate the limits of the conductivity when touching of particles occurs, two equations which approximate the dry soil or saturated soil condition are obtained.

For the lower limit De Vries considers the circumscribed cube, and the formula becomes:

$$4R^2 k = (4R^2 - \pi R^2) k_g + \int_0^R 2\pi k_S x dx + \int_y^R 2\pi \frac{h k_S k_g}{h k_S - 2(k_S - k_g)} x dx.$$

Integrated it becomes:

$$k = \frac{\pi r^2}{4R^2} k_S + \frac{\pi k_S k_g (R^2 - r^2)}{2R^2 (k_S - k_g)} \left( \frac{k_S}{k_S - k_g} \ln \frac{k_S}{k_g} - 1 \right) + \left( 1 - \frac{\pi}{4} \right) k_g.$$

The upper limit is given by the formula:

$$\frac{h}{k} = \int_0^h \frac{dz}{\frac{\pi}{4} (1 - \frac{z^2}{R^2}) (k_S - k_g) + k_0} ; \quad k = \frac{b h \pi (k_S - k_g)}{2R \ln \frac{bR+h}{bR-h}}$$

where:

$$b = \left( 1 + \frac{4 k_g}{\pi (k_S - k_g)} \right)^{1/2} \quad \text{for } k_S \gg k_g ;$$

when

$k_g = 0$  the combined equations yield:

$$\frac{\pi r^2}{4R^2} k_S \leq k \leq \frac{\pi h k_S}{2R \ln \frac{R+h}{R-h}}$$

De Vries concluded that the value of the equation is minimized by the fact that the limits are too far apart. Sample calculations for dry soil are given in Table 19.

The examples were taken from experimental work by Kersten (49), Smith (86) (87) and Smith and Yamauchi (84). The table contains the thermal conductivities as determined for the dry soils and also conductivities computed by means of the equations of Eucken (31), Smith (87), Nusselt (which is identical with the Birch and Clarke series treatment), Mickley, and De Vries for the lower limit. The conductivity of dry air  $k_g$  was taken as .00024 watt/cm deg C in all cases. The conductivity of the solid particles  $k_S$  was taken as given by the investigators whose experimental data were used. The value of  $k_S$  for the Chester soil (derived from gneiss) is given by Smith (87) as .025 watt per cm deg C, that of the Miami soils (glacial till) was .0293 watt per cm deg C.

For the soils investigated by Kersten the values were extrapolated to zero void space

TABLE 19  
SAMPLE CALCULATION FOR THERMAL CONDUCTIVITIES OF DRY SOIL

Soil	Composition, Percent	Porosity	Thermal Conductivity, watts/sq cm °C per cm						
			Measured	Calculated					
				Smith	Eucken	Nusselt	Mickley	De Vries	
Crushed quartz	95 quartz	0.37	0.00429	0.00351	0.0160	(0.00139)	0.00065	0.01076	0.0048
		0.275	0.00720	0.00380	0.0191	(0.00199)	0.00087	0.01345	0.0058
Lowell sand	72 quartz	0.40	0.00271	0.00259	0.0082	(0.00121)	0.0006	0.00975	0.00275
	22 feldspar	0.325	0.00357	0.00290		(0.00155)	0.00074	0.01148	0.00352
	6 pyroxene				0.0093				
Healy clay	23 quartz	0.604	0.00156	0.00166	0.0099	(0.0007)	0.0004	0.00583	0.00217
	55 kaolinite	0.48	0.00296	0.00209		(0.0010)	0.0005	0.0081	0.00352
	22 coal				0.0137				
Chester loam <sup>a</sup>	20-50 sand	0.439	0.00299	0.00295	0.0115	(0.0011)	0.00055	0.0091	0.00348
	20-50 silt								
	20-30 clay								
Miami silty clay <sup>b</sup>	50 sand	0.552	0.00137	0.00137	0.0103	(0.00088)	0.00043	0.00677	0.00268
	20 clay								
Miami silty clay <sup>c</sup>	0-30 sand	0.348	0.00353	0.00354	0.0162	(0.0015)	0.00069	0.01113	0.0048
	50-80 silt								
	20-30 clay								

<sup>a</sup>B horizon, red-brown clay loam

<sup>b</sup>A horizon, dark-brown silt loam

<sup>c</sup>C horizon, olive-drab silty clay loam

using his formula. For crushed quartz:  $k_s = .03$ ; Lowell sand:  $k_s = .016$ ; Healy clay:  $k_s = .0327$ . The bracketed data in column 6 are calculated assuming the air to be the continuous medium; the figures without brackets, assuming that the solid phase is continuous. De Vries' formula was modified to include the effect of porosity.

The conductivities were computed for a temperature of 50 deg C.

The theory of Maxwell (59) Burger (14) Eucken (31) gives according to de Vries the most promising results of the various theories treated. It assumes  $\epsilon^1 = \epsilon_0$  and  $E^1 = \bar{E}_0$  in the formula:

$$\epsilon = \frac{\sum_{i=0}^N \epsilon_i x_i \bar{E}_i}{\sum_{i=0}^N x_i \bar{E}_i}$$

Dividing through by  $\bar{E}_0$  it becomes:

$$\epsilon = \frac{\sum_{i=0}^N \epsilon_i x_i k_i}{\sum_{i=0}^N x_i k_i} \quad \text{where } k_i = \frac{\bar{E}_i}{\bar{E}_0}$$

Because of the tensorial relationship between  $\bar{E}_i$  and  $E^1$  the values of  $k_i$  is given by

$$k_i = \frac{1}{3} \left( \frac{1}{1 + \left( \frac{\epsilon_i}{\epsilon_0} - 1 \right) A_1} + \frac{1}{1 + \left( \frac{\epsilon_i}{\epsilon_0} - 1 \right) A_2} + \frac{1}{1 + \left( \frac{\epsilon_i}{\epsilon_0} - 1 \right) A_3} \right).$$

For ellipsoidal particles the value of  $A_1$  is given by Scholte (81). Introducing  $a$ ,  $b$  and  $c$  for the half-axes of the ellipsoid, we obtain for:

