Thermal Conductivity of Porous Catalysts

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A random pore model of catalytic pore structure is applied to the determination of the thermal conductivity of porous catalytic solids. The low thermal conductivities reported for such materials are explained by considering the microporous particles to consist of a packed bedlike assembly of smaller particles; heat transfer through the solid fraction occurs by conduction through individual small particles in contact with other particles. An expression for the effective thermal conductivity of a gas in the region between ordinary thermal conduction and free molecule conduction is used in determination of heat conduction through the void volume. Agreement of the theory with experimental data on alumina and silver catalysts over a wide range of conditions is good.

There has been a considerable interest in the recent literature on problems of estimation and measurement of transport properties within porous solids owing to the importance of such information in determination of catalytic effectiveness and selectivity. A majority of this work has concentrated on the question of diffusional mass transport within catalysts and thus on the measurement or estimation of effective diffusion coefficients within the porous matrix. Wakao and Smith (*1*) have presented a detailed model of catalytic pore structure which appears to explain the available data on diffusion through an important class of catalytic materials very well. In particular, their pore structure model refers to those solids exhibiting the bidisperse pore size distribution, commonly termed a *macropore* and *micropore structure,* which is typical of catalyst pellets produced by compression of individual powder particles. More detailed descriptions of this concept are given in a number of sources.

Simultaneous mass and heat transfer effects within porous catalysts have been analyzed by Carberry (*2*), Tinkler and Pigford (*3*), and Weisz and Hicks (*4*), among others. Catalytic effectiveness in such situations has been treated in terms of a nonisothermal effectiveness factor, defined analogously to the isothermal quantity; the problem of nonisothermal selectivity has not been discussed. The results of these studies indicate that considerable temperature gradients within catalyst particles can exist in the case of pronounced exothermic or endothermic reactions, as indicated theoretically by Wheeler (*5*) and Prater (*6*). The existence of these temperature gradients has recently been verified experimentally by Cunningham et al. (*7*).

Relatively little information is available concerning thermal conductivities of porous catalysts, although the magnitude of nonisothermal effects is very strongly dependent on this property. The question of the thermal conductivity of packed beds, a system which is comparable in some respects, has been studied extensively (*8*), but information on catalytic thermal conductivity has been given only by Sehr (*9*), Masamune and Smith (*10*), and Mischke and Smith (*11*). These studies have primarily been concerned with the experimental determination of thermal conductivity; analysis of the results in terms of the effect of the solid's pore structure on the thermal transport property is not reported. Though small in number, the three studies (and particularly the latter two) include an extensive range of variables including temperature, pressure, and void fraction. An ordinary, low conductivity catalyst support (alumina) and an extremely high conductivity material (silver) have been used as the solids in these studies. The primary objectives of the present work are to investigate the mechanism of thermal conduction within such porous solids and to propose a method whereby this important property may be estimated which is in agreement with the available experimental data.

CONDUCTION IN SOLIDS—MECHANISM

There are two primary questions which arise in the analysis of thermal conduction in porous solids: the mode of heat conduction in gases under conditions where the molecular mean free path is of the order of (or longer than) the characteristic dimension of the system, and the apparent thermal conductivity of the solid phase. Additional points concern the characteristic dimensions of the system and the effects of the porous structure itself on thermal conduction. The latter two questions shall be left for the moment to a subsequent section; however, the success of the pore structure proposal of Wakao and Smith (*1*) in describing diffusion indicates that such an approach, or one derived from it, may apply to the analysis of pore structure effects on thermal conduction.

Free molecule heat conduction is not strictly analogous to mass transport by Knudsen diffusion. The kinetic theory of gases teaches that a gas molecule striking a surface at temperature T_1 will leave that surface with energy corresponding to T_1 if the accommodation coefficient is unity, or with energy corresponding to a temperature $T < T_1$ if the accommodation coefficient is less than unity. This fact, of course, suggests the necessity of knowing the magnitude of the accommodation coefficient, but more important is the implication that energy is transported in this manner from T_1 to T_2 (where $T_2 < T_1$) in the absence of a temperature gradient in the gaseous phase. A temperature discontinuity may exist at the surfaces, but molecules retain their identity as far as energy is concerned between the surfaces. Under bulk transport conditions the Fourier's law expression for heat transport defines the thermal conductivity:

$$Q = -\lambda_m \nabla T \tag{1}$$

For free molecule transport, the energy transport equation requires the use of a finite temperature difference rather than the gradient:

