THERMAL CONDUCTIVITY OF HOMOGENEOUS MIXTURES

V. I. Loginov and V. G. Kucherov

UDC 536.223

The special and reference literature contains dozens of formulas for calculating the thermal conductivity of mixtures from data on their components. Among them are empirical correlations chosen for specific classes of mixtures and theoretical relations obtained with the use of fairly broad assumptions. Due to their construction, the latter should offer more possibilities for approximation. Which of these formulas should be given preference for calculating the properties of mixtures that have not yet been studied or have been examined only with a narrow compositional range? There is still no satisfactory answer to this question. There are also no quidelines that, if not permitting selection of the best theoretical relation, at least help compare the many variants that have been proposed.

The goal of the present investigation is to establish the general conditions that should be satisfied by formulas used to calculate the thermal conductivity of homogeneous mixtures within a broad range of compositions. We also want to construct a parametric class of functions for correlations between the thermal conductivities of homogeneous binary and multicomponent mixtures and their compositions. The theoretical results are substantiated by experimental data.

Two-Component Mixtures. We will consider a mixture homogeneous if its thermal conductivity for any fixed composition is independent of the method by which the mixture is obtained, i.e., whether the first component is added to the second or vice versa, whether or not two identical two-component mixtures are prepared from different batches of the same components, etc. All of the subsequent arguments will pertain only to such mixtures.

Let λ_Σ, λ_1, λ_2 be the thermal conductivities of a two-component mixture and its components. The fractional concentration of the components will be designated as φ_1 and φ_2. It is unimportant for the sake of subsequent discussion whether these concentrations are determined in the form of volume, mass, or mole fractions. It is important only that they satisfy the equality $\varphi_1 + \varphi_2 = 1$. We write the sought relation in the form of the system

$$\lambda_\Sigma = F(\lambda_1, \lambda_2, \varphi_1, \varphi_2),\ \varphi_1 + \varphi_2 = 1. \tag{1}$$

In order to determine the general properties that must be satisfied by the function F and its derivatives, we will assume that it is completely dependent on the above variables and is a physical relation which can be studied by dimensional analysis [1]. It follows from this assumption that the function F cannot include dimensional coefficients. Despite the obviousness of this condition, it is violated fairly often when the function F is found on the basis of approximation of empirical data. An example of this is the George–Kouts theoretical formula [2], the exponents of which contain two dimensional constants.

We will henceforth assume that the structure of Eq. (1) depends not only on the list of variables, but also on the order in which they are listed. In accordance with this, writing $F(\lambda_2, \lambda_1, \varphi_2, \varphi_1)$ means that this function is obtained from the original function $F(\lambda_1, \lambda_2, \varphi_1, \varphi_2)$ by permutation of the variables λ_1 and λ_2 in the latter. If such a permutation leaves the function unchanged, that indicates that the function has the property of evenness relative to the given permutation. If the permutation changes the sign of the function, then the latter will be considered odd in relation to this permutation.

To establish whether a function F is even or odd, we state the following obvious hypothesis: a sought function of the form (1) must not depend on the order of enumeration of the components of the mixture. Thus, Eq. (1) should remain valid with a relabeling of the components. This in turn means that the function F will be even relative to a simultaneous permutation of its variables λ_1, λ_2 and φ_1, φ_2. In other words, the function F should satisfy the equality

$$F(\lambda_1, \lambda_2, \varphi_1, \varphi_2) = F(\lambda_2, \lambda_1, \varphi_2, \varphi_1). \tag{2}$$

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 3, pp. 120-125, May-June, 1991. Original article submitted January 9, 1990.

