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THERMAL CONDUCTIVITY OF POROUS SYSTEMS

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Аннотация—Даны расчётные формулы для нахождения эффективной теплопроводности порошкообразных и твёрдых пористых материалов в широком диапазоне температур и различных газовых средах. Расчетные значения эффективной теплопроводности около 100 различных материалов сопоставлены с экспериментальными данными различных авторов, в том числе и авторов данной статьи. Изложена методика расчёта эффективной теплопроводности порошкообразных смесей, в частности смеси Al_2O_3-порошкообразный плексиглас. Показано, что путем смешивания различных порошкообразных материалов можно изменять эффективную теплопроводность засыпок в широких пределах в различных газах. Это особенно существенно для порошкообразных полимерных материалов при низких температурах, когда теплопроводность частиц становится близкой к теплопроводности газов в порах. Это относится также к контактной теплопроводности вакуумно-порошковой теплоизоляции при низких температурах, где доминирующим фактором является контактная теплопроводность, зависящая от внешней механической нагрузки, упругих свойств материала и состояния их поверхности.

Приведены экспериментальные и расчетные данные по теплофизическим свойствам твёрдых пористых систем (шамотная керамика) в широком диапазоне температур в различных газовых средах.

NOMENCLATURE

λ_{ef},	effective thermal conductivity of porous material;
λ_s,	thermal conductivity of material with zero porosity;
Π,	porosity;
λ_c,	contact thermal conductivity of granular material;
λ_g,	total molecular ($\lambda_g m$) and radiative (λ_{gr}) thermal conductivities in a pore;
λ'_g,	total molecular ($\lambda'_g m$) and radiative (λ'_{gr}) thermal conductivities in a micro-gap;
R,	thermal resistance;
R_{ef},	effective thermal resistance;
σ,	thermal conductance;
σ_{ef},	effective thermal conductance;
L,	characteristic size of an elementary cell (particle diameter);
l,	characteristic size of a pore;
h_r,	height of particle microroughnesses;
r_{sp},	radius of a contact spot;
μ,	Poisson coefficient;
E,	Young's modulus;
P,	strength of two particles pressure to each other;
λ_0,	thermal conductivity of gas at normal pressure;
ε,	emissivity of pore surface;
C,	Stefan–Boltzmann constant;
T,	mean absolute temperature of porous material;
k,	$= c_p/c_v$, ratio of gas heat capacities at constant pressure and volume;
$\bar{a}$,	accommodation coefficient;
Λ,	molecular free path of gas;
Λ_0,	gas molecular free path at normal pressure;
H_0,	normal gas pressure ($9{\cdot}93 . 10^4$ N/m^2);
H,	gas pressure in a pore;

δ,	thickness of granular filling;
b,	coefficient characterizing particle arrangement (it is four for cubic arrangement);
f_1,	coefficient of internal friction of filling;
n,	coefficient equal to one for a spherical pore;
λ_c',	contact thermal conductivity of free-packed granular material;
$\lambda(P)$,	contact thermal conductivity of granular material under extra mechanical load;
k_m, k_n,	empirical coefficients, $k_m = (h_r/L) . 10^{-3}$;
Kn,	Knudsen number;
Pr,	Prandtl number;
φ,	relative air humidity;
$D_{1,2}$,	coefficient of molecular water-vapour diffusion into the air;
ν,	mass flow coefficient, $\nu = (H/H - p)$;
M,	latent heat of water evaporation;
p,	partial pressure of water vapour;
ρ_v,	density of water vapour;
β,	$= \mathrm{d}p_v/\mathrm{d}T$;
p_{vs},	partial pressure of water vapour at $\varphi = 1$;
S,	contact area between two particles;
R_c,	thermal resistance of contact of two particles;
k_k,	coefficient of particle adhesion;
ρ,	density of powdered material;
ξ,	moisture content of porous material (per cent of dry weight).

INTRODUCTION

SCIENTISTS and engineers have been interested in thermal conductivity of porous systems since the end of the last century [1, 2]. By now vast experimental material has been accumulated and a lot of formulae have been proposed for the prediction of the effective thermal conductivity of porous systems. This great interest in porous systems is due to the fact that they have found rather a wide use in a number of industrial branches. Porous systems can be conventionally divided into solid porous materials with definite shape, granular materials and fibrous materials.

The present work deals with powdered systems and solid porous materials in which the processes of heat transfer have many similarities.

The reported data on thermal conductivities of pure materials (crystal and amorphous solid bodies, metals, gases, fluids) are rather numerous. The porous materials under consideration are composed of pure substances and, naturally, thermal conductivities of such systems depend on the properties and volumetric proportions of the pure materials they include. The knowledge of thermal properties of, and interaction beween, the elements in the heterogeneous systems allows the thermal conductivity of such systems to be calculated.

In nature there are many materials consisting of ten or more different components, and it is very difficult to determine the relation and interaction between them.

If, for example, pure quartz is only silica, then basalt is a compound of twelve and more components. However, many granular materials used in engineering are compounds of two or three components (for example, vacuum-powder insulation with addition of metal powder in the medium of rarefied gas or powder in the medium of binary gas mixture). Such materials as concretes, refractories, certain solutions, gas mixtures, alloys, etc. are composed of two or three components.

Generally speaking, porous systems consist of solid particles and of pores of complicated shapes and sizes. The analytical study of such systems with the help of basic hydrodynamic and thermodynamic equations applicable to continuous systems is difficult in this case. However, in the structure of such materials an elementary cell can be singled out whose properties will still not differ from those of the system as a whole.

Isolation of an elementary cell and consideration of the mechanism of heat transfer in it give an idea of the whole heterogeneous system.

The method of generalized conductivities is the most simple and widely used one for the study of heterogeneous systems. At one time Maxwell [2], Bruggeman [3], Eucken [4], Ollendorff [5] applied this method to the field of electricity. Eucken tried to use this method for the determination of the effective thermal conductivity of granular materials.

Odelevsky [6], Bogomolov [7] and others were among the Soviet scientists who applied the above method.

A good review of the present theoretical works is given in [18].

POROUS SYSTEM MODEL

The aim of the present work is to use the method of generalized conductivities for the calculation of the effective thermal conductivities of porous systems in the form of powders and solid materials over a wide range of temperatures and pressures of gases filling the pores. The results obtained are compared with the experimental data of the present authors and with the reported data.

Consider the applicability of the method of generalized conductivities for the determination of the effective thermal conductivity on the example of dry granular systems.

Let us express the effective thermal conductivity of a granular system as a function of a number of parameters

$$\frac{\lambda_{ef}}{\lambda_s} = f\left(\Pi, \frac{\lambda_g}{\lambda_s}, \frac{\lambda'_g}{\lambda_s}, \frac{\lambda_c}{\lambda_s}\right).$$

The shapes of real granular materials can be greatly diverse. The more fantastic are the shapes of the particles, the higher in general, is the overall porosity of the material. Most of the authors tend to consider granular materials as spheres in tetrahedral or cubic arrangement. The theoretical porosity of the most densely packed tetrahedral arrangement is 26 per cent. The porosity of a real granular system is approximately between 39 and 98 per cent.

Imagine an elementary cell in the form shown in Fig. 1. Assume the particles to be symmetric and consider only quarters of two particles adjoining each other.

Let V be the total volume of an elementary cell; V_1, the volume of solid phase of the elementary cell; V_2, the volume of the gaseous phase. Establish the relationship between the porosity and the ratio h/l (Fig. 1). Consider only one-quarter of the elementary cell. Denote the volumes V', V'_1, V'_2, respectively.

Then the following equalities are valid

$$V' = \tfrac{1}{4}L^3; \qquad V'_1 = \Delta^2(3L - 4\Delta);$$

$$\frac{V'_1}{V'} = \frac{V_1}{V} = 4\left(\frac{\Delta}{L}\right)^2\left(3 - 4\frac{\Delta}{L}\right);$$

$$\frac{\Delta}{L} = \frac{\Delta/l}{1 + 2\Delta/l}.$$

Denote $\Delta/L = x$, then the previous expression can be written in the form

$$4x^3 - 3x^2 + k = 0; \qquad k = \frac{1 - \Pi}{4}.$$

Solving this equation with respect to x and allowing for

$$h/l = \frac{x}{0{\cdot}5 - x}$$

obtain

$$\Pi = f(h/l).$$

Π	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1
h/l	∞	4·21	2·47	1·75	1·29	0·846	0·7	0·567	0·396	0·244	0

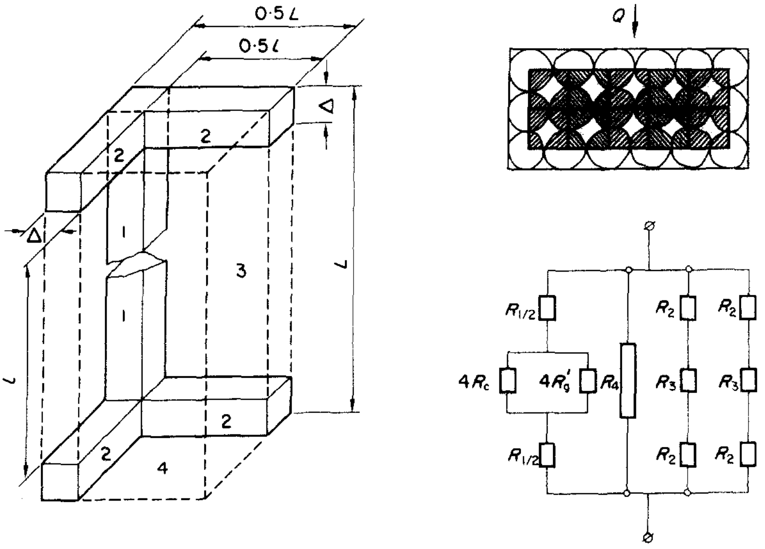

FIG. 1. One quarter of the porous system elementary cell and a diagram of its thermal resistances.

The present dependence is similar to $\Pi = f(h/l)$ [8] obtained for solid porous materials.