- (1) Prolate spheroid:  $a > b = c$ ;  $\frac{a}{b} = p$

$$A_1 = \frac{-1}{p^2 - 1} + \frac{p}{\sqrt{p^2 - 1}} \cdot \ln (p + \sqrt{p^2 - 1})$$

$$A_2 = A_3 \quad \text{and} \quad A_1 + A_2 + A_3 = 1$$

- (2) Oblate spheroid:  $a < b = c$ ;  $\frac{a}{b} = p$

$$A_1 = \frac{1}{1 - p^2} - \frac{p}{\sqrt{1 - p^2}} \cos^{-1} p$$

$$A_2 = A_3 \quad \text{and} \quad A_1 + A_2 + A_3 = 1$$

- (3) Sphere:  $a = b = c$

$$A_1 = A_2 = A_3 = \frac{1}{3}$$

- (4) Long cylinders with elliptical cross sections:

$$a = nb \quad c = \infty$$

$$A_1 = \frac{b}{a + b} ; \quad A_2 = \frac{a}{a + b} ; \quad A_3 = 0$$

(5) Laminae:  $b = c = \infty$   
 $A_1 = 1 \quad A_2 = A_3 = 0$

It was indicated that the error will be less than 20 percent using Eucken's formula when the ratio between the heat conductivity of the particles and that of the medium is less than approximately 20. In moist soil the water may be assumed as the medium over a wide range of moisture contents. The solid particles and air bubbles are treated as the inclusions. In this manner the requirements are satisfied. Also for inclusions having conductivities less than that of the medium the theory gives values that are too high and for inclusions having higher conductivity, values that are too low. In moist soil therefore the errors tend to compensate each other.

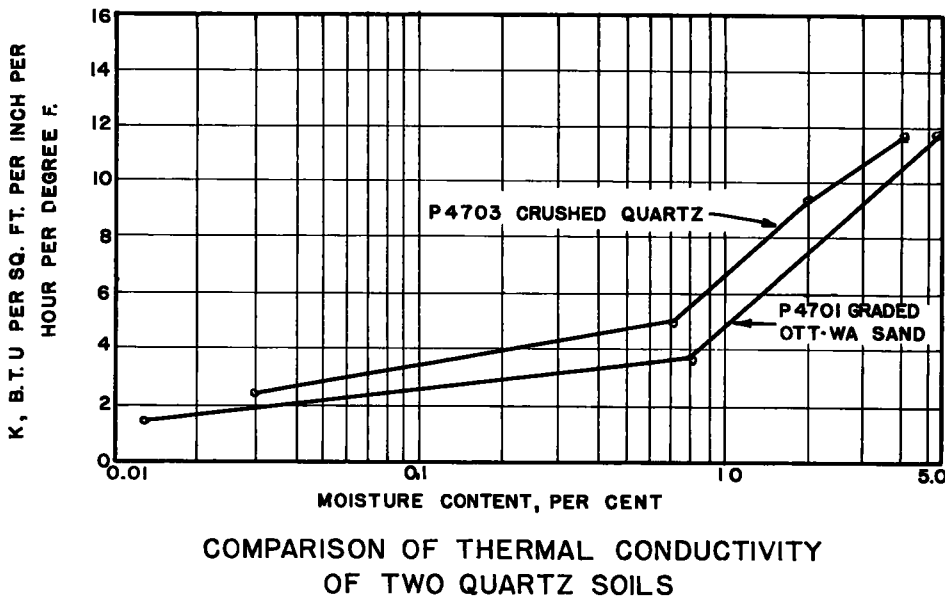
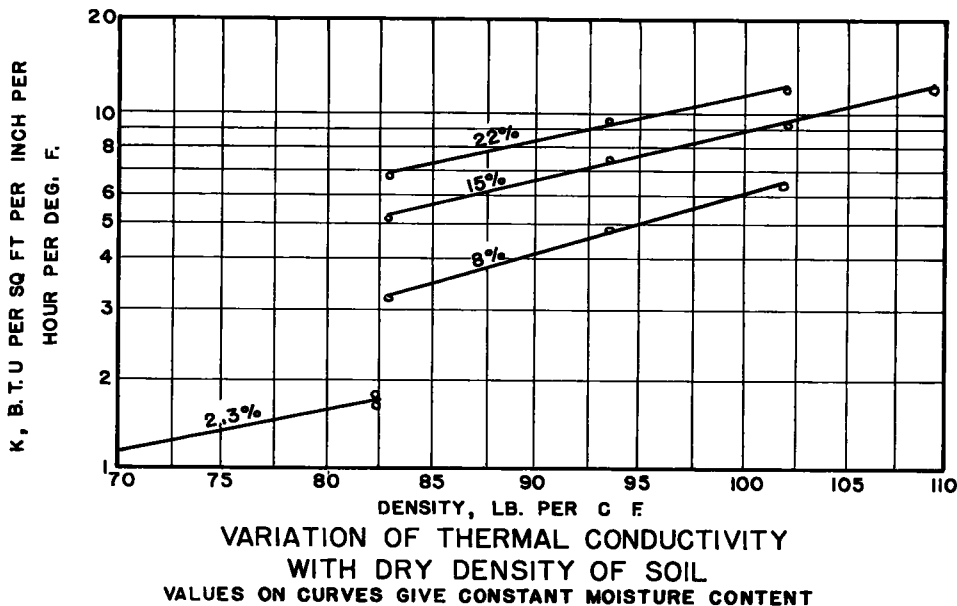


Figure 12.