$$Q = -\lambda_{eff}\,(T_2 - T_1) \tag{2}$$

The development of this relationship is discussed in many papers and texts on the kinetic theory of gases and applications, for example those of Kennard (*12*) and Dushman and Lafferty (*13*). It has been shown by Kennard that λ_{eff} in Equation (2) is given by

$$\lambda_{eff} = \frac{\lambda_m}{d + 2\beta L} \tag{3}$$

for the transport of energy between two parallel plane surfaces at T_1 and T_2, respectively, and separated by the distance d. The quantity β is a numerical constant which reflects the values of the accommodation coefficients for the two surfaces:

$$\beta = \frac{2-\alpha}{\alpha} \cdot \frac{2\delta}{\gamma+1} \tag{4}$$

where

$$\delta = \frac{9\gamma - 5}{4}$$

In the case where the mean free path L is very small, Equations (2) and (3) may be combined to

$$Q = -\frac{\lambda_m}{d}(T_2 - T_1) \tag{2a}$$

This is equivalent to the integrated form of Equation (1) in one dimension. The effective thermal conductivity for the intermediate region can be defined on the basis of this equivalence as

$$K'_{eff} = \frac{1}{\dfrac{1}{\lambda_m} + \dfrac{2\beta L}{d\,\lambda_m}} \tag{5}$$

For the case of conduction between T_1 and T_2, the limiting forms of this relationship are

$$K'_{eff} = \lambda_m \quad \text{for } d >> L \tag{6a}$$

$$K'_{eff} = \frac{\lambda_m}{2\beta L} \quad \text{for } d << L \tag{6b}$$

The form of this thermal conductivity expression for the intermediate region is illustrated in Figure 1 for air and helium at 1 atm. and 120°F., with d expressed in terms of the number of mean free path lengths. The intersection of the straight line predictions of the two limiting cases can be defined in terms of the break away or intersection pressure discussed by Masamune and Smith (*10, 14*). In terms of the properties of the system, the point of intersection is obtained from Equation (5) as

$$d = 2\beta L \tag{7}$$

Except for very small accommodation coefficients, the value of β for most materials will be such that this intersection occurs when d is in the general range of 5 to 10 mean free path lengths, as shown.

Two quantities involved in Equation (5) are unknown insofar as application to conductivity within porous materials is concerned: the dimension d and the accommodation coefficient α. The numerical value of d is dependent on the dimensions associated with the porous structure (pore diameters and lengths), and further discussion of this quantity will be given later. The accommodation coefficients of various surfaces have been measured experimentally and have been found to vary over a wide range for different gases and solids (*13*). One really has no way of predicting what the accommodation coefficients are within a porous solid, although it is not unlikely that such values would be typical of very rough surfaces and therefore near unity. In any event, however, the prediction of Equation (5) is not very sensitive to values of α. Except for very small accommodation coefficients, β is a constant of the order of unity, and the influence of α is small; for a range of $0.7 < \alpha < 1.0$ the value of K'_{eff} is almost constant with α. On this basis, the values of accommodation coefficients used in the following work are assumed to be unity.

APPARENT THERMAL CONDUCTIVITY OF THE SOLID PHASE

The apparent thermal conductivity of the solid material used to form a porous pellet presents a difficult problem. One striking experimental observation is that the

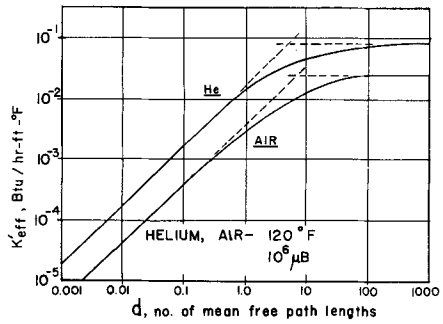

Fig. 1. Thermal conductivity of gases in the intermediate region.