If the lines of the heat flow are assumed parallel to the vertical generating lines of the elementary cell, then thermal resistances of the components of the one-quarter cell can be presented as

$$R_1 = \frac{L}{\lambda_s \Delta^2}, \quad R_2 = \frac{2}{\lambda_s l}, \quad R_3 = \frac{2}{\lambda_g \Delta}.$$

$$R_4 = \frac{4L}{\lambda_g l^2}, \quad R_g' = \frac{4h_r k_k}{\lambda_g' h^2}.$$

$$R_c = R_L + R_{sp} + R_0.$$

Let $h = 2\Delta$ be the thickness and width of the skeleton; R_L, the resistance determined by narrowing of the lines of the heat flow in the region adjacent to the place of contact; R_{sp} the resistance of microroughnesses at the place of contact; R_0, resistance of the oxidic film.

The effective thermal resistance of the one-quarter cell is

$$R_{ef} = \frac{4}{\lambda_{ef} \cdot L}.$$

Similarly, thermal conductance can be presented as

$$\sigma_1 = \frac{1}{R_1 + \dfrac{4}{\sigma_g' + \sigma_c}}; \quad \sigma_2 = \frac{\lambda_g \cdot l^2}{4L};$$

$$2\sigma_3 = \frac{1}{R^2 + \dfrac{R_3}{2}}; \quad \sigma_g' = \frac{\lambda_g' \cdot h^2 \cdot 10^3}{4Lk_m k_k};$$

$$\sigma_c = \frac{1}{R_L + R_{sp} + R_0}.$$

The effective thermal conductance

$$\sigma_{ef} = \sigma_1 + \sigma_2 + 2\sigma_3. \tag{1}$$

If the corresponding values of conductance are substituted into (1), then after some simple transformations we shall obtain

$$\frac{\lambda_{ef} L}{4} = \frac{1}{\dfrac{4L}{\lambda_s h^2} + \dfrac{4}{\sigma_c + \sigma_g'}} + \frac{\lambda_g l^2}{4L} + \frac{1}{\dfrac{2}{\lambda_s l} + \dfrac{2}{\lambda_g h}}. \tag{2}$$

Dividing (2) by $\lambda_s L/4$, find the initial formula for the calculation of the effective thermal conductivity of the porous system

$$\frac{\lambda_{ef}}{\lambda_s} = \frac{1}{\frac{1}{(h/L)^2} + A} + \nu_g(1 - h/L)^2 + \frac{2}{1 + h/l + \frac{1}{v_g h/L}}, \qquad (3)$$

where

$$A = \frac{1}{\frac{\lambda_c}{\lambda_s} + \frac{\nu'_g}{4k_k k_m}\left(\frac{h}{L}\right)^2 . 10^3}; \qquad L = l + h;$$

$$\frac{h}{L} = \frac{h/l}{1 + h/l}; \qquad \nu_g = \frac{\lambda_g}{\lambda_s}; \qquad \nu'_g = \frac{\lambda'_g}{\lambda_s}.$$

The value A expresses heat transfer through contact and gas microgap at the place of contact of two particles. With no thermal resistance at the joint of two particles $A = 0$ and the cell under consideration will be similar to that described for solid porous systems [8].

On the whole there are four independent modes of heat transfer from one contact surface to another: (a) heat conduction directly through the contact; (b) heat conduction through the medium filling the pores and the space between the projections of roughness of the contact surfaces; (c) radiative heat transfer between surfaces; (d) gas convection in pores. Limited sizes of pores and microgaps at the place of contact between the particles impede the onset of convective gas flows caused by the temperature gradient. It is known that with the values of $(Gr . Pr) < 10^3$ convective heat transfer in pores can be neglected [9]. This is true for the particles not larger than 4–5 mm in diameter. In this case only heat transfer due to the temperature gradient is considered. As shown in [10], in some cases of porous systems the heat flux with a temperature gradient is the cause of a gas flow with friction forces.

By enclosing gas in a porous system with comparatively large pores, one can obtain an increase of the pressure gradient which in its turn will give rise to a gas flow in the direction opposite to that caused by the temperature gradient and, by this means, decrease the effective thermal conductivity of the system. In some pressure tight systems this decrease can be 20 per cent.

POWDERS

Consider the above processes in application to granular systems:

It is well known that the contact surface of two particles represents an additional resistance to the heat flow from one particle to the other. However, until recently this problem has been given little attention. We can refer to some experimental works [11–14]. At present in a number of industrial branches, in particular in reactor power engineering, high heat flows occur from one surface to another through direct contact. Consequently even small contact resistances cause local overheating which is often extremely undesirable. In the present work the nature of thermal resistance of the contact between two particles *in vacuo* is studied and the model of this phenomenon is obtained.

In accordance with [16, 46] the heat flow from one particle to another contracts in the regions near the contact of two particles. Within the region of immediate proximity to the contact intensive interaction of phonons takes place which leads to excess thermal resistance.

If we present the contact spot of two particles as a circle with the radius r_{sp}, then the heat flow inside the particle passes through the region which is narrowing from the area h^2 to πr_{sp}^2.

In [46] the definition is given of the coefficient $g(x_L)$ allowing for the contraction of the passage for the heat flow

$$g(x_L) = 1 - 1{\cdot}40925\,x + 0{\cdot}29591\,x^3 + 0{\cdot}05254\,x^5 + 0{\cdot}02105\,x^7 + \ldots$$

where $x_L = 2r_{sp}/h$ is the contraction factor, $x_L \leqslant 0{\cdot}65$.

Due to the contraction of the passage for heat flow through two particles in contact, the thermal resistance is therefore:

$$R_L = \frac{g(x_L)}{2r_{sp}\lambda_s}.$$

For the majority of real granular systems the factor $g(x_L)$ is close to unity.

In [49] the thermal resistance of the circular contact area on a semi-infinite body is

$$R_L^T = 1/4r_{sp}\,.\,\lambda_s$$

provided that the temperature over the whole area is constant, and it is equal to

$$R_L^q = 8/3\pi^2 r_{sp}\lambda_s$$

provided that the heat flow on the area is constant.

The values of these expressions are close to each other.

In [50] the ratio of R_L to $2R_L^q$ is given for spherical particles as

$$\frac{R_L}{2R_L^q} = \frac{3\pi L/2}{16r_{sp}} \sum_{n=0}^{\infty} \frac{1}{2n+1} [P_{2n}(\cos\varphi) - P_{2n+2}(\cos\varphi)][1 + P_{2n+1}(\cos\varphi)];$$

$$\frac{r_{sp}}{L/2} = \sin\varphi.$$

This expression differs from unity very slightly (when $2r_{sp}/L$ changes from 0 to 0·4, $R_L/2R_L^q$ changes from 1 to 1·2).

Thus

$$R_L \cong \frac{1}{2r_{sp}\,.\,\lambda_s}.$$

Since real particles have various microroughnesses, the latter also constitute an additional resistance to the heat flow. Let us assume that the microroughness has some height h_r and is of the shape of a cylinder with the cross-sectional area πr_{sp}^2. Then the additional thermal resistance of the microroughness at the place of contact of the two particles can be expressed as

$$R_{sp} = \frac{h_r\,.\,k_k}{\pi r_{sp}^2\,.\,\lambda_s}.$$

Particles, especially metal ones, are often covered with an oxide film. This oxidizing film can produce a supplementary thermal resistance R_0 to the heat flow.

In the literature, unfortunately, there is little information about thermal resistance of films. As a rule, this resistance can be neglected [47]. At present the role of surface films is easier to be explained experimentally.

Thus contact resistance of granular systems can be presented as a sum of three components

$$R_c = R_L + R_{sp} + R_0.$$

Contact thermal conductivity can be presented as

$$\lambda_c = \frac{1}{R_c\,.\,L}. \tag{4}$$

To find λ_{ef}, insert λ_c into (3).

Apart from formula (4) in our calculations we have used the formula proposed by Riemann–Weber for the determination of contact thermal conductivity in cubic arrangement of congruent spherical particles L in diameter and with the radius of contact spot r_{sp}

$$\lambda_c = \lambda_s\left(\frac{L}{2r_{sp}} + \frac{1}{\pi}\ln\frac{L}{r_{sp}}\right)^{-1} \tag{5}$$

The radius of the contact spot for two spherical particles depends on pressure and can be determined by the Hertz formula [15]

$$r_{sp} = 0{\cdot}725\sqrt[3]{\left(\eta P\frac{L}{2}\right)}, \tag{6}$$

where

$$\eta = \frac{2(1-\mu^2)}{E}.$$

Assume

$$s = \pi r_{sp}^2.$$

For real particles with rough surfaces the contact area of two particles depends upon the nature of roughness. As shown in [16], with the ratio of thickness to the height of filling equal to 0·1, the following formula holds true for the determination of the contact spot between particles of free-packed powder

$$r_{sp} = 0{\cdot}575\frac{L}{2}\sqrt[3]{\left(\frac{\delta\rho\, b\eta}{f_1}\right)}. \tag{7}$$

In [17] the contact thermal conductivity of powdered systems is considered as a sum of contact thermal conductivity of free-packed material λ_c' which depends on the geometry of particles, their orientation to one another, weight and porosity and on the value $\lambda(P)$ being determined by the external mechanical load

$$\lambda_c = \lambda_c' + \lambda(P)$$

where

$$\lambda_c' = \frac{2{\cdot}82}{LQ}\frac{S}{h_r k_k}\lambda_s,$$

$$\lambda(P) = \frac{\lambda_s}{75}\frac{1}{Q}P^{\frac{2}{3}}k_c, \qquad (P < 3\,.\,10^5) \tag{8}$$

$$\lambda(P) = \frac{\lambda_s}{E^{\frac{4}{9}}}\frac{1}{Q}P^{\frac{4}{9}}k_b, \qquad (P > 3\,.\,10^5).$$

k_c and k_b are empirical coefficients. With changing mechanical load from $4\,.\,10^5$ N/m^2 to $12\,.\,10^5$ N/m^2, k_b changes almost linearly from 2·2 to 2·9. With changing mechanical load from 10^5 to $3\,.\,10^5$ k_c changes from 0·35 to 0·45.

In the above relations

$$Q = \sqrt[3]{\left(\frac{75}{100 - \Pi}\right)}.$$

At normal pressure the heat transfer is considerably effected by a microgap at the contact of two particles. The surface of real particles is rough. Thermal conductance of the microgap can be expressed by the following relation

$$\sigma_g' = \frac{\lambda_g' h^2}{4h_r k_k}. \tag{9}$$

The ratio $h_r/L = k_m\,.\,10^{-3}$ is rather a stable one for the particles of various sizes.