The shape of the solid particles is assumed to be ellipsoidal.  $A_1$  is calculated from data obtained from vapor diffusion measurements ( $A_1 = 0.144$ ). In this case "effective flattening" is considered which will not necessarily correspond to the real dimensions of the particles because it includes the effect of angularity and other deviations from ideal ellipsoidal form. The shape of the air particles is also taken as ellipsoidal but it changes with variation in moisture content. The conductivity of the air varies with the amount of free moisture in it and depends, therefore, on the temperature, the moisture content and the soil type. For the calculations of  $A_1$  of soil air De Vries made use of a simple calculation assuming linear interpolation. At 20 deg C and from experimental values of the thermal conductivity of a moist soil ( $A_1 = 0.144$  for soil) the formula is derived to be:

$$A_1 = 0.333 - 0.697x_g \text{ for air.}$$

The mean thermal conductivity  $k_s$  of the solid constituents is calculated according to their volume fractions and individual mean conductivities. A parallel treatment is assumed leading to the equation for  $N$  types of soil minerals.

$$k_s \text{ mean} = \sum_{i=1}^N k_i x_i$$

where

$k_i$  = thermal conductivity of the  $i$ -type of mineral

$x_i$  = volume fraction of the  $i$ -type

From data obtained experimentally on nineteen soils ranging from crushed rock and sand to clay and peat, Kersten (49) derived empirically formulas for calculation of the thermal conductivity of soil when the type of soil, density and moisture content are known. The variation of conductivity with density and moisture content is shown in Figure 12. From these relationships the following equations for prediction of thermal conductivity are derived and given by Kersten:

- (1) Silt and clay soils (more than 50 percent silt and clay); unfrozen:

$$k = [1.3 \log (\text{moisture content}) - 0.29] 10^{0.01S-3}$$

- (2) Silt and clay soils; frozen:

$$k = 1.44 \times 10^{0.022S-5} + 12.2 (\text{moisture content}) \times 10^{0.008S-5}$$

- (3) Sandy soils; unfrozen (less than 50 percent silt and clay):

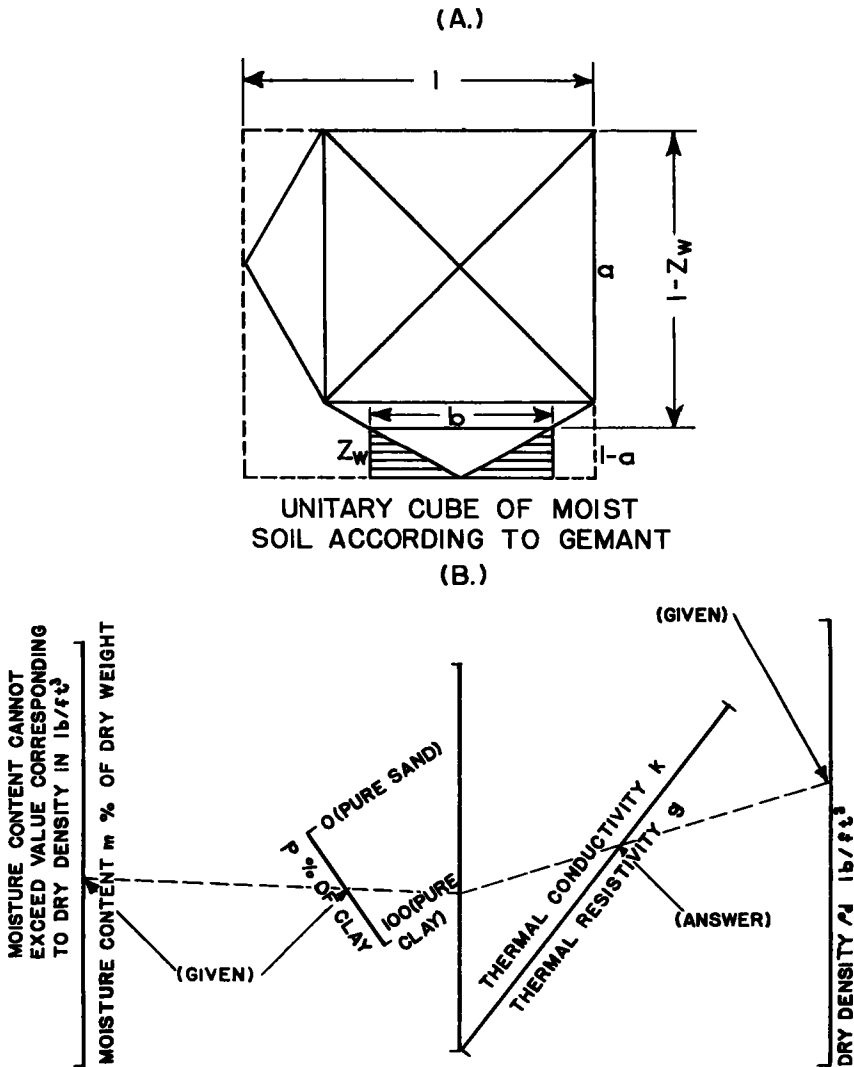
$$k = [1.01 \log (\text{moisture content}) + 0.58] 10^{0.01S-3}$$

- (4) Sandy soils; frozen:

$$k = 11.0 \times 10^{0.013S-5} + 4.6 (\text{moisture content}) \times 10^{0.0146S-5}$$

In these equations  $k$  is in watt/sq cm deg C per cm,  $S$  is the dry density in pounds per cubic foot and the moisture content is taken as a percentage of the dry soil weight. The equations for silt and clay are valid for moisture contents of 5 percent or more; for sandy soils at a moisture content, one percent or more. For a sandy soil with fairly high silt and clay content the average obtained from the two equations may be taken. The equations yield, with careful use, values of  $k$  within 25 percent accuracy.

In a later article Gemant (35) (36) took into account the effect of density, temperature, composition (sand-clay) and size of particles in developing an equation from a soil grain model shown in Figure 13(A). The temperature determines the amount of water absorbed on the grain  $m_0$  and this has to be subtracted from the total amount of water present to give the water collected between the grains  $m$ , taking part in the conduction of heat;  $a$ ,  $b$  and  $z_w$  are linear dimensions as shown in the figure. If  $s$  represents the density, and  $w$  the total moisture content we have:



NOMOGRAM FOR DETERMINATION OF  
THERMAL CONDUCTIVITY AND RESISTIVITY  
OF SANDY SOIL

Figure 13.

$$a = 0.078 \sqrt{s}$$

$$m = 0.16 \times 10^{-3} s w - m_0$$

$$b^2 = \left( \frac{a}{1-a} \right)^{2/3} \left( \frac{m}{2} \right)^{2/3}$$

$$z_w = \left( \frac{1-a}{a} \right)^{2/3} \left( \frac{m}{2} \right)^{1/3} = \frac{m}{2b^2}$$

Also  $k_s = 58.4 - 0.33p$  = thermal conductivity of the solid constituents, where  $p$  = percentage of clay in the mixture of sand and clay.