thermal conductivities of pellets made from very high conductivity solids such as silver (*10*) are of the same order of magnitude as those of pellets made from fairly low conductivity material (böhmite). Smith and coworkers (*10, 11*) report, for example, a silver-helium conductivity only about twice as large as böhmite-helium conductivity under roughly comparable conditions of pressure, temperature, and macrovoid fraction. Undoubtedly, one important factor contributing to this result is that conduction through the solid phase consists of transport through microporous particles (the agglomerate of which constitutes the pellet), and considerable resistance to heat transfer exists at points of contact between individual particles. In this respect, there is a strong relationship to the corresponding situation in a fixed bed. The study of electron microscope photographs of portions of the silver catalysts of Masamune and Smith (*10*) indicates the existence of a type of packed bed arrangement in which the microporous particles themselves consist of an assembly of smaller particles. The fact that there are large and probably controlling thermal resistances in the areas of contact between these smaller particles when incorporated into microporous particles is supported by measurements of the conductivity of the latter (that is microporous or powder particles). Such conductivities are, in the case of silver at least, only a small fraction of the thermal conductivity of the pure solid. The prediction of the apparent thermal conductivity of the solid phase is thus reduced to a problem of predicting the thermal conductivities of individual microporous particles which are viewed as themselves consisting of a psuedo fixed bed arrangement of smaller particles. Pore structure theory is not involved in this estimate but is employed to solve the subsequent problem of accounting for thermal conduction between the microporous particles.

Wilhelm et al. (*15*) proposed the following relationship for the contribution to the overall thermal conductivity of a fixed bed by conduction in the solid phase through individual particles in contact with other particles:

$$\log_{10}(\lambda'_s \cdot 10^5) = 0.859 + 3.12\frac{\lambda_s}{\sigma} \tag{8}$$

The result of Equation (8) is based on observations of heat transfer in packed beds over the range $0.185 < \sigma < 0.518$ and for λ_s up to 0.1 cal./cm.-sec.-°C. Values of σ for microporous particles, computed from micropore void fraction data, are normally within the range of Equation (8), as are the thermal conductivities of most solids employed in catalyst manufacture. It is proposed that Equation (8) may be used to compute at least the lower limit of the apparent thermal conductivity of microporous particles for a very large range of materials. For solids of moderate or low true thermal conductivity forming microporous particles of porosity of 0.3 to 0.5 [corresponding to the bulk of observations used to establish Equation (8)]

the thermal conductivity prediction can logically be expected to be much better than a lower limit.

CATALYTIC PORE STRUCTURE EFFECTS ON THERMAL CONDUCTIVITY

Analysis of heat conduction through the porous solid appears to be tractable when treated in terms of an extension of the random pore development of Wakao and Smith (*1*). From the proposals of that theory, conduction in the gas phase is considered through macropores, micropores, and a series combination of the two. In addition, conduction occurs through the solid phase contained in the microporous particles. It is assumed that area void fractions are the same as volume void fractions and that the effective area for transport is proportional to the square of the void fraction. Equation (5) will be used to describe the gas-phase conduction through pores in which the characteristic dimension is of the order of the molecular mean free path, and Equation (8) will be used to estimate the thermal conductivity of the solid fraction of the microporous particles.

It is postulated that the four mechanisms of conduction stated above operate in parallel fashion within a unit cell of the solid. This unit cell is formed by two adjacent microporous particles, and the dimension of the cell is taken to be the distance from the center of one microporous particle to that of its neighbor. Details of this assembly are given in reference *1*. The total heat flux, which may be obtained from the sum of the four modes of heat transfer within the porous matrix, is given for the unit cell of the model as

$$Q = K_{eff} \frac{\Delta T}{\Delta X} \tag{9}$$

The overall thermal conductivity K_{eff} is obtained from the sum of the individual conductivities of the four modes of conduction:

Gas-phase conduction in the macropores

$$k_a = \frac{1}{\dfrac{1}{\lambda_m} + \dfrac{2\beta L}{d_a \lambda_m}} \tag{10}$$

Gas-phase conduction in the micropores

$$k_i = \frac{\epsilon_i^2/(1-\epsilon_a)^2}{\dfrac{1}{\lambda_m} + \dfrac{2\beta L}{d_i \lambda_m}} \tag{11}$$

Conduction through micro and macropores in series

$$k_{series} = \frac{2}{\dfrac{1}{k_i + k_s} + \dfrac{1}{k_a}} \tag{12}$$

Conduction through the solid phase

$$k_s = \frac{\epsilon_s^2}{(1-\epsilon_a)^2} \lambda_s' \tag{13}$$

The four contributions are summed, including the appropriate area terms, to obtain K_{eff} for the unit cell:

$$K_{eff} = \epsilon_a^2 k_a + (1-\epsilon_a)^2 k_i + 2\epsilon_a(1-\epsilon_a)\, k_{series} + (1-\epsilon_a)^2 k_s \tag{14}$$

The derivation of Equations (10) to (12) follows directly from the pore structure theory and the assumptions concerning void fractions; Equation (13) combines the result of the apparent thermal conductivity prediction of Equation (8) with the effective solids area for contact between microporous particles. None of these quantities is strongly temperature dependent, and thermal conduction through a pellet in one dimension may be represented as conduction through a series of unit cells. Overall thermal conductivity of the pellet, then, is also given by Equation (14), and Equation (9) may be used to compute the heat flux through an entire pellet with the overall temperature gradient in place of $\Delta T/\Delta X$.