Since the structure of F is independent of the relative magnitudes of the quantities λ_1 and λ_2, then (1) will also be valid for $\lambda_1 = \lambda_2 = \lambda$. Physically, this can be likened to a situation in which the resulting mixture is prepared from two parts of the same substance. To distinguish between these parts, let us suppose that they are marked with an inert dye. For this mixture, naturally, the value of λ_Σ will be independent of the ratio of the components. This is equivalent to satisfaction of the equality

$$\lambda = F(\lambda, \lambda, \varphi_1, \varphi_2). \tag{3}$$

Along with the properties noted above, the function F should satisfy the following obvious equalities. These equalities can be regarded as limit properties of the function as φ_1 (or φ_2) approaches zero or unity:

$$\lambda_1 = F(\lambda_1, \lambda_2, 1, 0), \; \lambda_2 = F(\lambda_1, \lambda_2, 0, 1). \tag{4}$$

We begin our study of the properties of an arbitrary function F as follows. Let $\lambda_1 < \lambda_2$ and the function F change monotonically with a change in the variable φ_2. Then for any component ratio an increase in the fraction of the second component will lead to an increase in λ_Σ. If $\lambda_1 > \lambda_2$, then an increase in φ_2 will lead to a decrease in λ_Σ. In mathematical form, this fact can be represented in the form of the following inequalities

$$\frac{\partial}{\partial\varphi_2} F(\lambda_1, \lambda_2, \; 1-\varphi_2, \varphi_2) \begin{cases} >0 & \text{at} \quad \lambda_1 < \lambda_2, \\ =0 & \text{at} \quad \lambda_1 = \lambda_2, \\ <0 & \text{at} \quad \lambda_1 > \lambda_2 \end{cases} \tag{5}$$

or

$$\frac{\partial}{\partial\varphi_1} F(\lambda_1, \lambda_2, \; \varphi_1, 1-\varphi_1) \begin{cases} >0 & \text{at} \quad \lambda_1 < \lambda_2, \\ =0 & \text{at} \quad \lambda_1 = \lambda_2, \\ <0 & \text{at} \quad \lambda_1 > \lambda_2. \end{cases}$$

If the function F is not monotonic over the entire range of φ_2 (or φ_1), then it can be stated that (5) will always be valid in the neighborhood of the point $\varphi_2 = 0$ (or $\varphi_1 = 0$).

For monotonically increasing (decreasing) functions, it follows from inequalities (5) that the derivative of F will always contain a multiplier which depends only on λ_1 and λ_2. The sign of this multiplier will be determined by the relative magnitude of these quantities, in accordance with (5). Since φ_1 is expressed through φ_2 and vice versa, one of these variables can always be eliminated from the above relations. Making such an elimination and introducing new functional relations, we rewrite Eq. (1) in the form $\lambda_\Sigma = F(\lambda_1, \lambda_2, 1-\varphi_2, \varphi_2) \equiv F_1(\lambda_1, \lambda_2, \varphi_2)$ or $\lambda_\Sigma = F(\lambda_1, \lambda_2, \varphi_1, 1-\varphi_1) \equiv F_2(\lambda_1, \lambda_2, \varphi_1)$. The functions F_1 and F_2 must satisfy the equalities $F_1(\lambda_1, \lambda_2, 1-\varphi_1) = F_2(\lambda_1, \lambda_2, \varphi_1)$, $F_1(\lambda_1, \lambda_2, \varphi_2) = F_2(\lambda_1, \lambda_2, 1-\varphi_2)$. The property of evenness F, written in the form (2), will for F_1 and F_2 correspond to the equalities $F_1(\lambda_1, \lambda_2, \varphi_2) = F_1(\lambda_2, \lambda_1, 1-\varphi_2)$, $F_2(\lambda_1, \lambda_2, \varphi_1) = F_2(\lambda_2, \lambda_1, 1-\varphi_1)$.

The condition of the independence of λ_Σ of the ratio of the components when $\lambda_1 = \lambda_2 = \lambda$, expressed by (3), will for F_1 and F_2 have the form $\lambda = F_1(\lambda, \lambda, \varphi_2) = F_2(\lambda, \lambda, \varphi_1)$. The limit properties (4) of the function F will be found from the following expressions for F_1 and F_2

$$\lambda_1 = F_1(\lambda_1, \lambda_2, 0) = F_2(\lambda_1, \lambda_2, 1), \;\; \lambda_2 = F_1(\lambda_1, \lambda_2, 1) = F_2(\lambda_1, \lambda_2, 0). \tag{6}$$