The height of microroughness can be determined experimentally according to the class of surface purity. This is particularly important for metal powders where thermal resistance of a particle is much lower than the thermal resistance of a gas-filled microgap.

Besides microroughness, particles have various chops and macrowaves. In expression (9) thermal conductivity of the gas microgap is presented as the conductivity of a parallelepiped with the height $h_r k_k$ and base area h^2 since it is very difficult to calculate the real contact area. In this volume thermal conductivity of gas will naturally be somewhat different from that in a large pore. This fact is allowed for by the empirical coefficient k_n when molecular and radiative components of heat conduction in the microgap are being determined. Practice showed that the value k_n ranged from 0·5 to 1. Since micropores of the microgap are not closed, molecules served from the surfaces of adjoining particles inevitably penetrate into it. In a similar way also radiation penetrates. In this case both radiant energy quanta and molecules cover the way which is less than their path in a large pore.

In Table 1 are given the calculated values of λ for perlite obtained by formulae (4) and (5) and compared with the experimental data of [34]. The analysis of the calculated values by formulae (4) and (5) showed that formula (4) gives the values which are closer to the experimental results than does formula (5). It is reasonable to use formula (5) for tentative evaluation of λ_c when the ratio h_r/L is not known.

In Table 2 the values of λ are given for other materials.

In [34] it is pointed out that in high vacuum (10^{-2} N/m^2) within the temperature range 300–76°K the heat flow through perlite is greater than within the interval 300–20°K. Similarly, the heat flow through perlite at boundary temperatures 76–20°K is greater than at temperatures 70–4°K. This obvious thermal

Table 1. Contact thermal conductivity of perlite at various boundary temperatures (distance between the walls is 25·4 . 10^{-3} m, wall emissivity, 0·86 and gas pressure $H < 10^{-3}$ N/m^2)

Material	Boundary temperatures, °K		ρ	λ_s	$\lambda_{exp}\,10^4$	$\lambda_{calc}\,10^4$ accord. to (4)	$\lambda_{calc}\,10^4$ accord. to (5)
	T_1	T_2	kg/m^3	W/m deg	W/m deg	W/m deg	W/m deg
Perlite	304	76	1400	1·28	10 ± 0·5	12·8	40
(bulged)	304	20	1400	0·8	6·5 ± 0·5	6·15	25
L = 0·5 mm	76	20	1400	0·33	2·0 ± 0·5	2·4	10
[34]	76	4	1400	0·2	0·8	1·4	6

Table 2. Contact thermal conductivity of powdered materials at various boundary temperatures and gas pressure $H < 10^{-3}$ N/m^2

Material	Temperature °K	Porosity, Π per cent	λ_s W/m deg	Young modulus E 10^{10} N/m^2	$\lambda_{calc}\,10^4$ W/m deg (4)	$\lambda_{exp}\,10^4$ W/m deg
Stainless steel shot L = 0·071 mm [52]	315	40	16·3	21	178	173
Plumbum shot L = 0·159 mm [38]	315	42	34·3	1·6	132	122
L = 0·238 mm [38]	315	43·9	34·3	1·6	132	115
L = 0·318 mm [38]	315	41·6	34·3	1·6	131	124
L = 0·635 mm [38]	315	43·3	34·3	1·6	130	117
Tellurine L = 0·1 mm [51]	300–76	90	1·3	5·49	20	16
Perlite L = 0·3 mm [43]	304–76	95	1·28	5·49	10·5	6·5
Mgo L = 0·263 mm [52]	400	42	24·4	21	159	155

paradox, which remained obscure in [34], is well-explained when the structures of formulae (4) and (5) are considered for the determination of λ_c. For the temperature range 300–76°K the integral mean value λ_s for SiO_2, from which perlite is obtained, is higher than for the temperature range 300–20°K [11, 28]. Accordingly, within the range 76–20°K λ_s is higher than within 76–4°K. Due to this in the first case λ_c is higher than in the second.

Radiant heat conductivity can be found either by the formula

$$\lambda_{gr} = 2\varepsilon^2 C T^3 l, \qquad (10)$$

described in [18] or by the formula proposed by Loeb for porous systems

$$\lambda_{gr} = 4nl\varepsilon C T^3. \qquad (11)$$

Accordingly

$$\lambda'_{gr} = 2\varepsilon^2 C T^3 k_n l,$$

or

$$\lambda'_{gr} = 4nk_n l\varepsilon C T^3.$$

In both formulae the emissivity of the material surface is the function of temperature. The theoretical relation $\lambda_{gr} = f(T)$ therefore gives only an approximate idea about the value of the radiant component. However for powders with particles of relatively low diameter in low vacuum and at room temperatures the effect of radiant component is rather small. It is the effect of radiation that dominates at high vacuum and high temperatures.

Gas pressure in pores effects essentially the effective thermal conductivity of granular systems. According to the molecular–kinetic theory, the thermal conductivity of gas is a function of pressure, molecular mean free path, and the distance between surfaces exchanging heat. If the sizes of volumes filled with gas are comparable with the molecular mean free path, the so-called temperature jump greatly effects the thermal conductivity of gas. In granular materials the value of the molecular mean free path is often higher or commensurable with pore sizes. In such powders even at atmospheric pressure the phenomena observed in rarefied medium take place. In the literature some variants of theoretical pressure dependence of gas thermal conductivity are published. The most known of them are those proposed by Maxwell, Knudsen and Smoluchowski.

In the present work the equation published in [19] and convenient for practice is used

$$\lambda_g m = \frac{\lambda_0}{1 + \dfrac{2k}{k+1}\left(\dfrac{2-\bar{a}_1}{\bar{a}_1} + \dfrac{2-\bar{a}_2}{\bar{a}_2}\right)\dfrac{Kn}{Pr}}, \tag{12}$$

where

$$Kn = \frac{\Lambda}{l}, \qquad \Lambda = \frac{\Lambda_\infty}{1 + C/T}\cdot\frac{H_0}{H} = \Lambda_0\frac{H_0}{H}.$$

Assuming $\bar{a}_1 = \bar{a}_2$, we can express the above equation in the form

$$\lambda_g m = \frac{\lambda_0}{1 + B/Hl}, \tag{13}$$

where

$$B = \frac{4k}{k+1}\,\frac{2-\bar{a}}{\bar{a}}\,Pr^{-1}\Lambda_0 H_0.$$

In the literature, unfortunately, there is very little data on the value of the accommodation coefficient when various materials are interacting with gases within a wide temperature range [26]. In a number of cases it is not known how the value of Pr changes over a wide range of rarefication of the medium.

A fairly large amount of experimental material is available on the effective thermal conductivity of granular material as a function of gas pressure in the pores. The experimental relation $\lambda_{ef} = f(H)$ in semi-logarithmic coordinates has the form of an S-shaped curve. A particularly great amount of experimental data is obtained for various types of powder-vacuum insulation.

It was Smoluchowski and Dewar who have already noticed that, when filling the space between the walls of some vessels with finely divided powders, one can obtain almost the same effect as high vacuum between the walls of low emissivity.

The comparison of the experimental and predicted relations $\lambda_{ef} = f(H)$ (Fig. 2 and Table 3) showed their good agreement. The experiments and calculations showed that in finely divided powder-vacuum insulation it is advisable to use rarefied gas with maximum molecular (for example helium, hydrogen) free path though the thermal conductivity of these gases is relatively high.

The analysis of the S-shaped curves showed that at low rarefactions the effective thermal conductivities of granular systems do not depend on pressure until the pressure is reduced to the value when the molecular mean free path becomes commensurable with the characteristic pore size ($Kn \leqslant 1$). With further decrease in pressure the thermal conductivity of fillings changes proportionally to the pressure variation. The slope of S-shaped curves depends on the pore sizes and gas characteristics.

In some cases when the investigations are carried out within the region of low pressures, the existence of thermomolecular diffusion should be taken into consideration. The true pressure in the bed of porous material can be different due to diffusion. The value of the correction for the thermomolecular diffusion is measured in [20] as a function of pressure, temperature, diameter of channels and kind of gases.

Thus in formula (3)

$$\lambda_g = \frac{\lambda_0}{1 + B/Hl} + \lambda_{gr}, \tag{14}$$

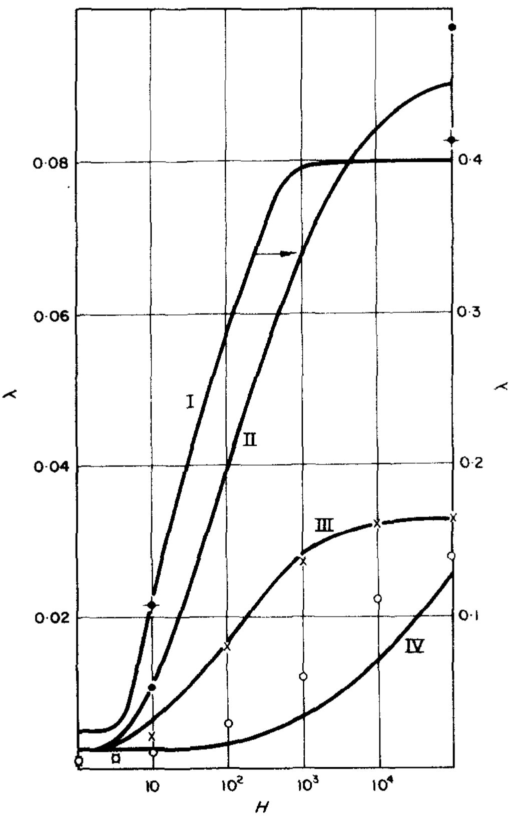

FIG. 2. λ_{ef} of nonmetallic granular material as a function of H.

1. Quartz sand ($L = 0{\cdot}4 \,.\, 10^{-3}$ m), + experimental data.
2. Powdered plexiglass ($L = 50 \,.\, 10^{-6}$ m), ● experimental data.
3. Perlite ($L = 0{\cdot}5 \,.\, 10^{-3}$ m) [34], × experimental data
4. Silica gel ($L = 5 \,.\, 10^{-6}$ m) [43], ○ experimental data.

$$\lambda'_g = \frac{\lambda_0}{1 + B/Hk_n l} + \lambda'_{gr}. \qquad (15)$$

As an example calculate the effective thermal conductivity of perlite for which the relation $\lambda_{ef} = f(H)$ found experimentally was given in [34].