The final equation for the resistivity  $r$  of the soil:

**TABLE 20**  
**CALCULATED THERMAL CONDUCTIVITIES OF MOIST SOIL**  
in  $10^{-3}$  °C per cm

Soil	Moisture Weight Percent	Content Volume	Dry Density lb/cu ft	Porosity	Conduct. Meas.	Mickley	Gemant (2nd)	Burger Eucken	Kersten	Nomograph
Crushed quartz	1.9	0.0312	102.8	0.379	13.72	23.1	3.9	18.1	9.13	8.5
	4.3	0.0706	102.7	0.380	18.5	23.5	12.2	18.7	13.0	13.4
	2.1	0.0403	119.6	0.276	23.6	28.5	11.0	24.7	14.2	13.5
	3.7	0.0535	120.2	0.273	30.4	29.1	19.7	25.3	18.3	19.5
Lowell sand	4.1	0.0656	99.8	0.400	12.23	22.5	11.4	11.9	11.9	13.0
	11.8	0.211	111.9	0.329	22.53	27.7	19.9	15.2	21.8	20.0
	14.0	0.253	112.8	0.323	22.22	28.6	16.0	16.8	23.3	21.5
Healy clay	10.7	0.143	83.6	0.482	6.38	12.6	8.4	10.5	7.2	8.8
	22.7	0.304	83.6	0.482	9.11	13.8	11.4	11.7	10.1	11.0
	34.8	0.450	80.6	0.500	12.63	14.6	12.3	12.4	10.2	11.5
Chester loam B-horizon	7.49	0.094	75.5	0.545	2.53	14.1	7.68	8.7	4.8	8.5
	14.8	0.170	69.2	0.583	3.03	13.4	8.92	8.5	6.1	9.0
	25.2	0.324	77.3	0.534	4.28	16.2	13.7	10.4	9.1	12.5
I.S. Clay	30.0	0.337	70	0.575	8.57	10.0	8.26	9.6	8.17	7.65
	50.0	0.560	70	0.575	10.55	11.7	9.80	11.1	9.63	8.8
	18.0	0.318	110	0.331	13.0	16.6	15.80	15.5	16.7	16.2

$$r = \frac{1}{k} = \left[ \frac{(1-a)}{a} \right]^{\frac{4}{3}} \frac{\tan^{-1} \sqrt{\frac{k_s - k_w}{k_w}}}{\left( \frac{m}{2} \right)^{\frac{1}{3}} \left[ k_w (k_s - k_w) \right]^{\frac{1}{2}}} + \frac{1 - z_w}{k_{sa}} f \left( \frac{b^2}{a} \right)$$

where:

$k_w$  = conductivity of water = 6

$f \left( \frac{b^2}{a} \right)$  is an experimental function of given linear dimensions  $a$  and  $b$ ;  
 $k$ ,  $k_s$  and  $k_w$  are all measured in  $10^{-3}$  watt/sq cm deg C per cm.

According to Makowski and Mochlinski (57) the previous formula has the same form as the Kersten formula expressed by them as:

$$k = (a \log_{10} m + b) 10^{\frac{s-3}{100}} \text{ watt/sq cm deg C per cm}$$

in which  $a$  and  $b$  represent linear functions of the clay content  $p$ .

$$a = 1.42408 - 0.00465p \text{ and } b = 0.4192 - 0.00313p.$$

The two authors constructed a nomograph using the Gemant and Kersten formulas from which can be read directly the resistivity or conductivity when the clay content, moisture content and dry density are given. The nomograph is of the form shown in Figure 13(B).

They discussed the Mickley, Gemant and Kersten equations and indicate that Gemant's give the best results for sandy soils, relatively high moisture contents and high densities. It is not reliable for moisture contents below one or two percent and low densities.

Calculated values of the thermal conductivity of moist soil are shown in Table 20. The experimental data used were obtained from the same investigators as for the dry soil computations. The value of  $k_g$  used in the calculation of conductivities by the Mickley and Gemant (second equation (35), (36)) equations were computed from the formula (57):

$$k_g = 58.4 - 0.33p \text{ in milliwatts/cm deg C}$$

where  $p$  is the percentage of clay in the soil. The conductivity of water was taken as:

$$k_w = 6 \text{ milliwatt/cm}^2 \text{ deg C per cm}$$

In the Mickley and Burger-Eucken equations, the conductivity of air was assumed to be that of moist air at approximately 40 deg C.:

$$k_g = 2.5 \text{ milliwatt/cm}^2 \text{ deg C per cm.}$$

The equation of Burger-Eucken was used following the interpretation of De Vries (25).

## DISCUSSION OF RESULTS

In the preceding treatment, the best available theories of thermal conduction in single, di- and multiphase systems have been discussed and the results of their application have been compared with experimental data. The purpose of a theory is, firstly, to permit a visualization of the action mechanism of a physical or chemical phenomenon, preferably in terms of the science of mechanics, and, secondly, to provide a simple mathematical formulation of the phenomenon with the least possible number of physical parameters and of necessary assumptions. In the normal development of a theory, the visualization precedes the mathematical formulation.



The final mathematical formulation may follow immediately the first visualization or may be separated from it by a shorter or longer chain of development. In fact, the latter may be so long that the original visualization is forgotten, or the phenomenon may be so complex that it cannot be completely expressed by a simple picture, but requires a set of differential equations. Whatever be the final mathematical formulation, in the beginning is the picture, and the picture, if it is essentially correct, leads not only to an understanding of the phenomenon and to its expression in mathematical form but also indicates physical or chemical means by which the phenomenon may be changed qualitatively or quantitatively. If such change is the purpose of a study, then a relatively crude visualization may be more important than the refined mathematical formulation.

The picture of the actual thermal phenomena, occurring in soil systems of interest to the engineer, is quite complex with heat conduction, heat convection and material convection taking place in multiphase systems. In order to develop an understanding systematically, the present treatment was restricted to heat conduction. Because of the presence of gaseous, liquid and solid phases in normal soils, the theories of heat conduction in gases, liquids and solids were introduced and discussed before treatment of the more complex granular systems and especially of soils was attempted.

The theory developed for the gaseous phase conforms with the hypothesis of the molecular kinetic theory and is in good agreement with experimental data; in fact, the success of the theory to explain experimental data also in heat conduction was a proof of the kinetic theory of heat. The expression for heat conduction holds for an ideal gas over a large pressure and temperature range. In the case of non-ideal gases or more complex situations the basic concept remains the same but modification has become necessary.