We checked the 26 formulas encountered most often in the literature for calculating the thermal conductivities of homogeneous mixtures. All of them satisfy limit properties (4) and five of them satisfy parity property (2), but only the following three satisfy property (5):

$$\lambda_\Sigma = \lambda_1^{\varphi_1} + \lambda_2^{\varphi_2},$$

$$\lambda_\Sigma = \left[\lambda_1\lambda_2 \frac{\varphi_1\lambda_1 + \varphi_2\lambda_2}{\varphi_1\lambda_2 + \varphi_2\lambda_1}\right]^{1/2}, \quad \lambda_\Sigma = \left[\varphi_1\lambda_1^r + \varphi_2\lambda_2^r\right]^{1/r} \tag{7}$$

(r is a coefficient). The first two formulas were proposed by Lichtenecker [3], while the third was proposed by Vredeveld [2]. It is usually referred to as the generalized additivity formula. Which of these formulas should be given preference in evaluating the thermal conductivity of a new mixture? How should they be modified so as to construct new correlations?

To answer these questions, let us return to Eq. (1) and analyze the dimensionality of the sought relation. Assuming that it is differentiable, it can be written in differential as well as integral form. In this case, the constants λ_1 and λ_2, entering explicitly into integral relation (1), can be present only in the boundary conditions of the differential equation. They can enter the equation itself only as a ratio corresponding to a dimensionless constant. Taking all this into account, we write the differential form of the sought relation as*

$$\Phi(\partial\lambda_\Sigma/\partial\varphi_2,\ \lambda_\Sigma,\ \varphi_2,\ \lambda_2/\lambda_1) = 0,\ \lambda_\Sigma(0) = \lambda_1,\ \lambda_\Sigma(1) = \lambda_2. \tag{8}$$

Changing over in Eq. (8) to dimensionless variables (of which there will be three: $\dot{\lambda}_\Sigma/\lambda_\Sigma$, φ_2, and λ_2/λ_1) and solving it for the first of them, we write the result in the form of the differential equation

$$\frac{1}{\lambda_\Sigma}\frac{\partial\lambda_\Sigma}{\partial\varphi_2} = f\left(\frac{\lambda_2}{\lambda_1},\ \varphi_2\right),\quad \lambda_\Sigma(0) = \lambda_1,\quad \lambda_\Sigma(1) = \lambda_2,$$

Solving this equation with the initial condition $\lambda_\Sigma(0) = \lambda_1$ and using the equality $\lambda_\Sigma(1) = \lambda_2$, to normalize the function $f(\lambda_1/\lambda_2,\ \varphi_2)$ we obtain

$$\frac{\lambda_\Sigma}{\lambda_1} = \exp\left\{\int_0^{\varphi_2} f\left(\frac{\lambda_2}{\lambda_1},\ \varphi_2\right) d\varphi_2\right\},\quad \int_0^1 f\left(\frac{\lambda_2}{\lambda_1},\ \varphi_2\right) d\varphi_2 = \ln\frac{\lambda_2}{\lambda_1}. \tag{9}$$

In order to parameterize the function f, we expand it into a series in a certain system of functions $\psi_i(\varphi_2)$ which are orthogonal on the interval [0, 1]. We thus obtain

$$f\left(\frac{\lambda_2}{\lambda_1},\ \varphi_2\right) = \alpha_0\left[1 + \sum_{i=1}^{n}\alpha_i\psi_i(\varphi_2)\right],\quad \alpha_0 = \ln\frac{\lambda_2}{\lambda_1},\quad \psi_0(\varphi_2) = 1. \tag{10}$$

In the general case, the coefficients α_i are functions of the ratio λ_2/λ_1 such that parity property (2) is satisfied when (10) is substituted into (9). Since we are examining the construction of approximating relations for specific mixtures, we will henceforth assume that the coefficients α_i are constants determined experimentally.