The diameter of distended perlite particles is 0·5 mm, porosity $\Pi = 0{\cdot}947$; $h/l = 0{\cdot}14$; $h/L = 0{\cdot}123$; the width of the vertical layer between the walls with emissivity 0·8 is $2{\cdot}54 \,.\, 10^{-2}$ m; boundary temperatures are 304–76°K; integral mean thermal conductivity λ_s for the above temperature range is 1·28 W/m deg; integral mean thermal conductivity of air within the above temperature range is 0·0168 W/m deg; the ambient pressure, 10^2 N/m²; $B/Hl = 2{\cdot}19$; assume $\lambda_g = \lambda'_g$; density $\rho = 1400$ N/m³.

$$E = 5{\cdot}49 \,.\, 10^{10}\ \text{N/m}^2; \qquad \mu = 0{\cdot}25;$$

$$f_1 = 0{\cdot}3; \qquad b = 4.$$

We have

$$\lambda_g m = \frac{0{\cdot}0168}{1 + 2{\cdot}19} = 52{\cdot}7 \,.\, 10^{-4}\ \text{W/m deg}$$

$$\lambda_{gr} = 9{\cdot}2 \,.\, 10^{-2} \,.\, 27 \,.\, 0{\cdot}41 \,.\, 0{\cdot}25 \,.\, 10^{-3} = 2{\cdot}55 \,.\, 10^{-4}\ \text{W/m deg}$$

$$\lambda_g = 52{\cdot}7 + 2{\cdot}55 = 55{\cdot}25 \,.\, 10^{-4}\ \text{W/m deg}$$

$$v_g = \frac{55{\cdot}25 \,.\, 10^{-4}}{1{\cdot}28} = 43{\cdot}2 \,.\, 10^{-4}.$$

Find the radius of the contact spot by formula (7)

$$r_{sp} = 0{\cdot}575 \,.\, 0{\cdot}25 \,.\, 10^{-3} \sqrt[3]{\left(\frac{0{\cdot}025 \,.\, 1400 \,.\, 4.2 \,.\, 0{\cdot}94}{5{\cdot}49 \,.\, 10^2 \,.\, 0{\cdot}3}\right)} = 0{\cdot}36 \,.\, 10^{-6}\ \text{m}$$

$$k_k = 1{\cdot}5; \qquad k_m = 1; \qquad \lambda_c = 1{\cdot}4 \,.\, 10^{-3}\ \text{W/m deg}$$

$$\frac{\lambda_{ef}}{\lambda_s} = \left\{1\Big/\left[66 + \left(1\Big/\frac{1{\cdot}4 \,.\, 10^{-3}}{1{\cdot}28} + \frac{43{\cdot}2 \,.\, 10^{-4}}{4.1 \,.\, 1{\cdot}5} \,.\, 0{\cdot}0151 \,.\, 10^3\right)\right]\right\} + 43{\cdot}2 \,.\, 10^{-4}(1 - 0{\cdot}123)^2 + \left[2\Big/\left(1 + 0{\cdot}14 + \frac{1}{43{\cdot}2 \,.\, 10^{-4} \,.\, 0{\cdot}123}\right)\right] = 121 \,.\, 10^{-4}$$

$$\lambda_{ef} = 1{\cdot}28 \,.\, 121{\cdot}0 \,.\, 10^{-4} = 155 \,.\, 10^{-4}\ \text{W/m deg}$$

$$\lambda_{\text{exp}} = 155 \,.\, 10^{-4}\ \text{W/m deg.}$$

Table 3. Effective thermal conductivity of some granular materials in air medium of various density

Powder	L	H	Π	λ_s	$\lambda_g \cdot 10^4$	$\lambda_{exp} \cdot 10^4$	$\lambda_{calc} \cdot 10^4$	Ref
1	2	3	4	5	6	7	8	9
Quartz sand T = 300°K	0·78	10^5	0·354	13·68	260	4400	4400	authors' data
	0·435	10^5	0·377	13·68	260	4150	4000	authors' data
	0·435	10^4	0·377	13·68	253	—	4000	authors' data
	0·435	10^3	0·377	13·68	210	—	3940	authors' data
	0·435	10^2	0·377	13·68	76·5	—	2840	authors' data
	0·435	10^1	0·377	13·68	13·2	1060	1040	authors' data
	0·435	10^0	0·377	13·68	3·25	—	260	authors' data
	0·435	10^{-1}	0·377	13·68	2·9	—	260	authors' data
	0·15	10^5	0·400	13·68	260	3700	3700	authors' data
Powdered plexiglass T = 300°K	$50 \cdot 10^{-3}$	10^5	0·400	0·19	260	880	900	authors' data
	$50 \cdot 10^{-3}$	10^4	0·400	0·19	217	—	840	authors' data
	$50 \cdot 10^{-3}$	10^3	0·400	0·19	87	—	668	authors' data
	$50 \cdot 10^{-3}$	10^2	0·400	0·19	12·6	—	400	authors' data
	$50 \cdot 10^{-3}$	10^1	0·400	0·19	1·54	108	107	authors' data
	$50 \cdot 10^{-3}$	10^0	0·400	0·19	0·38	—	16·2	authors' data
	$50 \cdot 10^{-3}$	10^{-1}	0·400	0·19	0·26	—	12·8	authors' data
Perlite T = 300°K	—	10^5	0·98	1·28	260	285	279	[42]
	—	10^5	0·96	1·28	260	351	348	[42]
	—	10^5	0·92	1·28	260	460	455	[42]
T = 77–300°K	0·5	10^5	0·947	1·28	168	325	328	[34]
	0·5	10^4	0·947	1·28	167	320	319	[34]
	0·5	10^3	0·947	1·28	138	275	284	[34]
	0·5	10^2	0·947	1·28	55·2	143	155	[34]
	0·5	10^1	0·947	1·28	10·2	60	68	[34]
	0·5	10^0	0·947	1·28	3·31	16	13	[34]
	0·5	10^{-1}	0·947	1·28	2·55	16	12	[34]
Silica gel T = 77–300°K	$5 \cdot 10^{-3}$	10^5	0·95	1·28	138	277	256	[43]
	$5 \cdot 10^{-3}$	10^4	0·95	1·28	53	221	147	[43]
	$5 \cdot 10^{-3}$	10^3	0·95	1·28	8·4	119	65	[43]
	$5 \cdot 10^{-3}$	10^2	0·95	1·28	7·95	40	25	[43]
	$5 \cdot 10^{-3}$	10^1	0·95	1·28	3·2	20	14	[43]
	$5 \cdot 10^{-3}$	10^0	0·95	1·28	3·1	16	12	[43]

In Table 4 the values of λ_{ef} are given for a number of granular non-metallic materials in the atmosphere of various gases at normal pressure. Experimental values of λ_{ef} are compared to the ones calculated by formula (3) and also by formulae of Maxwell and Bruggeman for a wide range of porosity variation (35–98 per cent).

As seen from Table 4, formula (3) gives a good agreement of the results with the experimental data.

At present the studies of thermal properties of granular materials in the media of various gas mixtures are of great interest. Porous materials can be applied as filters for gas mixture separation. In this their thermal conductivities are rather important since the higher is the temperature drop on the surface of porous material, the more effective the separation of gas mixtures. In the literature a number of formulae are reported for the calculation of the effective thermal conductivity of gas mix-

Table 4. Thermal conductivity of granular materials

	Materials	λ_s W/m deg	λ_0 W/m deg	L mm	Π per cent	λ_{exp} W/m deg	Calculated values W/m deg $\lambda_{(3)}$	$\lambda_{Maxwell}$	$\lambda_{Bruggeman}$	$\frac{\lambda_{exp}}{\lambda_{(3)}}$	$\frac{\lambda_{exp}}{\lambda_{Maxwell}}$	$\frac{\lambda_{exp}}{\lambda_{Bruggeman}}$
1	2	3	4	5	6	7	8	9	10	11	12	13
1.	Glass beads–air [39]	1·09	0·029	3·8	40	0·180	0·192	0·134	0·230	0·940	1·344	0·785
2.	Glass beads–air [40]	1·09	0·024	0·16	35	0·159	0·188	0·138	0·250	0·845	1·15	0·635
3.	Glass beads–H_2 [39]	1·09	0·147	4	40	0·460	0·490	0·460	0·500	0·938	1·0	0·920
4.	Glass beads–He [40]	1·09	0·139	0·16	35	0·360	0·460	0·480	0·545	0·782	0·75	0·660
5.	Glass beads–CO_2 [41]	1·09	0·016	0·17	40	0·234	0·130	0·080	0·159	1·800	2·93	1·470
6.	Quartz sand–air T = 300°K	1·37	0·026	0·78	35·4	0·440	0·400	0·148	0·299	1·100	3·18	1·570
7.	Quartz sand–air T = 300°K	1·37	0·026	0·435	37·7	0·415	0·400	0·138	0·266	1·035	3	1·560
8.	Quartz sand–air T = 300°K	1·37	0·026	0·150	47	0·370	0·370	0·105	0·179	1·000	3·53	2·060
9.	Quartz sand–helium T = 100°K	20·65	0·070	0·435	38	0·303	0·294	0·247	0·290	1·030	1·23	1·045
10.	Plexiglass beads–air T = 300°K	0·19	0·026	0·050	40	0·095	0·090	0·079	0·093	1·050	1·2	1·025
11.	Plexiglass beads–He T = 300°K	0·19	0·16	0·050	40	0·141	0·149	0·177	0·095	0·945	0·795	1·485
12.	Plexiglass beads–He T = 100°K	0·142	0·070	0·050	40	0·058	0·064	0·108	0·061	0·906	0·536	0·950
13.	Perlite–air T = 77–300°K [42]	1·28	0·02	—	98	0·0285	0·028	0·021	0·022	1·020	1·35	1·295
14.	Perlite–air T = 77–300°K [42]	1·28	0·02	—	96	0·0351	0·035	0·022	0·023	1·000	1·595	1·525
15.	Perlite–air T = 77–300°K [42]	1·28	0·02	—	92	0·0460	0·045	0·025	0·026	1·020	1·84	1·770
16.	Perlite–air T = 77–300°K [42]	1·28	0·016	0·500	95	0·0325	0·033	0·019	0·024	0·985	1·71	1·350
17.	Perlite–air T = 77–300°K [43]	1·28	0·026	0·005	95	0·0277	0·026	0·023	0·023	1·065	1·205	1·205
18.	Perlite–H_2 T = 77–300°K [34]	1·28	0·123	0·5	95	0·146	0·144	0·137	0·137	1·013	1·065	1·065
19.	Perlite–He T = 77–300°K [34]	1·28	0·105	0·5	95	0·126	0·126	0·180	1·200	1	0·106	0·105
20.	Tellurine–CO_2 [44]	1·51	0·0163	0·2	71	0·099	0·100	—		0·99	—	—
21.	Tellurine–CH_4 [44]	1·51	0·0384	0·2	71	0·0152	0·162	—	—	0·94	—	—
22.	Tellurine–gas oil [44]	1·51	0·0314	0·2	71	0·134	0·142		—	0·945	—	—

tures [21–23]. Practically no works are available on the effective thermal conductivity of porous materials in gas mixture media.