In many cases of interest, the micropore contribution to transport processes occurring within the porous solid is very small and may be neglected. This may be the result of $d_i << L$, or of a small micropore void fraction. Equation (14) becomes

$$K_{eff} = \frac{\epsilon_a^2}{\dfrac{1}{\lambda_m}\left(1 + \dfrac{2\beta L}{d_a}\right)} + \frac{4\epsilon_a(1-\epsilon_a)}{\dfrac{(1-\epsilon_a)^2}{\epsilon_s^2 \lambda_s'} + \dfrac{1}{\epsilon_a^2 \lambda_m}\left(1 + \dfrac{2\beta L}{d_a}\right)} + \epsilon_s^2 \lambda_s' \tag{15}$$

The contribution of the gas phase to the effective thermal conductivity is given by the first three terms of Equation (14) if the micropore contribution is important, or by the first two terms of Equation (15) if it may be neglected.

For catalysts made from relatively high conductivity solid, $\epsilon_s^2 \lambda_s' >> (1-\epsilon_a)^2$, and the effective thermal conductivity is given by

$$K_{eff} = \frac{\epsilon_a^2}{\dfrac{1}{\lambda_m}\left(1 + \dfrac{2\beta L}{d_a}\right)} + \frac{4\epsilon_a(1-\epsilon_a)}{\dfrac{1}{\epsilon_a^2 \lambda_m}\left(1 + \dfrac{2\beta L}{d_a}\right)} + \epsilon_s^2 \lambda_s' \tag{16}$$

THERMAL CONDUCTION IN THE GAS PHASE

It has been shown that observed rates of mass diffusion are well explained by the theory on summing macropore, micropore, and series contributions to the diffusional flux. Knudsen diffusion in the macroporous and microporous structures is treated by the use of Knudsen diffusivities based on the mean macro and micropore diameters. Since free molecule conduction is not entirely analogous to Knudsen diffusion, it follows that micro and macropore diameters are not necessarily the characteristic dimensions associated with heat transport. Indeed, thermal conductivities computed from Equation (5) with pore diameters are an order of magnitude smaller than observed values.

This brings forward an important point concerning the postulation of parallel heat conduction mechanisms within the unit cell. Unless macropores are very large (that is pore wall effects are small), it is unlikely that heat transport in, say, the axial direction of the macropore will occur wholly in the gas phase. If this were true, the proper characteristic dimension would be ΔX. There are, of course, very strong pore wall effects which result in essentially a series interaction between gas and solid along the macropore length. The true gas-phase conduction mechanism is, thus, more nearly a heat transport process between interior surfaces of the pore. This series interaction between gas and solid renders the prior statement concerning parallel mechanisms within the unit cell inaccurate in the strictest sense. However, it is important to note that a relationship such as Equation (5) allows the transport of heat between solid surfaces to be expressed in terms of an effective transport property of the gas phase. Even though the series gas-solid interaction is involved in heat transport within the unit cell, this process may be described by an appropriate gas-phase thermal

conductivity and summed with the other mechanisms to obtain total heat flux.

If the role of the gas phase is, accordingly, visualized in terms of free molecule heat conduction between surfaces, one should be able to estimate the proper dimension from the length traversed before a large fraction, say 99%, of the molecules emanating from a point on the interior pore surface strike another surface. The average of such point values over the surface would provide a value of d_a for the macropore. An estimate of the magnitude of d_a may be obtained by simplifying the geometry to the case of a single pore and carrying out such computations with a range of diameters (1,000 to 10,000 Å) and pore lengths (ΔX = 20 to 150 μ) typical of the dimensions which have been reported for porous catalysts. The results of this indicate that d_a varies from 0.05 to 0.15 ΔX for the extremes of the dimensions above.* Such results are not precise (nor can they be in view of the complex geometry involved in the pore structure), but they do show the order of magnitude in terms of some measurable property of the macropore structure. The relatively small variation of d_a obtained for the range of dimensions indicates that one may be able to estimate this quantity with reasonable confidence for a given catalyst if information is available on pore size distribution or microporous particle dimensions.