With allowance for (10), we reduce sought relation (9) to the form

$$\frac{\lambda_\Sigma}{\lambda_1} = \left(\frac{\lambda_2}{\lambda_1}\right)^{\varphi_2 + \sum\limits_{i=1}^{n}\alpha_i I_i(\varphi_2)},\quad I_i(\varphi_2) = \int_0^{\varphi_2}\psi_i(\varphi)\, d\varphi. \tag{11}$$

It is evident from this that at n = 0 the relation just obtained coincides with the first formula of (7). As the functions $\psi_i(\varphi)$, it is convenient to use polynomial functions that are orthogonal on the interval [0, 1]. Considering that $\psi_0(\varphi) = 1$, we write two such functions in the following form†

$$\psi_1(\varphi) = 1 - 2\varphi,\ \psi_2(\varphi) = 1 - 6\varphi + 6\varphi^2. \tag{12}$$

If necessary, subsequent polynomials can be constructed on the basis of established orthogonalization methods [4]. However, we were not able to find experimental data which – with allowance for its accuracy – would have required the use of approximation (11) with $n \geq 2$.

---

*If we take φ_2 instead of φ_1, then as the boundary conditions we need to use $\lambda_\Sigma(0) = \lambda_2$, $\lambda_\Sigma(1) = \lambda_1$ [see (6)].

†The functions $\psi_i(\varphi)$ cannot be normalized in this case because they are multiplied by unknown coefficients α_i.

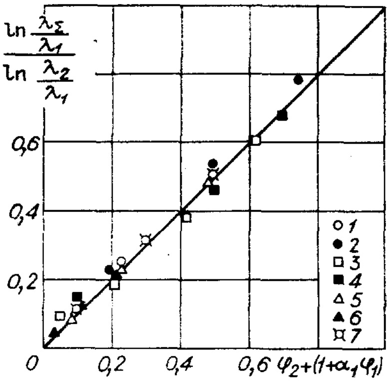

Fig. 1

TABLE 1

Type of mixture and its components	λ_1	λ_2	φ_2	α_1	δ, %
	W/(m·K)				
Normal organic liquids: cyclohexane–benzene [5]	0,218	0,145	0—1	0	1,6
Associated organic liquids: methyl alcohol–butyl alcohol [5]	0,200	0,151	0—1	0	0,9
Aqueous alcohol solutions: ethyl alcohol–water [6]	0,167	0,603	0—1	0 0,3	13,5 3,4
Inorganic liquids with water: orthophosphoric acid–water [7]	0,442	0,603	0—1	0 —1,07	6,8 2,0
Straight emulsions: coolant "Ukrinol-1" in water [8]	0,160	0,603	0—0,3	0	1,3
Reverse emulsions: emulsion of water in oil from the Karatyubinsk deposit [9]	0,603	0,147	0—0,5	0	1,2

The integrals in (11) corresponding to functions (12) can be written either as functions just of concentration φ_2 or in the form of mixed functions of φ_1 and φ_2. For practical calculations, the latter functions are more convenient:

$$I_1=\varphi_2-\varphi_2^2=\varphi_1\varphi_2,\quad I_2=\varphi_2-3\varphi_2^2+2\varphi_2^3=\varphi_1\varphi_2(\varphi_1-\varphi_2),\quad \varphi_1+\varphi_2=1.$$

We used 20 different mixtures to check the expediency of using the above class of parametric relations to construct theoretical formulas. The experimental data on the parameters of the mixtures was taken from different literature sources. The most characteristic of these results are shown in Table 1 and Fig. 1 (points 1 for cyclohexane–benzene [5]; 2 – methyl alcohol–butyl alcohol [5]; 3 – ethyl alcohol–water [6]; 4 – glycerin–water [6]; 5 – orthophosphoric acid–water [7]; 6 – coolant "Ukrinol-1" in water [8]; 7 – emulsion of water in oil from the Karatyubinsk deposit [9]). In Table 1, δ represents the relative error between the experimental data and approximate relation (11).