The liquid state is easily recognized and circumscribed in a general way, but it is scientifically more complex than the solid and gaseous states. This is the reason why in its scientific exploration the liquid has been treated for a long time either as an imperfect gas or as a disturbed crystal, or as something intermediate between gas and crystal. Only now is evolving a molecular theory of liquids deserving of its name. Unfortunately, already in its present state this theory has become so abstract and has left its physical model concepts so far behind that its most modern version cannot be profitably applied to our problem. In addition, in soils one is dealing with a very peculiar liquid "water".

The equation derived by Bridgman for the heat conduction in liquids has the advantage of simplicity but gives only approximative results. The average error is 15.2 percent with a maximum error of 39 percent (85). Some assumptions made by Kardos are erroneous as was pointed out by Smith (85) and his equation must be considered as only semi-empirical. However, in view of the close agreement of his calculated values with experimental data some physical significance may be attributed to his concepts. The velocity of sound through the medium may be regarded as a measure of the rate of energy exchange between molecules. To which degree the theoretical equation of Bridgman will correspond with actual values at different temperatures and pressures, is not known because of the inadequate experimental data.

The theory of the crystal state is much more advanced than that of the liquid state; however, no heat conductivity theory has been developed as yet for the solid state of the same validity and simplicity as that of Bridgman for liquids. The expression of Debye with modifications and additions by Peierls (72) (73) and Makinson, involves parameters that cannot be obtained accurately by computation or by direct measurement. Yet evidence is not sufficient to disprove the basic principles on which the theory of Debye is based.

As was pointed out by such investigators as Birch and Clarke, Eucken, De Haas and Biermasz, some additional variables, or different expression of the variables involved, must be taken into account to provide for the differences in experimental data. It is true and also logical that different workers in the field obtain different results, but the data should be within experimental error and should not differ as much as those which are found in the literature for the heat conductivity of crystals. As was mentioned, variation in purity and "micro structure" may account for some of the differences.

The influence of these factors is hard to evaluate because the degree of purity and "mosaic structure" developed is difficult to determine and is usually not given with the other data.

A further test of a theory is to apply it in explanation for the different heat conductivities in different directions occurring in anisotropic crystals. Neither the theory of Wooster (103) which attempts to correlate thermal conductivity with the crystal structure, nor that of Eucken and Kuhn (32) which explains variation in conductivity in crystals in terms of their respective hardness (strength of chemical bonds) appears to be very successful.

This is about as far as any theory went. From Tables 12, and, especially, 13 it must be concluded that Eucken and Kuhn's theory regarding aggregates cannot be valid. The data on mixed crystals presented by Eucken and Kuhn cannot be explained unless the contact between the crystals gives rise to the large deviation from the formulas in Table 14. In contrast to the data in Table 14, the calculated values in Table 15 show reasonable agreement with the experimental data. It must be pointed out, however, that this good agreement is obtained only after adjusting the formulas or after experienced use of the equations and after knowledge of the governing factors in the material under consideration had been obtained.

In glasses, the thermal conductivity increases with increase in temperature. This is the case with all non-crystalline substances including liquids. By following this analogy and by applying Bridgman's formula for liquids the distance between heat propagating units is in the order of the distance between silica atoms in glass. If we consider the silicon atom the center of the "unit cell" (from the crystal concept), the analogy between liquids and glasses becomes more apparent. However, as was pointed out by Birch and Clarke there exist the already mentioned basic differences.

In granular systems the discontinuity of energy and temperature that exists on a solid-gas interface has been recognized and experimentally proven. It is reasonable to assume that a similar phenomenon exists between a solid and a liquid phase. The reduction in conductivity which occurs when an aggregate is substituted for a pure crystal suggests the probability that an interfacial phenomenon exists also on solid-solid phase boundaries. From Kersten's data on the relationship between heat conductivity and crushed quartz content and gradation, it was found that, for the same temperature and the same low moisture content (0.02 percent), the logarithm of the thermal conductivity plotted against density gave two parallel straight lines. The conductivity of the crushed quartz was higher than that of the sand. Since crushed stone sand possesses greater mechanical resistance than rounded natural sand, it is difficult to decide to what extent the increased thermal conductivity of the former at the same density was due to macro-factors of interlocking and contact or to micro-factors such as the different physico-chemical character of the fresh and old grain surfaces, respectively.

The importance of the interfacial resistance has been recognized but not quantitatively evaluated. Even the qualitative picture of what is happening on the boundary between two phases has in many instances defied comprehension. It is felt that a thorough investigation of this point will add markedly to the understanding of soil systems, not only with respect to thermal conductivity but also in regard to most of the important physical characteristics of soils.

The total basic knowledge available on thermal conductivity is not very impressive. No simple equation could be developed even for pure crystals. This situation indicates that a large deal of theoretical work must be accomplished before heat conduction in complex, multiphase systems such as soils can be thoroughly comprehended. On the other hand, the very primitive state in which the theory finds itself gives hope that its further rational development will bear fruits of practical as well as academic importance. At the present time only empirical or semi-empirical equations have been developed to calculate the thermal conductivities of different soil types at different moisture and density conditions. These equations are all based on simplified assumptions concerning the geometry of the grains in contact. They vary from the purely empirical formulas of Kersten to what may be considered the more theoretical equations of De Vries, and Maxwell-Burger-Eucken. Tables 19 and 20 show the reliability

of these approaches. It is obvious that none of the equations is able to give consistently dependable results. The greatest deviation of calculated from experimental values was found for the structured soils – a situation which is likely to be encountered in the field. All the theories mentioned try to express the thermal conductivity of the whole system in terms of the various conductivities of its constituents; however, in their practical use the value of the solid phase conductivity is commonly selected so as to fit the experimental data. This may be practically justified because of temperature discontinuities existing at the boundaries but it stamps the methods as no better than semi-empirical. However incomplete, the equations do give an indication of the order of magnitude of the thermal conductivity of a soil in equilibrium. They are, in a way, all valuable because each makes use of some different approach which may