The magnitude of d_a given by the estimate above is supported by the data of Masamune and Smith (*10*) on the variation of thermal conductivity with pressure for silver catalysts. Effective pore widths determined from the reported mean free path lengths in accordance with Equation (5) are in the range of 0.05 to 0.08 of the average microporous particle diameter of 60 μ. Data on the thermal conductivity of packed beds of spherical particles as a function of pressure (*14*) are also in agreement with the proposed method for estimation of macropore dimension.

It is concluded that, for estimating gas-phase thermal conductivity in the macropore structure, d_a for the average of the macropores will be of the order of one tenth the dimension of the unit cell, that is one tenth the average diameter of the microporous particles. The calculations of effective thermal conductivity to be presented indicate that the uncertainty involved in estimation of other quantities such as void fraction is more influential in the precise estimation of the effective thermal conductivity than the uncertainty in d_a. The value of d_a can be determined experimentally by the analysis of the variation of effective thermal conductivity with pressure (*10, 14*); such data in combination with independent measurements of macropore diameter would be most useful in further study of the problem.

If the micropore contribution is important, the micropore dimension d_i can be determined by analogy to the macropore case, although somewhat more speculation is involved. The average length of a micropore is taken to be of the order of the volume to surface ratio of the microporous particle ΔX_i. The length to diameter ratio for these pores is larger than those involved with the macropores, but compensating for this is the fact that the micropore network is much more interconnected. The characteristic dimension for free molecule conduction in the micropores, thus, is taken to be 0.1 ΔX_i. Unfortunately, for the low and moderate density materials on which the bulk of the available and reliable experimental data have been reported, the micropore contributions to heat or mass transport are small, and no real test of this estimate is provided. On the other hand, such data provide a meaningful test of the macropore dimension.

* This is not to imply that d_a is independent of pore diameter. In effect, d_a is a function of the diameter to length ratio, and reporting it in terms of ΔX is arbitrary; alternatively one might say that in this range d_a is of the order of ten times the pore diameter.

TABLE 1. SUMMARY OF CATALYST PROPERTIES AND EXPERIMENTAL CONDITIONS

System**	ϵ_a	σ	d_a 10^5, ft.	d_i 10^5, ft.	λ'_s, B.t.u./hr.-ft.-°F.
Alumina-air	0.134	0.223	2.95	0.49	0.475
Alumina-helium	0.275	0.246	2.95	0.49	0.483
Alumina*	0.450	0.251	2.95	0.49	0.485
Silver-helium					
Silver-air	0.610	0.448	1.97	0.33	3.50
Silver-carbon dioxide	0.408	0.446	1.97	0.33	3.50
Silver†	0.289	0.449	1.97	0.33	3.50
Silver-helium Silver	0.144	0.450	1.97	0.33	3.50

* Vacuum conditions, 25 μ Hg total pressure.
† Vacuum conditions, 10 μ Hg total pressure.
** Data of Smith and co-workers (*10, 11*).

PREDICTION OF THERMAL CONDUCTIVITY

The studies of Masamune and Smith (*10*) and Mischke and Smith (*11*) present experimental data on alumina and silver catalysts over a wide range of macropore void fraction and pressure with air, helium, and carbon dioxide as the gases. Some of the information on these systems is summarized in Table 1. The development of Equations (10) to (14) has been used to predict values of thermal conductivity which may be compared with these data. The reported results of Sehr (*9*) do not contain sufficient information on void fraction to be included in these comparisons.

In Figure 2 is given a comparison of the predicted thermal conductivities with experimental data for alumina-helium and alumina-air at 1 atm. and for alumina at 25 μ total pressure. Curve III represents essentially the solid phase thermal conductivity as computed from Equations (8) and (13); the gas-phase contribution is negligible under these conditions. Agreement with the experimentally determined conductivities is very good for the solid under vacuum conditions, and Equation (8) apparently provides a quite reliable estimate for the microporous particles of böhmite. Prediction of the alumina-helium conductivities at 1 atm. is also in good agreement with the data over the range of macro void fractions. The estimation for the alumina-air system results in the poorest agreement; the computed thermal conductivity at ϵ_a = 0.45 is about 15% below the measured value. Predictions of Equations (14) and (15) are equivalent for these samples at $\epsilon_a > 0.30$.