The unknown coefficients α_1 and α_2 were determined by the least squares method. If only one coefficient α_1 was found, it was calculated from the formula

$$\alpha_1=\frac{b_1}{a_{11}},\quad b_1=\sum_{j=1}^{k}y^{(j)}I_1(\varphi_2^{(j)}),$$

$$a_{11}=\sum_{j=1}^{k}I_1^2(\varphi_2^{(j)}),\quad y^{(j)}=\frac{\ln\frac{\lambda_\Sigma^{(j)}}{\lambda_1}}{\ln\frac{\lambda_2}{\lambda_1}}-\varphi_2^{(j)}.$$

Here, the superscript j determines the serial number of the experimental point, characterized by the coordinates $\lambda_\Sigma^{(j)}$ and $\varphi_2^{(j)}$. In the case of the determination of two coefficients α_1

TABLE 2

α_1	α_2	β_1	β_2	δ, %
0	0	0	0	4,6
0	0	−0,093	0	2,3

and α_2, they are calculated from the formulas

$$\alpha_1 = \frac{b_1 a_{22} - b_2 a_{12}}{\Delta}, \quad \alpha_2 = \frac{a_{11} b_2 - a_{12} b_1}{\Delta},$$

$$\Delta = a_{11} a_{22} - a_{22}^2, \quad b_2 = \sum_{j=1}^{k} y^{(j)} I_2\left(\varphi_2^{(j)}\right),$$

$$a_{12} = \sum_{j=1}^{k} I_1\left(\varphi_2^{(j)}\right) I_2\left(\varphi_2^{(j)}\right),$$

$$a_{22} = \sum_{j=1}^{k} I_2^2\left(\varphi_2^{(j)}\right).$$

An analysis of the results of the calculations shows that the use of just one term of the series in the exponent of the right side of (11) (the Lichtenecker formula) makes it possible to obtain satisfactorily accurate results only for straight and reverse emulsions and mixtures in which the components have similar thermal conductivities. We should also point out that the sign of the coefficient α_1 is different for different mixtures – which means that a correction for the sign should be introduced into the Lichtenecker formula.

Multicomponent Mixtures. To examine the procedure for the construction of approximate relations for the thermal conductivities of homogeneous multicomponent mixtures, we will use the example of a three-component mixture with the component concentrations φ_{13}, φ_{23}, φ_{33} and the corresponding thermal conductivities λ_1, λ_2, λ_3. The second digit of the subscript denotes the quantity of the given component in the mixture. If the components φ_{13} and φ_{23} (in the general case, any two components) are hypothetically combined into one component, then the mixture can be regarded as a two-component mixture with the component concentrations $(\varphi_{13} + \varphi_{23})$, φ_{33} and the corresponding thermal conductivities λ_1^* and λ_3. We calculate λ_1^* from Eq. (11) with the condition that

$$\lambda_1^* = \lambda_\Sigma, \ \lambda_1 = \lambda_1, \ \lambda_2 = \lambda_2, \ \varphi_1 = \varphi_{13}/(\varphi_{13} + \varphi_{23}), \ \varphi_2 = \varphi_{23}/(\varphi_{13} + \varphi_{23}).$$

We also obtain the desired result from (11) by assuming that in this equation

$$\lambda_1 = \lambda_1^*, \ \lambda_2 = \lambda_3, \ \varphi_1 = \varphi_{13} + \varphi_{23}, \ \varphi_2 = \varphi_3.$$

The result of using the above-described procedure to construct an approximate relation for a homogeneous three-component mixture can be formally written in the form

$$\frac{\lambda_\Sigma}{\lambda_1} = \left(\frac{\lambda_2}{\lambda_1}\right)^{\eta_1(1-\eta_2)} \left(\frac{\lambda_3}{\lambda_1}\right)^{\eta_2}, \quad \eta_1 = \frac{\varphi_{23}}{\varphi_{13} + \varphi_{23}} + \frac{\varphi_{13}\varphi_{23}}{(\varphi_{13} + \varphi_{23})^2}\left(\alpha_1 + \alpha_2 \frac{\varphi_{13} - \varphi_{23}}{\varphi_{13} + \varphi_{23}}\right),$$
$$\eta_2 = \varphi_{33} + (\varphi_{13} + \varphi_{23})\varphi_{33}[\beta_1 + \beta_2(\varphi_{13} + \varphi_{23} + \varphi_{33})]. \tag{13}$$

The coefficients α_1, α_2 and β_1, β_2 are determined from the approximation of the thermal conductivities of binary mixtures of components with the thermal conductivities λ_1, λ_2 and λ_1^*, λ_3, respectively.