TABLE 21  
VARIATION OF THERMAL CONDUCTIVITY OF CORUNDUM POWDER  
with Grain Size in  $10^{-3}$  watt/cm<sup>2</sup> °C per cm

Average Grain Size mm	Measured Density lb/cu ft	Measured Conductivity	Calculated Conductivity at 113.8 lb/cu ft Density	
0.60	106.8	3.44	4.28	(4.05)
0.45	113.8	5.89	5.89	(5.89)
0.30	111.6	5.04	5.39	(5.30)
0.175	94.7	3.74	6.27	(5.80)
0.125	103.7	4.17	5.70	(5.27)
0.090	104.4	4.80	6.42	(5.96)
0.075	99.8	4.08	6.30	(5.64)
0.015	66.0	2.14	9.94	(6.44)
0.006	58.5	1.78	9.94	(6.35)

bear fruit in the comprehension of the total situation. The most rapid methods are the nomograms of Makowski and Mochlinski and Kersten's equations. The Maxwell-Burger-Eucken theory has the better mathematical basis, while that of Gemant gives physically the best interpretation. For dry soil the formula of De Vries is considered to be the most representative.

The influence of particle size on conductivity is not clearly pointed out in the formulas treated. Its effect is included in the designation sand, silt and clay (from a size classification). However, the difference in mineralogical character of the different size fractions makes this effect dependent on mineral type as well as on size characteristics. The work of Patten (71) on dry carborundum powder of varying grain sizes produced the first data of real value in this respect. Table 21 gives the variation of the thermal conductivity as a function of the grain size of carborundum powder. The conductivities were calculated back to one density using Kersten's formula for conductivity-density relationships in dry, crushed quartz.

The calculation of the figures in brackets employs the equation found by Kersten for fine crushed quartz. However, the use of the formulas in this respect is somewhat debatable because, as Kersten's formulas show, the particle size has an effect on the influence of the density. The equations can be a useful practical tool in evaluating conductivities but may in certain cases hide the real mechanism of conductivity. Although not quite clear from his data, Patten concludes that for the same moisture content coarse quartz has a higher conductivity than fine quartz flower. He explains it by the assumption that less water is absorbed on the surface of large particles and that the available water can therefore accumulate between the grains and consequently

increase the conductivity. The specific and over-all effect of granulometry still remains to be formulated. Little doubt exists about the importance of size, shape and packing of component particles on the physical properties of soils including their thermal conductivities. Investigation of these granulometric and structural factors will be given primary emphasis in the Princeton research.

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### REFERENCES

1. Arrhenius, S., "Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuern," *Zeitschrift f. physik. Chem.*, 4: 226-48 (1889).
2. \_\_\_\_\_, *Meddel. Vetenskapsakad. Nobelinstit.*, 3: 20 (1916).
3. Bates, K. O., Hazard, G. and Palmer, G., "Thermal Conductivity of Liquids," *Ind. Eng. Chem.*, 10: 6, 314-8 (1938).
4. Bates, K. O., "Thermal Conductivity of Liquids," *Ind. Eng. Chem.*, 28: 4, 494-8 (1936).
5. \_\_\_\_\_, "Thermal Conductivity of Liquids," *Ind. Eng. Chem.*, 25: 4, 431-7 (1933).
6. \_\_\_\_\_, "Thermal Conductivity of Liquid Silicones," *Ind. Eng. Chem.*, 41: 9, 1966-8 (1949).
7. Baum, E., "Über den Temperaturkoeffizienten der Viskosität von Flüssigkeiten," *Kolloid-Zeitschrift*, 135: 176-82 (1954).
8. Birch, F. and Clark, H., "The Thermal Conductivity of Rocks and its Dependence upon Temperature and Composition," *Amer. Journ. Sci.*, 238: 529-58, 613-35 (1940).
9. Bragg, W. H. and Bragg, W. L., "X-Rays and Crystal Structure," 4th Ed., Bell & Sons, Ltd., London (1924).
10. Bridgman, P. W., "The Thermal Conductivity of Liquids," *Proc. Nat. Acad. Science*, 9: 341-5 (1923).
11. Bromley, L. A. and Wilke, C. R., "Viscosity Behavior of Gases," *Journal Engineering Chemistry*, 43: 7, 1641-48 (1951).
12. Bruggeman, D. A. G., "Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen," *Annalen der Physik*, V, 24: 636-79 (1935).
13. Buddenberg, J. W. and Wilke, C. R., "Calculation of Gas Mixture Viscosities," *Ind. Eng. Chem.*, 41: 7, 1345-47 (1949).
14. Burger, H. C., "Das Leitvermögen verdünnter mischkristallfreier Legierungen," *Phys. Zeitsch.* 20: 73-76 (1919).
15. Chapman, S., "The Kinetic Theory of a Gas Constituted of Spherically Symmetrical Molecules," *Royal Society of London Phil. Trans. (a)*, 211: 433-84 (1912).
16. Chapman, S. and Cowling, T. G., "Mathematical Theory of Non-Uniform Gases," Cambridge University Press (1939).
17. "Chemical Engineer's Handbook," McGraw-Hill, N. Y., 824 (1934).
18. Comings, E. W. and Egly, R. S., "Viscosity of Gases and Vapors at High Pressures," *Ind. Eng. Chem.*, 32: 5, 714-18 (1940).
19. Cornelissen, J. and Waterman, H. I., *Chem. Eng. Science*, London, 4: 239-46 (1955).