The present work studies the effective thermal conductivity of granular materials in water vapour–air mixture. Krisher and Ronalter showed in 1940 that for a gaseous mixture of water vapour and air one can use a fictitious thermal conductivity coefficient which includes the ordinary thermal conductivity coefficient plus the expression allowing for the diffusion of vapour under the action of the temperature gradient with the effect of distillation

$$\lambda = \lambda_{\mathrm{air}} + \varphi v \beta M D_{1,2}. \tag{16}$$

De Vries [24] gives the following expression for λ

$$\lambda = \lambda_{\mathrm{air}} + M D_{1,2} \frac{H}{H - p} \rho_v \frac{1}{p_{vs}} \frac{\mathrm{d}p_{vs}}{\mathrm{d}T}. \tag{17}$$

He also presents numerous values of $\varphi v \beta M D_{1,2}$ for $\varphi = 1$ together with the thermal conductivity coefficients of air and water. The effect of vapour diffusion increases with the increase in temperature.

Example. The moisture content of the quartz sand ($\rho = 1810$ kg/m^3, $L = 0{\cdot}78$ mm) $\xi = 1{\cdot}3$ per cent. The volumetric fraction of water in the sand is 2·4 per cent and that of water vapour–air mixture, 31·1 per cent. The temperature is 293°K. The thermal conductivity of crystal quartz is 15 W/m deg, the thermal conductivity λ_{ef} of the water vapour–air mixture 0·08 W/m deg [24]. The thermal conductivity of water vapour in the microgap is 0·028 W/m deg. $v' = 0{\cdot}028/15 = 0{\cdot}00186$; $v = 0{\cdot}08/15 = 0{\cdot}00533$; $h/l = 1{\cdot}75$; $h/L = 0{\cdot}637$; $k_m = 4$: $k_k = 1{\cdot}5$; $\lambda_c \approx 0$. The calculation is done by formula (3);

$$\lambda_{ef} = 0{\cdot}77 \text{ W/m deg}; \qquad \lambda_{\mathrm{exp}} = 0{\cdot}76 \text{ W/m deg}.$$

While in a large pore thermal diffusion of water vapour with the effect of distillation is important, in a microgap heat is basically transferred by the water vapour heat conduction. In [24] a method is proposed for the determination of the effective thermal conductivity of wet porous systems with high moisture content ($\xi > 2{\cdot}5$ per cent for quartz sand). This model allows calculation of porous systems with low moisture content.

Let us consider the application of the method of generalized conductivity for the determination of the effective thermal conductivity of metal powdered systems. Metal granular systems are widely used in engineering as thermal insulation at high temperatures as well as insulation which can bear high mechanical loads due to their high mechanical strength. Metal fillings are often used in atmospheres of various active and inert gases. The effective thermal conductivity of metal fillings is much less than the real conductivity of the metal of which they are made of. As to the values of the ratio λ_s/λ_g, they are 10–300 for thermally insulating materials and can be up to 1500–2000 and above for metal materials. It is natural that in many cases the thermal conductivity of such metal systems depends on the resistance of contact between the particles, conductance of the gas microgap and to a small degree, on the thermal resistance of the particles themselves. In calculations concerning metal fillings with $\lambda_s/\lambda_g > 700$–$1000$, the thermal resistance of the particles themselves can be neglected. In this case formula (3) assumes the form

$$\lambda_{ef} = \lambda_g' \frac{L}{4 k_k h_r} \left(\frac{h}{L}\right)^2 + \lambda_c + \lambda_g \left(1 - \frac{h}{L}\right)^2 + \lambda_g \frac{h}{L}. \tag{18}$$

λ_c is determined by formula (4).

All the above considerations of the modes of heat transfer in granular systems are also applicable to this case. One of the most essential factors of heat transfer in metal fillings at normal pressure of gas in the pores is the thermal conductivity of a gas microgap compared to which the thermal conductivity of gas in a pore is rather low. To determine the effective thermal conductivity of metal powders it is very important to know the particle surface purity, height of microroughness and how the particles are pressed to one another. The height of microroughness is determined by the class of the material finish or by experiment with an electron microscope.

As investigations showed, the ratio of the microroughness height to the particle diameter is rather stable. For some metal fillings it is $(2–4) . 10^{-3}$ (lead and steel particles). When calculating a number of metal fillings we take this ratio equal to $3 . 10^{-3}$ and $k_k = 1{\cdot}5$ (Table 5).

In formula (18) the factor k_k shows the mutual arrangement of microroughness of two particles in contact. In an overwhelming majority of cases k_k is 1·5–2. For glass spheres the ratio h_r/L is $(4–5) . 10^{-3}$. Optical measurements of the height h_r for spheres 2–2·5 mm in diameter gave values of $(8–10) . 10^{-3}$ mm.

In Table 4 when calculating fillings of glass balls in various gas media we took $h_r/L . 10^{-3} = 4$ at $k_k = 2$.

In this connection it is reasonable to perform regular measurements of the ratio h_r/L for the fillings of various materials and to compose tables of the ratio h_r/L for a wide class of materials. This will improve the accuracy of the calculation of the effective thermal properties of powders.

Some influence on thermal conductivity through contact in fillings is exerted by mechanical load. The dependence of $\lambda_c = f(P)$ on mechanical load can be determined by formulae (4, 5, 8). It should be pointed out that mechanical load little changes the height of microroughness within the range of elastic deformation of particles.

An experimental investigation was carried out in [11, 12] of the conductivity of contact surfaces and also of contact pairs particle-flat or convex–concave surface.

It should be noted that in a number of cases metal fillings should be calculated by formula (3) if the ratio λ_s/λ_g is within the range < 500.

As an example consider the effective thermal conductivity of steel spheres in air (experimental data are given in [35]).

Calculations are carried out using formulae (3) and (18) since in this case λ_s/λ_g is 1475.

Reference data: $L = 3{\cdot}18 . 10^{-3}$ m; $\Pi = 38$ per cent; $\lambda_s = 38{\cdot}4$; $\lambda_0 = 0{\cdot}026$; $T = 320°$K; $h/l = 1{\cdot}34$; $h/L = 0{\cdot}573$; $H = 10^5$ N/m^2; $v_g = v'_g = 0{\cdot}677 . 10^{-3}$; $k_m = 3$; $k_k = 1{\cdot}5$; $\lambda_c = 0{\cdot}03$.

According to formula (3)

$$\frac{\lambda_{ef}}{\lambda_s} = \left[\!\left[1 \Big/ \left\{\frac{1}{0{\cdot}573^2} + \left[1 \Big/ \left(\frac{0{\cdot}03}{38{\cdot}4} + \frac{0{\cdot}677 . 10^{-3} . 0{\cdot}573^2}{4.3 . 10^{-3} . 1{\cdot}5}\right)\right]\right\}\right]\!\right] + 0{\cdot}677 . 10^{-3} (1 - 0{\cdot}573)^2$$

$$+ \left[2 \Big/ \left(1 + 1{\cdot}34 + \frac{1}{0{\cdot}677 . 10^{-3} . 0{\cdot}573}\right)\right] = 13{\cdot}6 . 10^{-3}$$

$$\lambda_{ef} = \lambda_s . 13{\cdot}6 . 10^{-3} = 38{\cdot}4 . 13{\cdot}6 . 10^{-3} = 0{\cdot}523 \text{ W/m deg.}$$

According to formula (18)

$$\lambda_{ef} = 0{\cdot}026 . \frac{10^3}{4.3 . 1{\cdot}5} 0{\cdot}573^2 + 0{\cdot}03 + 0{\cdot}026(1 - 0{\cdot}573)^2 + 0{\cdot}026 . 0{\cdot}573 = 0{\cdot}524 \text{ W/m deg.}$$

The thermal conductivity λ_{ef} measured experimentally is equal to 0·525 W/m deg [37].

In this case according to formula (18) the calculations are considerably simplified.