As an example, we calculated the approximate relation for the thermal conductivity of a ternary mixture of isopropyl alcohol, isobutyl alcohol, and water. The calculations were based on the data in [10]. The concentrations of the initial components were changed within the ranges (0-0.46), (0-0.43), (0-0.64), respectively, while the thermal conductivities of these components were equal to $\lambda_1 = 0.140$, $\lambda_2 = 0.153$, $\lambda_3 = 0.613$. Table 2 shows theoretical values of α_1, α_2, β_1, β_2 found from Eq. (13) and the corresponding maximum errors of the approximation δ.

The case when $\alpha_1 = \alpha_2 = \beta_1 = \beta_2 = 0$ corresponds to approximation of the binary intermediate components on the basis of the Lichtenecker formula (7).

LITERATURE CITED

1. G. Hantley, Dimensional Analysis [Russian translation], Mir, Moscow (1970).
2. R. Read, J. Prausnitz, and T. Sherwood, Properties of Liquids and Gases [Russian translation], Khimiya, Leningrad (1982).
3. K. Lichtenecker, "Zur Wider standsberechung mischkristallfreie Legierungen," Phys. Z., 10, No. 25 (1909); No. 22 (1929).
4. G. A. Korn and T. M. Korn, Handbook for Scientists and Engineers, 2nd ed., McGraw-Hill, New York (1968).
5. G. Kh. Mukhamedzanov and A. G. Usmanov, Thermal Conductivity of Organic Liquids [in Russian], Khimiya, Leningrad (1971).
6. G. N. Dul'nev and Yu. P. Zarichnyak, Thermal Conductivity of Mixtures and Composite Materials [in Russian], Énergiya, Leningrad (1974).
7. A. Misnar, Thermal Conductivity of Solids, Liquids, and Gases and Their Mixtures [Russian translation], Mir, Moscow (1968).
8. G. I. Cherednichenko, G.-B. Froishteter, and P. M. Stupak, Physicochemical and Thermophysical Properties of Lubricants [in Russian], Khimiya, Leningrad (1986).
9. V. G. Kucherov, Thermophysical Properties of Water-Oil Emulsions and a Method of Calculating Them for Oil Recovery and Refining Conditions. Engineering Sciences Candidate Dissertation [in Russian], Moscow (1987).
10. Yu. L. Rastorguev and Yu. A. Ganiev, "Thermal conductivity of liquid solutions," Inzh.-fiz. Zh., 14, No. 4 (1968).

DYNAMIC CONTACT PROBLEM FOR A TWO-LAYER HALF-SPACE WITH A SPHERICAL CAVITY

A. A. Lyapin, A. N. Rumyantsev, and M. G. Seleznev

UDC 539.3:534.1

This article examines the problem of exciting steady harmonic vibrations in an elastic two-layer half-space with a spherical cavity. The vibrations are excited by impact of a rigid die against the plane surface. The deformation of the medium is presumed to be axisymmetric. The boundary-value problem is solved in two steps. In the first step, we study the problem of the excitation of steady harmonic vibrations in an elastic two-layer half-space with a deep-set spherical cavity. Here, the vibrations are excited by a weightless rigid circular die with a flat base. With allowance for the radiation conditions, the boundary-value problem is reduced to a system of integrodifferential equations. These equations are studied by asymptotic methods and the method of approximate factorization of matrix functions. With the assumption that the amplitude of the load acting on the die is constant, we find the distribution law for the contact stresses and the amplitude—frequency characteristics of points of the base of the die. In the second step, we consider the effect of the mass of the die by examining the equation of its motion as a rigid mass under the influence of an assigned external load and the reaction of its complex elastic base. The reaction of the base is found from the first step for the given frequency range.

Results are presented from study of the basic laws governing the behavior of the amplitude—frequency characteristics in relation to the mass of the die and the location of the cavity in the medium for different ratios of the stiffnesses of the layer and the half-space.

Rostov-on-Don. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 3, pp. 125-129, May-June, 1991. Original article submitted September 21, 1989; revision submitted January 26, 1990.

0021-8944/91/3203-0418$12.50