20. Debye, P., "Vorträge über die kinetische Theorie der Materie und Elektrizität," Leipzig und Berlin (1914).
21. De Guzman, J., *Annales soc. espan. fis. quim.*, 353 (1913).
22. de Haas, W. J. and Biermasz, T. "Die Wärmeleitfähigkeit von Kristallen bei tiefen Temperaturen," *Physica*, 5:320-24 (1938).
23. \_\_\_\_\_, "The Thermal Conductivity of Diamond and Potassium-Chloride," *Physica*, 5:47-53 (1938).
24. DeSanarmont, *Annalen Chim. Phys.*, (1848, 1850, 1887).  
Poggendorfs *Annalen*, (1848, 1849, 1850).  
Wiedemanns *Annalen*, (1848, 1850).
25. DeVries, D. A., "Het warmtegeleidings vermogen van grond," Doctor's Thesis. Rijksuniversiteit te Leiden (1952).
26. Drude, P., "Zur Elektronentheorie der Metalle," *Annalen der Physik*, IV, 1: 566-613 (1900).
27. Eucken, A., "Allgemeine Gesetzmässigkeiten für das Wärmeleitvermögen verschiedener Stoffarten und Aggregatzustände," *Forschung a. d. Geb. d. Ingenieurwes*, 2:6 (1940).
28. \_\_\_\_\_, "Die Wärmeleitfähigkeit einiger Kristalle bei tiefen Temperaturen," *Phys. Zeitschrift*, 12:1005-8 (1911).
29. \_\_\_\_\_, "Über das Wärmeleitvermögen, die spezifische Wärme und die innere Reibung der Gase," *Phys. Zeitsch.* 14:324-32 (1913).
30. \_\_\_\_\_, "Über die Temperaturabhängigkeit der Wärmeleitung fester Nichtmetalle," *Annalen der Physik*, IV, 34:185-221 (1911).
31. \_\_\_\_\_, *Verein deutscher Ingenieure, Forschungsheft No. 353*, Berlin (1932).
32. Eucken, A. and Kuhn, G., "Ergebnisse neuer Messungen der Wärmeleitfähigkeit fester krystallisierter Stoffe bei 0° und -190° C," *Zeitschrift für phys. Chem.*, 134:193-219 (1928).
33. Fairbanks, D. F. and Wilke, C. R., "Diffusion Coefficients in Multi-Component Gas Mixtures," *Ind. Eng. Chem.*, 42:3, 471-5 (1950).
34. Gehrcke, E., "Über die Wärmeleitung verdünnter Gase," *Annalen der Physik*, IV, 2:102-114 (1900).
35. Gemant, A., "Die Wärmeleitfähigkeit des Bodens," *Archiv der Elektrischen Übertragung*, 5:539 (1951).
36. \_\_\_\_\_, "How to Compute Thermal Soil Conductivities," *Heating, Piping and Air Conditioning*, 122-123 (Jan., 1952).
37. \_\_\_\_\_, "The Thermal Conductivity of Soil," *Journal of Applied Physics*, 21: 750-4 (1950).
38. Glasstone, S., Laidler, K. J. and Eyring, H., "The Theory of Rate Processes," McGraw-Hill, N. Y. (1941).
39. Grunberg, L. and Nissan, A. H., "Viscosity of Highly Compressed Fluids," *Ind. Eng. Chem.*, 42:5, 885-91 (1950).
40. Hildebrand, J. H., "The Liquid State," *Proc. Phys. Soc. London*, 56:221-39 (1944).
41. Hirschfelder, J. H., Bird, R. B. and Spotz, E. L., "The Transport Properties of Non-Polar Gases," *Journal Chem. Phys.*, 16: 968-81 (1948).
42. Ingen-Houtz, J., "Sur les métaux comme conducteurs de la chaleur," *Jour. de Phys.*, 34 (1786).
43. Jakob, M., "Heat Transfer," John Wiley & Sons, 1: (1949).
44. \_\_\_\_\_, "Wärmeleitung," *Handbuch der Physik*, Band XI (1926).
45. Johnson, A. I. and Huang, C. J., "Thermal Conductivity Chart for Gases," *Chem. Eng.*, 61:204-5 (Feb. 1954).
46. Johnson, E. F., "Molecular Transport Properties of Fluids,"  
*Ind. Eng. Chem.*, 46:889-93 (1954).  
*Ind. Eng. Chem.*, 47:599-604 (1955).  
*Ind. Eng. Chem.*, 48:582-85 (1956).
47. Johnstone, H. F., Jacobson, H. G. and Preckshot, G. W., "Heat Conductivity of Zinc Oxide," *Ind. Eng. Chem.*, 33:1, 106-7 (1941).