In Table 5 the experimental values of λ_{ef} are given for a number of metal fillings in various gas media at normal pressure. The experimental data are compared with the predicted ones by formula (3) for hydrogen and by formula (18)

Table 5. Thermal conductivity of metal powders in various gas media

	Materials	λ_s	λ_g	λ_s/λ_g	Π, %	L, mm	λ_{exp}	$\lambda_{Maxwell}$	$\lambda_{Bruggeman}$	$\lambda_{(18)(3)}$	$\frac{\lambda_{exp}}{\lambda_{Maxwell}}$	$\frac{\lambda_{exp}}{\lambda_{Bruggeman}}$	$\frac{\lambda_{exp}}{\lambda_{(18)(3)}}$	References
1.	Steel–H_2	26·2	0·19	136	37	1·26	2·34	1·14	2·9	2·8	2·34	0·81	0·84	[36]
2.	Plumbum–H_2	35	0·19	184	35	0·62	2·18	1·00	2·76	2·02	2·18	0·8	1·08	[35]
3.	Steel–air	38·4	0·0263	1460	38	3·2	0·52	0·155	0·46	0·53	3·4	1·13	0·99	[37]
4.	Steel–air	45	0·0272	1650	42·3	8·0	0·52	0·138	0·34	0·49	3·8	1·5	1·05	[38]
5.	Steel–air	45	0·0272	1650	41·3	3·2	0·40	0·142	0·376	0·51	2·8	1·07	0·78	[38]
6.	Steel–air	45	0·0272	1650	40·6	3·2	0·60	0·146	0·398	0·54	4·1	1·52	1·11	[38]
7.	Steel–air	45	0·0272	1650	40·2	4·0	0·43	0·146	0·41	0·523	2·9	1·04	0·82	[38]
8.	Steel–air	45	0·0272	1650	39·4	4·8	0·51	0·151	0·435	0·52	3·4	1·16	0·98	[38]
9.	Steel–air	45	0·0272	1650	39	6·4	0·52	0·155	0·448	0·53	3·4	1·16	0·98	[38]
10.	Plumbum–air	34·3	0·029	1190	41·7	6	0·493	0·147	0·386	0·493	3·3	1·28	1·00	[39]
11.	Plumbum–air	34·3	0·0273	1260	45	8	0·356	0·126	0·292	0·44	2·8	1·21	0·81	[38]
12.	Plumbum–air	34·3	0·0273	1260	42	1·6	0·418	0·138	0·356	0·490	3·0	1·18	0·86	[38]
13.	Plumbum–air	34·3	0·0273	1260	43·3	6·4	0·404	0·134	0·336	0·473	3·0	1·23	0·86	[38]
14.	Steel–CH_4	26·5	0·038	700	38	3·18	0·655	0·205	0·61	0·73	3·2	1·07	0·90	[35]
15.	Steel–C_3H_8	38·4	0·019	2060	38	3·18	0·40	0·109	0·33	0·385	3·7	1·23	1·05	[35]
16.	Steel–CO_2	38·4	0·0157	2450	38	3·18	0·37	0·092	0·284	0·318	4·0	1·31	1·13	[35]

for other gases and also with the data by the formulae of Maxwell and Bruggeman [3].

A closer agreement is obtained by formulae (3) and (18).

In Fig. 3 the experimental and predicted [by formulae (18) and (3)] relations $\lambda_{ef} = f(H)$ are given for some metal fillings.

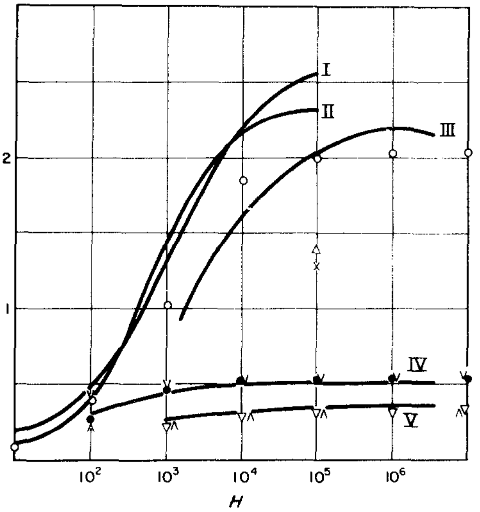

FIG. 3. λ_{ef} of metal granular materials as function of H.
△ steel balls in hydrogen [36],
× plumbum shot in hydrogen [36].
1. Plumbum shot ($L = 0{\cdot}62 \,.\, 10^{-3}$ m) in hydrogen [35]
○ calculated values.
2. Steel balls ($L = 1{\cdot}26 \,.\, 10^{-3}$ m) in hydrogen [35].
3. Steel balls ($L = 3{\cdot}18 \,.\, 10^{-3}$ m) in hydrogen [35].
4. Steel balls ($L = 3{\cdot}18 \,.\, 10^{-3}$ m) in air [35],
● calculated data according to (3),
V calculated data according to (18).
5. Steel balls ($L = 3{\cdot}18 \,.\, 10^{-3}$ m) in CO_2 [35],
▽ calculated data according to (3),
Λ calculated data according to (18).

Not only metal powders but also the powders made of metal oxides are characteristic of high values of λ_s/λ_g. In reference [48] the data are given on the effective thermal conductivity of powdered Al_2O_3, MgO, ZrO_2 oxides within a wide temperature range. In Figs. 4–6 and Table 6 the experimental data are compared with the calculated values. The calculations were carried out using formulae (3) and (18).

For the above crystal powders the ratio of the microroughness height to the characteristic particle size is $h_r/L = 4 \,.\, 10^{-3}$.

The coefficient k_k of particle arrangement was chosen equal to 1·5 as in most calculations.

It is interesting to point out that the thermal conductivities of Al_2O_3 and MgO skeletons considerably differ from that of ZrO_2 skeleton (Table 6). While for Al_2O_3 and MgO the thermal conductivities of their skeletons sharply decrease with the increase in temperature, for ZrO_2 a slight increase of λ_s with temperature is observed. However due to high thermal resistance of gas in pores the effective thermal

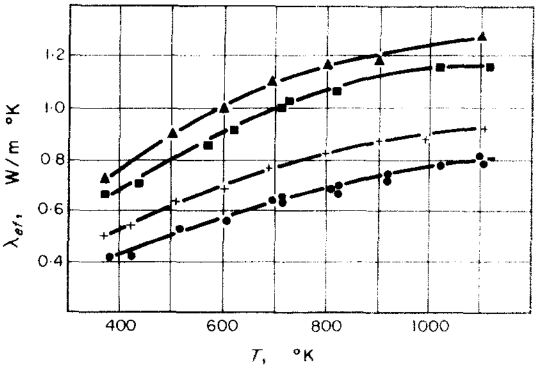

FIG. 4. Calculated effective thermal conductivity of MgO in air.
● Π = 45 per cent—experimental data [48],
+ Π = 39 per cent—experimental data [48],
■ Π = 36 per cent—experimental data [48],
▲ Π = 35 per cent—experimental data [48].

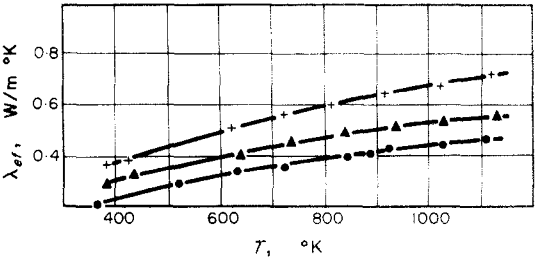

FIG. 5. Calculated effective thermal conductivity of ZrO_2 in air.
● Π = 42 per cent—experimental data [48],
▲ Π = 36 per cent—experimental data [48],
+ Π = 30 per cent—experimental data [48].

Table 6. Effective thermal conductivity of powdered MgO, ZrO$_2$ *and* Al$_2$O$_3$ *in air*, H = 10^5 N/m^2 [48]

Material	T°K	Π, %	λ_s	λ_0 air	λ_{exp}	λ_{calc}	Formula	$\frac{\lambda_{exp}}{\lambda_{calc}}$
MgO								
L = 0·268 mm	375	42	24·4	0·0318	0·433	0·425	(18)	1·02
	502·4	42	27·9	0·0387	0·502	0·515	(18)	1·03
	572·1	42	22·1	0·045	0·552	0·556	(3)	0·99
	723	42	16	0·0533	0·661	0·67	(3)	0·98
	810	42	13	0·056	0·666	0·68	(3)	0·98
ZrO$_2$								
L = 0·292 mm	343	36	2	0·03	0·291	0·31	(3)	0·94
	430	36	2	0·0348	0·339	0·336	(3)	1·01
	825·7	36	2·1	0·059	0·493	0·51	(3)	0·96
	883	36	2·1	0·0615	0·523	0·54	(3)	0·97
Al$_2$O$_3$								
L = 0·263 mm	373	42	30·2	0·0319	0·42	0·428	(18)	0·98
	573	42	22·1	0·0388	0·479	0·49	(3)	0·97
	673	42	12·8	0·0505	0·6	0·61	(3)	0·98
	873	42	9·3	0·0615	0·695	0·72	(3)	0·96

conductivity of powders increases slowly with temperature.

If, for example, at a temperature of 373°K the ratio λ_s/λ_g for MgO is 760 then at a temperature of 810°K it is 232. In the first case formula (18) can be used for the calculations, whereas in the second formula (3) must be employed.

Powdered mixtures of various materials

From the foregoing a number of conclusions can be made: At low temperatures and high vacuum the effective thermal conductivities of powdered systems depend on the thermal conductivity of the skeleton, porosity, elastic properties of the material (elasticity modulus E) and the degree of the material transparency to heat radiation, and the state of the particle surface.

If the thermal conductivity λ_s of amorphous materials is lower than that of crystal materials or metals, other conditions being equal, then the Young modulus for crystals is much higher than for amorphous bodies. With a certain ratio of crystal and amorphous powders in mixture heat insulation can be obtained whose properties will be better than heat insulating properties of the mixture components.

By mixing powders made of various materials we can obtain heat insulation with prescribed properties.

To verify this hypothesis some experiments were carried out with the mixture of plexiglass and Al$_2$O$_3$ powders.

Assume that the mixture obtained has zero porosity. Al$_2$O$_3$ particles are dispersed in a continuous plexiglass medium.

Find the effective thermal conductivity of such a system with zero porosity by the formulae of Odelevsky (19) and Maxwell (20) when $\lambda_s/\lambda_g \leqslant$ 1–200 or by Bruggeman's formula [3] when $\lambda_s/\lambda_g \geqslant 1000$.

After having determined the real porosity of the obtained mixture by formula (3) find the effective thermal conductivity of the system allowing for the porosity. In Table 7 experimental and calculated values of the effective thermal conductivity of Al$_2$O$_3$ and powdered plexiglass mixture are given.

In addition to decreasing the contact thermal conductivity, the mixing of various powders decreases the radiative heat transfer through particles. Such materials as aerogel, perlite, silica gel are known to be semi-transparent for heat radiation through the particles themselves.

The addition of fine metal powder or small crystals of metal oxides into such powders will close this window for heat radiation.