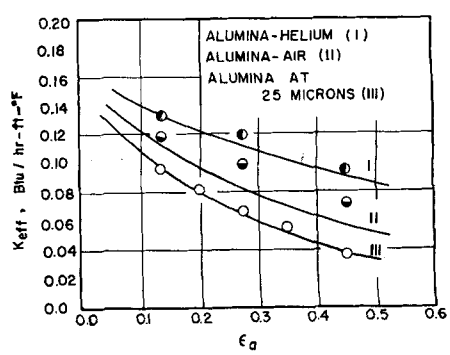

Fig. 2. Prediction of thermal conductivity: alumina-air, alumina-helium 120°F. (*11*).

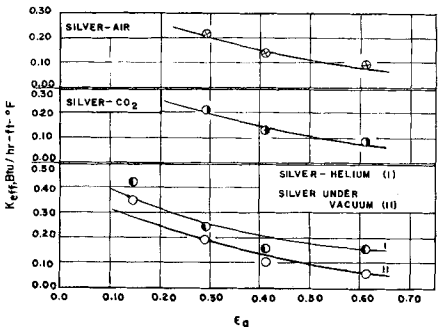

Fig. 3. Prediction of thermal conductivity, pelleted silver with air, carbon dioxide, and helium, 93°F. (*10*).

The effect of temperature on thermal conductivity is also well correlated by the method. A variation of less than 1% in thermal conductivity of the alumina under vacuum conditions, over a temperature range of 100° to 350°F., was computed, which agrees well with reported values for a range of macro void fractions (*11*). Further computation for the alumina-helium system at 1 atm. indicates a small increase in effective thermal conductivity over the same temperature range, 3% for $\epsilon_a = 0.14$ and 8% for $\epsilon_a = 0.45$. The values of d_a and d_i used for these computations were based on an average microporous particle diameter of 90 μ.

Estimation of the thermal conductivities for the silver pellets (*10*) involves difficulties with Equation (8), since the conductivity of silver is about ten times larger than the largest thermal conductivity involved in the observations used to establish that relationship. Calculation of λ_s' for silver with the void fraction data reported for the silver catalysts, in fact, results in a larger conductivity than that of the pure solid. A procedure for the estimation of the lower limit on the apparent thermal conductivity is easily devised by noting that the results of Equation (8) for higher thermal conductivity materials ($0.05 < \lambda_s < 0.20$ in cal./cm.-sec.-°C.) are as well represented by a linear plot on logarithmic coordinates as by the form of Equation (8). The thermal conductivity of the microporous silver particles thus estimated is 3.5 B.t.u./hr.-ft.-°F., and the comparison with measured conductivities of the silver pellets under vacuum conditions is given by curve II of Figure 3. A comparison of predicted conductivities with experimental data at 1 atm. for silver-helium, silver-air, and silver-carbon dioxide is also presented in this figure. Agreement is generally good with the exception of the data for ϵ_a of 0.14, as shown by curves I and II. The discrepancy here is not considered significant, since it was reported that the value of ϵ_a for this pellet is subject to some uncertainty owing to the method of calculation used and that the high pressure used in forming this pellet may have produced deformations within the microporous particles hence increasing their apparent thermal conductivity. The gas-phase contribution to thermal conductivity for the three systems at this point is well predicted by the theory, however, as indicated by curves I and II for the silver-helium system.

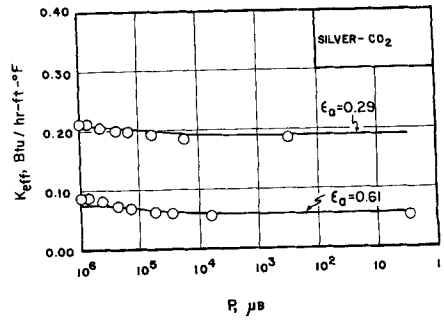

Fig. 5. Pressure effect on thermal conductivity, silver-carbon dioxide, 93°F. (*10*).

Variation of the thermal conductivity with total pressure provides a very severe test of the method of prediction. In Figures 4, 5, and 6 are given the comparisons for two of the catalysts reported in Figure 3 with all three gases. The different shapes of the curves for helium and for air and carbon dioxide are due to the effect of free molecule conduction. At higher pressures for the latter two gases the mean free path is small compared with d_a and d_i, whereas for helium at 1 atm. the effects of free molecule conduction are quite significant. The agreement between measured and computed values can be improved somewhat by using values of d_a and d_i determined from the thermal conductivity-pressure data available for these systems. The values shown, however, are computed in accordance with the proposed estimation procedure and are based on an average microporous particle diameter of 60 μ. It is seen that the method of estimation provides a reliable prediction of the magnitude and form of the dependence of effective thermal conductivity on pressure.