48. Kardos, A., "Theorie der Wärmeleitung von Flüssigkeiten," *Forschung auf der Gebiete des Ingenieurwes*, 5:14 (1934).
49. Kersten, M. S., "Thermal Properties of Soils," *Bulletin* 28, Eng. Exp. Station, University of Minnesota (1949).
50. Kistler, S. S. and Caldwell, A. G., "Thermal Conductivity of Silica Aerogel," *Ind. Eng. Chem.*, 26:6, 658-662 (1934).
51. Kundt, A. and Warburg, E., "Über Reibung und Wärmeleitung verdünnter Gases," *Annalen der Physik (Poggendorffs Annalen)*, 155: 337 & 525 (1875).
52. Lagemann, R. T., "Molecular Refraction-Viscosity Constant Nomograph," *Ind. Eng. Chem.*, 37:6, 600 (1945).
53. Lasareff, P., "Über den Temperatursprung an der Grenze zwischen Metall und Gas," *Annalen der Physik IV*, 37. 233-46 (1912).
54. Lindsay, A. L. and Bromley, L. A., "Thermal Conductivity of Gas Mixtures," *Ind. Eng. Chem.*, 42:8, 1508-11 (1950).
55. Loeb, L. B., "Kinetic Theory of Gases," McGraw Hill Book Co., N. Y. (1927).
56. Makinson, R. E. B., "The Thermal Conductivity of Metals," *Proc. Camb. Phil. Soc.*, 34:474-97 (1938).
57. Makowski, M. W. and Mochlinski, K., "An Evaluation of Two Rapid Methods of Assessing the Thermal Resistivity of Soil," *Proc. Inst. of Electrical Eng.*, 103: Part A (1956).
58. Mason, R. B., "Thermal Insulation with Aluminum Foil," *Ind. Eng. Chem.*, 25:3, 245-55 (1933).
59. Maxwell, C., "Treatise on Electricity and Magnetism," Oxford, 365 (1873).
60. Meissner, A., "Leistungssteigerung durch thermische Verbesserung der Isolierstoffe," *Elektrotech. und Maschinenbau*, 53: 25, 289-93 (1935).
61. Mickley, A. S., "The Thermal Conductivity of Moist Soil," *Trans. American I. E. E. Tech. Paper* 51-326, 70: 1789.
62. Mitra, S. S., "Relation between Vapor Pressure and Viscosity of Liquids," *Jour. Chem. Phys.*, 22: 349-50 (1954).
63. Mitra, S. S. and Chakravarty, D. H., "Vapor Pressure and Viscosity of Liquids," *Jour. Chem. Phys.*, 22: 1775-6 (1954).
64. Moore, W. J., "Physical Chemistry," Prentice-Hall Co., N. Y. (1950).
65. Mukherjee, A. K., *Journ. Indian Chem. Soc.*, 30:725-7 (1953).
66. Nusselt, W., *Zeitschrift d. Bayer. Revisionsver.* No. 13 & 14 (1913).
67. Ollendorff, F., *Arch. fur Elektrotechn.*, 25:436-447 (1931).
68. Othmer, D. F. and Conwell, J. W., "Correlating Viscosity and Vapor Pressures of Liquids," *Ind. Eng. Chem.*, 37:11, 1112-5 (1945).
69. Othmer, D. F. and Josefowitz, S., "Correlating Viscosities of Gases with Temperature and Pressure," *Ind. Eng. Chem.*, 38:1, 111-6 (1946).
70. Palmer, G., "Thermal Conductivity of Liquids," *Ind. Eng. Chem.*, 40:1, 89-92 (1948).
71. Patten, H. E., "Heat Transference in Soils," U. S. Dept. of Agriculture, Bureau of Soils, *Bulletin* 59 (1909).
72. Peierls, R., "Zur kinetischen Theorie der Wärmeleitung in Kristallen," *Annalen der Physik*, 3:1055-1101 (1929).
73. Poincaré, H., "Quelques propriétés typiques des corps solides," *Ann. Inst. H. Poincaré*, 5:177-222 (1935).
74. Polder, D. and Van Santen, J. H., "The Effective Permeability of Mixtures of Solids," *Physica*, 12:257-71 (1946).
75. Powell, R. E., Roseveare, W. E. and Eyring, H., "Diffusion, Thermal Conductivity, and Viscous Flow of Liquids," *Ind. Eng. Chem.*, 33:4, 430-5 (1941).
76. Powell, R. W. and Griffiths, E., "The Variation with Temperature of the Thermal Conductivity and the X-Ray Structure of Some Micas," *Proc. Royal Society*, 163:189-98 (1937).
77. Prins, J. A., Schenk, J. and Schram, A. J. G. L., "Heat Conduction by Powders in Various Gaseous Atmospheres at Low Pressure," *Physica*, 16:379-80 (1950).
78. Rayleigh, W. R., "On the Influence of Obstacles Arranged in Rectangular Order Upon the Properties of a Medium," *Phil. Mag.*, 34: 481-502 (1892).

79. Riedel, L., *Chem. Ing. Tech.*, 27:209-13 (1955).
80. Sakiadis, B. C. and Coates, J., Paper 39 presented at the Annual Meeting of the Am. Inst. Chem. Engrs. (December 1954).
81. Scholte, Th. G., "A Contribution to the Theory of the Dielectric Constant of Polar Liquids," *Physica*, 15: 5-6, 437 (1942).
82. Schudel, W., *Schweiz. Ver. Gas- und Wasserfach, Monats-Bull.*, 22:112-131 (1942).
83. Schulz, K., "Die Wärmeleitung in Mineralien, Gesteinen und den künstlich hergestellten Stoffen von entsprechender Zusammensetzung," *Fortschritte der Mineralogie, Kristallographie und Petrographie*, 9: 345-535 (1924).
84. Smith, G. S. and Yamauchi, T., "Thermal Conductivity of Soil for Design of Heat Pump Installations," *Heating, Piping and Air Conditioning*, 129-35 (July 1950).
85. Smith, J. F. D., "The Thermal Conductivity of Liquids," *Trans., American Soc. Mech. Engrs.*, 58:719-25 (1936).
86. Smith, W. O., "Thermal Conductivities in Moist Soils," *Proc. Soil Science Society of America*, 4:32-40 (1939).
87. ———, "The Thermal Conductivity of Dry Soil," *Soil Science*, 53:6, 435-59 (1942).
88. Smith, W. R. and Wikes, G. B., "Thermal Conductivity of Carbon Blacks," *Ind. Eng. Chem.*, 36:12, 1111-2 (1944).
89. Smoluchowski, M. R. von Smolan, *Wiener Berichte* 107 IIA, 304 (1898).
90. ———, *Krakauer Anzeiger (A)*, 129 (1910).  
Report on the 2nd International Congress on Heat, 2: 166 Wien (1910).
91. Stokes, G. G., "On the Conduction of Heat in Crystals," *Coll. Papers Bd. 3*, S. 203, Cambridge University Press (1901).
92. Sutherland, W., "The Viscosity of Mixed Gases," *Phil. Mag.*, 40: 421-31 (1895).
93. ———, "The Viscosity of Gases and Molecular Forces," *Phil. Mag.*, 5(36): 507-31 (1893).
94. Thelen, P., "The Differential Thermal Conductivities of Certain Schists," University of California Publication, *Bulletin of the Dept. of Geology*, 4:11, 201-26 (1904-06).
95. Thiesen, M., "Zur Theorie der Diffusion," *Verhandl. deut. physik. Ges.*, 4: 348-60 (1902).
96. Uyehara, O. A. and Watson, K. M., *National Petroleum News*, 36: 764 (1944).
97. Voigt, W., "Lehrb. d. Kristallphysik," Leipzig und Berlin, B. G. Treubner, 403 (1910).
98. Wassiljew, A. "Wärmeleitung in Gasgemischen," *Physik. Zeits.*, 5: 737 (1904).
99. Wilke, C. R., "Diffusional Properties of Multi-Component Gases," *Chem. Eng. Prog.*, 46: 95-104 (1950).
100. ———, "A Viscosity Equation for Gas Mixtures," *Jour. Chem. Phys.*, 18:517 (1950).
101. Wilkes, G. B., "Reflective Insulation," *Ind. Eng. Chem.*, 31:7, 832-8 (1939).
102. Wood, W. A., "The Variation with Temperature of the Thermal Conductivity and the X-Ray Structure of Some Micas," *Proceedings, Royal Society*, 163:199-204 (1937).
103. Wooster, W. A., "Thermal Conductivity in Relation to Crystal Structure," *Zeitschrift für Kristallographie*, 95: 138-49 (1936).