An experimental investigation has been carried out on the apparatus and by the methods described in [25]. The powders were put into a cup made of copper foil and surrounded by an adiabatic enclosure, the temperature of which within the experiment was automatically kept equal to the temperature of the lateral surface of the copper cup. Inside the cup with the radius was placed a heater of constant power in the form of a cylinder of copper foil with manganin wire 0·1 mm in diameter wound on its lateral surface. At the radii $r_1 = 0$, $r_2 = 5 . 10^{-3}$ m and $r_3 = 10 . 10^{-3}$ m temperature measurers (thermocouples and resistance thermometers or germanium diode thermometer) were placed. The calorimeter made in this way was placed in a cryostat and cooled to the temperature of liquid nitrogen and then heated by the constant power source up to the room temperature. During heating were measured the rate of temperature increase in the centre of the sample, the temperature drop in two points of the sample and, in the experiments with rarefied media, the pressure in the chamber.

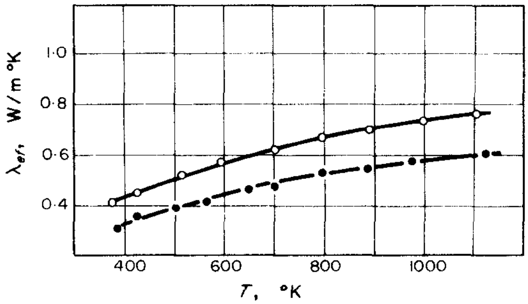

FIG. 6. Calculated effective thermal conductivity of Al_2O_3 in air.

○ = 42 per cent—experimental data [48].

● = 51 per cent—experimental data [48].

Solid porous systems

To show the applicability of the method of generalized conductivities for the investigation of the effective thermal conductivity of solid porous materials, consider chamotte ceramics as a material widely used in engineering as refractory and thermal insulation in a wide temperature range, for manufacturing ceramic filters, under the conditions of transpiration cooling, etc.

The chamotte ceramics selected as a sample for investigation had the following chemical composition (per cent by volume): SiO_2—64·5%, Al_2O_3—32·8%, Fe_2O_3—0·6%, TiO_2—1·5%, CaO—0·6%. Since the admixtures of Fe_2O_3, TiO_2 and CaO make up a negligible fraction in the volume, it appeared possible to neglect them and consider the solid basis (skeleton) of ceramics as a two-phase system consisting of silicon dioxide and aluminum oxide if we

Table 7. Effective thermal conductivity of powdered mixture of Al_2O_3 *and plexiglass in air,* $H = 10^5$ N/m^2

Material	V of plexiglas, %	V Al_2O_3, %	Π %	λ_s W/m deg	λ_{calc} W/m deg	λ_{exp} W/m deg	$\frac{\lambda_{exp}}{\lambda_{calc}}$
Powdered plexiglass L = 0·05 mm T = 300°K	100	0	40	0·192	0·085	0·089	1·05
Al_2O_3 L = 0·06 mm T = 300°K	0	100	75	32	0·165	0·171	1·03
Al_2O_3–plexiglass mixture							
T = 300°K	73	27	52	0·36	0·093	0·098	1·06
T = 273°K	73	27	52	0·481	0·104	0·109	1·05
T = 80°K	73	27	52	0·317	0·048	0·049	1·02
T = 300°K	44	56	70	7	0·13	0·13	1

assume [27] that the component greater in volume forms continuous medium in which the particles of the second, smaller in volume, phase are dispersed.

The temperature dependence of thermal conductivity of this two-phase system was determined using the relation of Odelevsky:

$$\frac{\lambda_s}{\lambda_{SiO_2}} = 1 - \frac{V_{Al_2O_3}}{\dfrac{1}{1 - \lambda_{Al_2O_3}/\lambda_{SiO_2}} - \dfrac{1 - V_{Al_2O_3}}{3}} \qquad (19)$$

obtained for the calculation of the conductivity of a matrix two-phase heterogeneous system. By "matrix" system we mean one in which one phase forms a coherent matrix with its arbitrary volumetric concentration. In the case considered SiO_2 is a matrix. To calculate the thermal conductivity coefficient of the ceramics skeleton in a wide temperature range it is necessary to know the temperature relations of the thermal conductivity coefficients of the skeleton components. The appropriate data for amorphous SiO_2 were taken from [28, 29, 30] and for crystal Al_2O_3, from [31, 32].

The results calculated by (19) completely coincide with those obtained from the Maxwell–Eucken relation

$$\frac{\lambda_s}{\lambda_{SiO_2}} = \frac{1 + 2V_{Al_2O_3}\dfrac{1 - \lambda_{SiO_2}/\lambda_{Al_2O_3}}{2\lambda_{SiO_2}/\lambda_{Al_2O_3} + 1}}{1 - V_{Al_2O_3}\dfrac{1 - \lambda_{SiO_2}/\lambda_{Al_2O_3}}{2\lambda_{SiO_2}/\lambda_{Al_2O_3} + 1}}. \qquad (20)$$

This confirms the conclusion made, in particular, in [18] about the good agreement between the results obtained when the thermal conductivity was calculated by the above formulae.

The determination of the ceramics effective thermal conductivity was the next step in the calculation. Since chamotte is a material with communicating pores, Dulnev's relation obtained for the determination of the thermal conductivity of the two-component disperse system with connecting pores was used [8]

$$\frac{\lambda_{ef}}{\lambda_s} = \left(\frac{h}{L}\right)^2 + v_g\left(1 - \frac{h}{L}\right)^2 + \frac{2v_g\dfrac{h}{L}\left(1 - \dfrac{h}{L}\right)}{1 - \dfrac{h}{L}(1 - v_g)}. \qquad (21)$$

When calculating by means of this relation it is necessary to know the porosity of the material. This was determined experimentally. A ceramic sample was weighed and then put into a vacuum chamber from which air was pumped out to a vacuum of 1 N/m^2. After the sample was kept in the rarefied medium for two days, the vessel with the sample was filled with benzine. The repeated weighing of the sample allowed the value of the open porosity to be found equal to 40 per cent.

The calculations carried out with the application of the specific weights and volumetric relations between ceramics components, showed that there is a small amount (about 5 per cent) of closed pores in the material.

The inspection of pore distribution along the radii showed that 2–5 μ is a dominating pore size of the ceramics.

As in the case of granular materials heat in pores can be transferred by the mechanism of molecular heat conduction of gas, convection and radiative heat transfer. To calculate the molecular heat conduction of gas in the pores of the material the above generalized equation (12) was used. The necessity for using this equation is explained by the fact that the studied chamotte ceramics was rather a thin-pore material in which the pore size becomes commensurable with the mean free molecular path of the gas (the value of the criterion Kn is of the order of 10^{-2}).

For the above pore sizes and small temperature gradients the effects of convective heat transfer in pores can be neglected [18].

The effect of radiation in the pores of the material was estimated by relation [18]

$$\lambda_{gr} = 2\varepsilon^2 C T^3 l. \qquad (22)$$

The calculation using this formula showed that the coefficient of radiative heat conduction in the pores over the whole temperature range is no more than 1·5 per cent of the coefficient of molecular heat conduction.

In Table 8, data are presented on the temperature dependence of the heat-conduction coefficients of the skeleton components of the ceramics; of the filling gas; the calculated values of temperature dependences for the heat-conduction coefficient of the skeleton and the effective thermal conductivity of the chamotte ceramics.

The experimental work was done by two methods. The studies over the temperature range 80 to 500°K in vacuum and in various gases (air, Freon-12, helium) at atmospheric pressure were carried out on the above installation by the method described in [25] (Figs. 7–9). The studies over the temperature range 400–1200°K in air at atmospheric pressure were carried out by the method set forth in [45].

The high-temperature installation was a furnace with silite heaters and cylindrical sample $110 \,.\, 10^{-3}$ m long and $30 \,.\, 10^{-3}$ m in diameter. The heater (a constant power source) was mounted along the axis of the sample. Under quasi-stationary heating conditions, when the ambient temperature changed at a constant rate, the thermal diffusivity coefficient of the ceramics was determined by measuring the temperature difference at two points along the cylinder radius with the help of Chromel–Alumel thermocouples with the axial heaters off, and the effective thermal conductivity, by measuring the temperature difference at the same points but with the heater being switched on and its power being registered.

Comparison of the predicted and experimental values shows their fairly good agreement. The differences are about 10 per cent. The fact that the experimental values are below the calculated ones can be explained by the presence of some closed pores in the ceramics. It should be pointed out that the greatest discrepancy between the calculated and experimental values is typically enough for Freon-12, i.e. for the gas for which the molecular free path ($\Lambda = 0{\cdot}024 \,.\, 10^{-6}$ m) is less than for air ($\Lambda = 0{\cdot}06 \,.\, 10^{-6}$ m), and less than for helium ($\Lambda = 0{\cdot}2 \,.\, 10^{-6}$ m). From [10] we can suppose for Freon-12 and to some degree for air the presence of a directed gas flow in the ceramics due to the pressure gradient arising under the influence of the temperature gradient which is the reason of the decrease in the coefficient of the effective thermal conductivity of the ceramics in the atmosphere of these gases.

In Fig. 10 plotted are the curves for the temperature dependence of the thermal conductivity coefficients of the ceramics skeleton components and the skeleton in the total, the calculated curve for the effective thermal conductivity coefficient of the ceramics in the air at atmospheric pressure and the experimental data (points).