COMMENTS ON THE PORE STRUCTURE MODEL

The pore structure model which has been employed in this development is vulnerable to criticism in several respects; in particular the assumptions regarding the equality of volume and area void fractions and the statistical arguments involved in utilizing the square of area void fractions in computation of flux terms can be questioned. For these reasons the user must be cautioned to avoid a too literal interpretation of the results of a development based on such a model.

An alternative procedure suggested by Woodside and Messmer (*16*) proposes the effective thermal conductivity of a heterogeneous material to be uniquely determined by void fraction in accordance with the following relationship:

$$K_{eff} = \lambda_d \left(\frac{\lambda_c}{\lambda_d}\right)^{1-\mu} \tag{17}$$

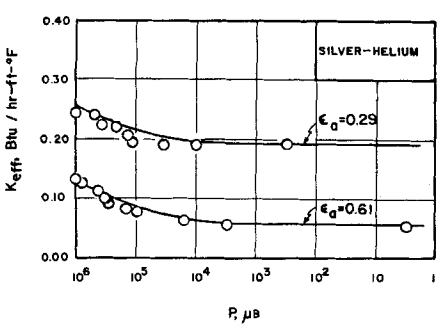

Fig. 4. Pressure effect on thermal conductivity, silver-helium, 93°F. (*10*).

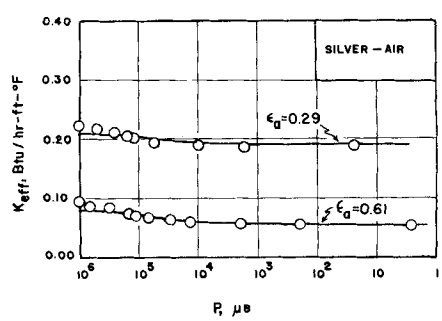

Fig. 6. Pressure effect on thermal conductivity, silver-air, 93°F. (*10*).

This equation may be applied to the macropore-micropore structure without the need of making any assumptions concerning volume-area void fractions, although it is now necessary to select continuous and discontinuous phases. If the microporous structure, including solids, is taken to be the continuous phase, effective thermal conductivities for the particle may be quickly determined from Equation (17). The results computed by this method are in very poor agreement with experimental data, although this may arise from the arbitrary definition of continuous and discontinuous phases and their inclusion in Equation (17) rather than from any fundamental inconsistency in the approach of Woodside and Messmer.

A study of the relationship between volume and area void fractions has been reported by Tsao (17), who gives an equation derived from a probabilistic model whereby the area void fraction may be computed from observed data. Such an expression would be of great value in explaining the apparent dependence of transport rates on the square of the void volume and in providing a more sound basis for this than the arbitrary assumptions of the random pore model. The probabilistic development, however, appears to suffer from several defects (*18*), and it does not appear possible to use it for the purpose of studying independently the assumptions of the pore structure model.

The results of the present work show that the dependence of thermal conductivity on void fraction, temperature, and pressure are well correlated by the theory based on the random pore model. Although it would be a serious error to assume that the representation of what is happening is correct in each detail, presumably the concepts which are utilized by the method result in an appropriate overall evaluation of the process.

SUMMARY

Thermal conductivity data which have been reported for some types of catalysts have been interpreted in terms of the porous nature of such materials. The very low conductivities observed are explained by considering the apparent thermal conductivity of the microporous particles of solid to be analogous to that of a fixed bed arrangement in which heat is transferred by conduction in the solid phase through individual particles in contact with other particles.

The determination of thermal conduction in pores whose diameter is of the order of the molecular mean free path has been discussed. The development of a proper characteristic pore dimension to describe this process is a complex problem involving detail on pore structure which is not available, but a procedure is proposed for estimation of the dimension in terms of microporous particle size. Such characteristic dimensions may also be determined from experimental data on thermal conductivity variation with pressure. In those systems normally encountered, in which the micropore contribution to conductivity is small, the suggested estimation procedure appears adequate for engineering purposes without the requirement of separate experimental information.

An extension of the random pore model proposed by Wakao and Smith is utilized to describe pore structure effects on conduction in the heterogeneuos material. Although the agreement of predicted conductivities with experimental values is good, the method does not avoid the assumptions of the random pore model and thus should not be taken as presenting a verification of the detail of that model.

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NOTATION

d = characteristic length for free molecule heat transport, ft.
d_a = characteristic dimension, macropores, ft.
d_i = characteristic dimension, micropores, ft.
K'_{eff} = gaseous thermal conductivity in intermediate region B.t.u./hr.-ft.-°F.
K_{eff} = effective thermal conductivity of catalyst pellet, B.t.u./hr.-ft.-°F.
k_a = macropore thermal conductivity, B.t.u./hr.-ft.-°F.
k_i = micropore thermal conductivity, B.t.u./hr.-ft.-°F.
k_s = solids thermal conductivity, B.t.u./hr.-ft.-°F.
k_{series} = micropore-macropore series thermal conductivity, B.t.u./hr.-ft.-°F.
L = molecular mean free path, ft.
$P_{\mu B}$ = pressure, millibars
Q = heat flux, B.t.u./hr.-sq. ft.-°F.
T = temperature, °F.
ΔT = temperature difference across unit cell, °F.
ΔX = length of unit cell, ft.
ΔX_i = volume to surface ratio for microporous particles, ft.

Greek Letters

α = accommodation coefficient
β = numerical constant determined from specific heat ratio and accommodation coefficient
γ = specific heat ratio
δ = numerical constant determined from specific heat ratio
ϵ_a = macropore void fraction
ϵ_i = micropore void fraction
ϵ_s = fraction of solids
λ_c = thermal conductivity of continuous phase, B.t.u./hr.-ft.-°F.
λ_{eff} = effective thermal conductivity of Equation 2, B.t.u./hr.-sq. ft.-°F.
λ_d = thermal conductivity of discontinuous phase, B.t.u./hr.-ft.-°F.
λ_s' = apparent thermal conductivity of solid phase in microporous particles, B.t.u./hr.-ft.-°F. [cal./sec.-cm.-°C. in Equation (8)]
λ_m = molecular thermal conductivity of gas, B.t.u./hr.-ft.-°F.
λ_s = true thermal conductivity of solid phase, B.t.u./hr.-ft.-°F.
μ = discontinuous phase fraction of total volume
σ = porosity of microporous particles, determined as $\epsilon_i^2/(1-\epsilon_a)^2$

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Solution of Problems Involving Conventional and Complex Distillation Columns at Unsteady State Operation

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The θ method of convergence has been applied to conventional and complex columns at unsteady state operation. A different holdup for each stage may be specified in terms of molal, mass, or volumetric units. Plate efficiencies were used, and the K values and enthalpies were taken to be polynomials in temperature.

The combination of the calculational procedure of Thiele and Geddes (*27*) and the θ method of convergence (*11*) has been applied to solve problems involving conventional and complex distillation columns at unsteady state operation. A conventional column is one which has one feed stream and two product streams, the distillate and the bottoms. A complex column has any number of feeds and/or one or more side stream withdrawals in addition to the distillate and bottoms. In the interest of simplicity, the equations are developed for a conventional column, and then a brief description of their extension to include complex columns is presented.

The differential equations that represent a component-material balance, a total-material balance, and an enthalpy balance for plate j are as follows:

$$v_{j+1,i} + l_{j-1,i} - v_{ji} - l_{ji} = \frac{du_{ji}}{dt} \qquad (1)$$

$$V_{j+1} + L_{j-1} - V_j - L_j = \frac{dU_j}{dt} \qquad (2)$$

$$V_{j+1}H_{j+1} + L_{j-1}h_{j-1} - V_jH_j - L_jh_j = \frac{d(U_jh_j)}{dt} \qquad (3)$$

These differential-difference equations were first presented by Marshall and Pigford (*13*). In the statement of the material and enthalpy balances, the holdup in the vapor phase was omitted because it is generally negligible. Equation (1) implies that the composition of the liquid is the same at each point on plate j at any time t. This assumption is made throughout the course of the developments.

In order to complete the description of a plate, the equilibrium relationship

$$y_{ji} = E_{ji}K_{ji}x_{ji} \qquad (4)$$

is needed. The instantaneous vaporization efficiency (*7*, *26*) is defined as

$$E_{ji} = y_{ji}/Y_{ji}, \text{ and } Y_{ji} = K_{ji}x_{ji} \qquad (5)$$

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