Let us dwell upon one more essential and interesting case which follows from the inspection of relation (21). It is evident that if the value of λ_{ef} of the material is determined experimentally, for example, in the air, then, the porosity of this material being known, from relation (21) we can find the thermal conductivity of its skeleton. Therefore when λ_s and the thermal conductivity of any other gas are known, λ_{ef} in the atmosphere of this gas can be calculated by the same relation. It should be pointed out that most of the existing installation for the determination of the thermal properties of the materials in the temperature range 400–1200°K are not provided with vacuum facilities and hence cannot be used for the investigations with various gaseous media. The calculations of this kind can therefore considerably extend the studies of thermal properties of porous materials used in the atmospheres different from the air. Moreover, if in addition the temperature dependence of the heat capacity of the material or its effective thermal diffusivity coefficient in air are known, the possibility arises of calculating the thermal diffusivity of porous material in the atmosphere of various

Table 8. Predicted and experimental values of the coefficient of effective thermal conductivity of porous chamotte ceramics as a function of temperature in various gas media

T°K	$\lambda_{Al_2O_3}$	λ_{SiO_2}	λ_s	λ_{calc}	λ_{exp}	λ_0 10^3 [33]
		Helium. H = 0·993 . 10^5 N/m^2				
40	70·0	0·25	0·58	0·22	—	34
100	120·0	0·63	1·52	0·56	0·55	70
180	50·0	0·98	2·22	0·83	0·82	108
220	43·7	1·10	2·50	0·90	0·91	124
293	32·5	1·28	2·85	1·05	0·95	150
340	28·5	1·33	3·00	1·16	0·99	168
		Freon-12. H = 0·993 . 10^5 N/m^2				
300	32·5	1·28	2·85	0·90	0·81	10·8
340	28·5	1·33	3·00	0·91	0·84	12·3
		Air. H = 0·133 N/m^2				
300	32·5	1·28	2·85	0·90	0·81	
400	23·5	1·50	3·11	1·02	0·85	
		Air. H = 0·993 . 10^5 N/m^2				
100	120	0·63	1·52	0·51	0·51	9·6
180	50	0·98	2·25	0·73	0·71	16·3
220	43·7	1·10	2·50	0·81	0·80	20·4
300	32·5	1·28	2·85	0·94	0·86	26·5
400	23·6	1·53	3·24	1·07	0·96	34·0
600	14·3	1·72	3·28	1·10	1·08	46·0
800	10·0	2·05	3·46	1·17	1·13	57·4
1000	7·7	2·91	4·06	1·38	1·32	68·4
1200	6·3	4·40	4·98	1·68	1·57	77·7

gases. In other words, having found experimentally the temperature dependence of the effective thermal conductivity coefficients and the coefficients of thermal diffusivity (or heat capacity) in air knowing porosity of the material we can calculate the temperature dependence of λ_{ef} and a_{ef} in another gas.

CONCLUSIONS

1. A method is developed for the calculation of the effective thermal conductivity of porous materials which allows inspection of the effects of temperature, porosity, material skeleton thermal conductivity, thermal conductivity of the gas in the pores, pore size, mechanical load

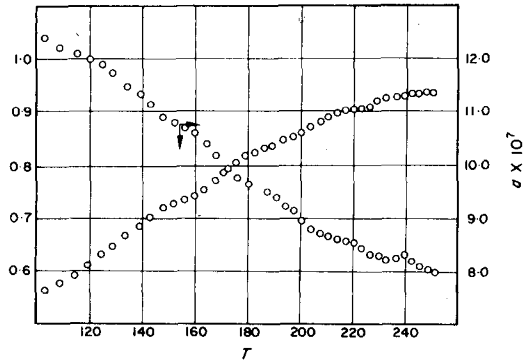

FIG. 7. λ_{ef} and a_{ef} of chamotte ceramics (Π = 40 per cent), in helium at H = 10^5 N/m^2. The authors' experimental data.

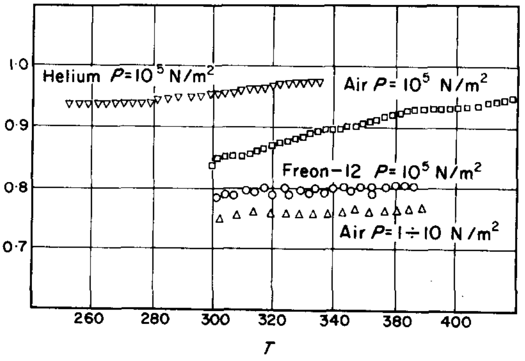

FIG. 8. λ_{ef} of chamotte ceramics (Π = 40 per cent) in various gas media. The authors' experimental data.

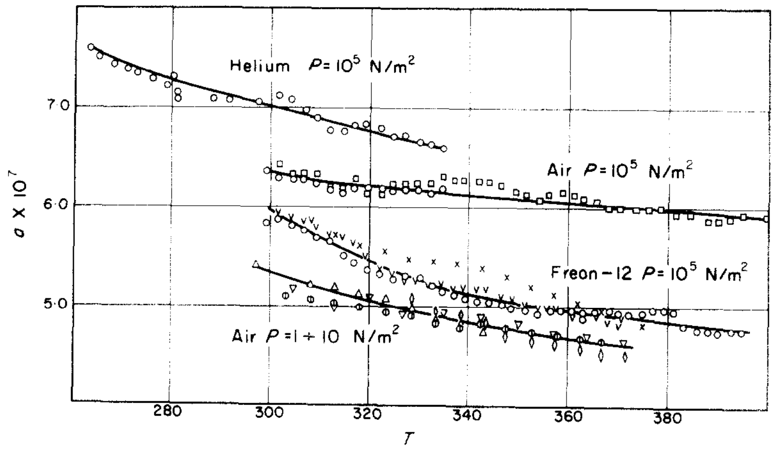

FIG. 9. a_{ef} of chamotte ceramics (Π = 40 per cent) in various gas media. The authors' experimental data.

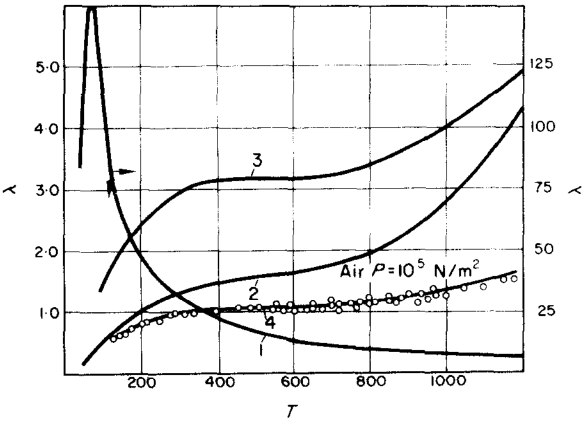

FIG. 10. Thermal conductivity of chamotte ceramics and its components:

1—$\lambda_{Al_2O_3}$; 2—λ_{SiO_2}; 3—λ_s; 4—calculated values; ○—experimental data.

on porous material, radiation and optical and surface properties of the material particles upon the effective thermal conductivity.

2. A method is developed for the calculation of the effective thermal conductivity of mixtures of powdered and solid porous materials. It is shown that with a certain relation λ_s/λ_g the effective thermal conductivity of a mixture *in vacuo* can be less than the effective thermal conductivity of its components under the same conditions.

3. On the basis of the studies carried out some recommendations can be given for the synthesis of porous systems with the required effective thermal conductivity within a wide temperature range.

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Abstract—Predicted formulae are given for the determination of the effective thermal conductivity of powdered and solid porous materials in a wide temperature range and various gas media. The calculated values of the effective thermal conductivities of about 100 various materials are compared with the experimental values of different authors including the authors of the paper. The methods for calculating the effective thermal conductivity of powdered mixtures, in particular of Al_2O_3 and powdered plexiglass mixture, are set forth. It is shown that mixing different powdered materials can change the effective thermal conductivity of fillings over wide ranges for various gases. This is mostly essential for powdered materials at low temperatures when thermal conductivity of particles becomes close to that of gases in the pores. This also refers to contact thermal conductivity of vacuum-powder thermal insulation at low temperatures where the contact thermal conductivity on external mechanical load, the elasticity of the material and the state of the material surface, appear as a dominating factor.

Experimental and calculated data on thermal properties of solid porous systems (chamotte ceramics) are given for a wide temperature range and various gas media.

Résumé—On donne des formules calculées pour déterminer la conductivité thermique effective de matériaux poreux en poudre et consolidés dans une gamme étendue de températures et avec différentes milieux gazeux. Les valeurs calculées des conductivités thermiques effectives d'environ 100 matériaux différents sont comparées avec les valeurs expérimentales obtenues par plusieurs auteurs dont ceux de l'article actuel. On a établi des méthodes de calcul de la conductivité thermique effective de mélanges de poudres, en particulier d'un mélange de Al_2O_3 et de plexiglas en poudre. On montre qu'en mélangeant différents matériaux en poudre, la conductivité thermique effective de remplissages peut changer dans des conditions très variables et avec différents gaz. Ceci est surtout essentiel pour des matériaux en poudre à de basses températures lorsque la conductivité thermique des particules devient voisine de celle des gaz dans les pores. Ceci a trait également à la conductivité thermique de contact de poudres dans lesquelles on a fait le vide pour l'isolement thermique aux basses températures lorsqu'il y a prédominance de la conductibilité thermique de contact dépendant de la charge mécanique exterieure, de l'élasticité du matériau et de son état de surface.

Les résultats expérimentaux et calculés pour les propriétés thermiques de systèmes poreux consolidés (céramique en chamotte) sont donnés dans une gamme étendue de températures et pour différents milieux gazeux.

Zusammenfassung—Zur Bestimmung der effektiven Wärmeleitfähigkeit von pulverförmigen und festen porösen Materialien wurden für einen grossen Temperaturbereich und für verschiedene Grössen Gleichungen aufgestellt. Die berechneten Werte der effektiven Wärmeleitfähigkeit von etwa 100 verschiedenen Materialien wurden mit Versuchswerten verschiedener Autoren, einschliesslich jener der vorliegenden Arbeit verglichen. Die Methoden zur Berechnung der effektiven Wärmeleitfähigkeit von pulverförmigen Gemischen insbesonders von Al_2O_3 und einer pulverisierten Plexiglasmischung sind dargelegt. Es wird gezeigt, dass die Mischung verschiedener pulverisierter Materialien die effektive Wärmeleitfähigkeit von Füllungen für verschiedene Gase in einem weiten Bereich ändern kann. Das ist vor allem für pulverförmige Materialien bei tiefen Temperaturen wichtig, wenn die Wärmeleitfähigkeit der Teilchen jener des Gases in den Poren nahekommt. Das gilt aber auch für den Kontaktwiderstand von Vakuumpulver-Isolierungen bei tiefen Temperaturen, wobei der Kontaktwiderstand von der äusseren, mechanischen Belastung, der Materialelastizität und dem Oberflächenzustand des Materials abzuhängen scheint.

Durch Versuche gefundene und berechnete Werte für die thermischen Eigenschaften von festen porösen Systemen (Schamottekeramik) sind für einen weiten Temperaturbereich und verschiedene Gase angegeben.