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CALCULATION OF THERMAL CONDUCTIVITIES OF TERNARY GAS MIXTURES

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A semi-empirical method is suggested for calculating the thermal conductivity of a gas mixture by using the first-order Padé approximant. Examples are provided to show high accuracy of the method and the adequacy of fitting parameters that are determined from experimental data in a wide temperature range. The possibility of using the thermal conductivities of the binary gas mixtures constituting the ternary mixture is investigated.

Introduction. The requirements of intensification and control of technological processes demand reliable transfer coefficients. At present reliable data on transfer coefficients in gas mixtures can be obtained mainly from specialized thermophysical experiments. Available calculation methods based both on rigorous relations of the kinetic theory of gases [1] and on semi-empirical relations [2-4] often fail to provide the accuracy required in practice. An experimental study of transport properties of gaseous mixtures is expensive and requires much time since these properties, as a rule, must be known in a rather wide range of parameters (composition and temperature). As our experience shows, it is difficult to find data on transfer coefficients of a particular ternary mixture because of the large number of available mixtures. This requires derivation of new semi-empirical relations for determining with an accuracy approaching the experimental one transfer coefficients of gaseous mixtures that take into account, as much as possible, a priori information on mixture composition and the transfer coefficients of the components.

We suggest a semi-empirical formula for calculation of transfer coefficients that is based on unique properties of Padé approximants and whose accuracy is close to the experimental one. Unlike conventional calculation schemes, the suggested formula may be used for a minimum number (no more than two) of experimental values of the transfer coefficients of a considered mixture obtained at different concentrations of its components. This allows not only substantial improvement in the accuracy of the values obtained but also considerable reduction in the volume of experimental investigations on transfer coefficients of gaseous mixtures. It is pertinent to note that this method has been successfully employed to describe the concentration dependence of viscosity coefficients and thermal conductivities of binary gas mixtures in a sufficiently wide temperature range [5].

Mathematical Model. We shall assume that the transfer coefficient of a ternary mixture at temperature T is completely specified by the expression

$$\lambda = F_1 (\lambda_i, x, y), \tag{1}$$

where λ_i is the transfer coefficient of the i-th gas constituting a gaseous mixture; F_1 is an unknown function that we seek to determine from a priori and experimental information; x, y, and z are the numerical molecular concentrations of the first, second, and third gas constituting a ternary mixture, respectively. Since the condition

$$x + y + z = 1,$$

is fulfilled, the variable z does not enter the arguments in the right-hand side of (1). Proceeding from dimensional theory [6] we may reduce expression (1) to the form

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$$\lambda(x, y) = \lambda_3 F_2(\lambda_1/\lambda_3, \lambda_2/\lambda_3, x, y), \tag{2}$$

where F_2 is a dimensionless function of its dimensionless arguments. Representing the dependence of F_2 on its arguments in the form of a [1/1] Padé approximant in x and y [7], we arrive at the following expression:

$$\lambda(x, y) = \lambda_3 \frac{A_0 + A_1 x + A_2 y}{1 + B_1 x + B_2 y}. \tag{3}$$

To determine the unknown coefficients A_1, A_2, A_3, B_1, and B_2, we use natural conditions, namely:

at $x = 1$

$$\lambda(1, 0) = \lambda_1; \tag{4}$$

at $y = 1$

$$\lambda(0, 1) = \lambda_2 \tag{5}$$

and, finally, at $x = y = 0$

$$\lambda(0, 0) = \lambda_3. \tag{6}$$

From conditions (4)-(6) it follows that

$$A_0 = 1, \quad A_1 = \lambda_1/\lambda_3 (1 + B_1) - 1, \quad A_2 = \lambda_2/\lambda_3 (1 + B_2) - 1. \tag{7}$$

We now may write expression (3) with account for (7) as

$$\lambda(x, y) = \lambda_3 \frac{(1 - x - y) + \lambda_1/\lambda_3 (1 + B_1) x + \lambda_2/\lambda_3 (1 + B_2) y}{1 + B_1 x + B_2 y}. \tag{8}$$

To determine B_1 and B_2, we need, as was mentioned in the introduction, additional information. Let two experimental values of the transfer coefficient λ^* and λ^{**} obtained for different compositions of a ternary mixture be available. Then successive substitution of these data into (8) yields a linear system of two equations for B_1 and B_2. Solving it, we easily determine these parameters. As is shown in [5], we need only one experimental transfer coefficient for a binary mixture. In the case of a large number of experimental values, the least-squares method may be used in view of the linearity of the system of equations.

We shall illustrate the suggested method by calculating the thermal conductivities of He-Ar-Xe and Ne-Ar-Kr mixtures, for which sufficiently detailed experimental data are available, which allows both the calculation of concentration dependences and the comparison of calculated and experimental results. Table 1 lists thermal conductivity values calculated by (8) for the He-Ar-Xe mixture with $B_1 = 3.276$, $B_2 = 2.288$. For their determination, use was made of two experimental values from [8] obtained at 38°C. As is seen, the deviation of the calculated values from the experimental ones does not exceed 5%.

Similarly, Table 2 cites thermal conductivities of the Ne-Ar-Kr mixture with $B_1 = 1.606$, $B_2 = 2.225$. Experimental data are also taken from [8]. As in the previous case, the deviation does not exceed 5%. Moreover, both tables list the thermal conductivities and relative errors produced by calculations of B_1 and B_2 in which one experimental value of thermal conductivity is used for the ternary mixture and one value is used for the binary mixture and, finally, only two values of thermal conductivity are used for binary mixtures. It is noteworthy that B may be formally determined, as follows from (8), at $y = 0$, i.e., using data for a binary mixture not containing gas B. Analogously, the parameter B may be determined independently from data for another mixture (B, C). The discrepancy between the experimental and predicted data is at its maximum in the case where two binary mixtures are employed, but, nevertheless, it is always lower that 10% (see the tables).

TABLE 1. Comparison of Calculated and Experimental Thermal Conductivities ($\lambda \cdot 10^3$ W/(m·K)) of the He-Ar-Xe (*A*-*B*-C) Ternary Mixture

Mixture composition, %			λ_{exp}	λ_{1calc}	δ_1, %	λ_{2calc}	δ_2, %	λ_{3calc}	δ_3, %
A	*B*	*C*							
9.67	18.00	62.33	16.76	16.42	−2.03	18.67	11.40	18.68	11.46
39.01	36.75	24.24	35.36	33.84	−4.30	36.56	3.39	37.42	5.83
32.02	60.65	7.33	35.28	33.68	−4.53	34.45	−2.35	35.66	1.08

TABLE 2. Comparison of Calculated and Experimental Thermal Conductivities of the Ne-Ar-Kr (*A*-*B*-*C*) Ternary Gaseous Mixture

Mixture composition, %			λ_{exp}	λ_{1calc}	δ_1, %	λ_{2calc}	δ_2, %	λ_{3calc}	δ_3, %
A	*B*	*C*							
18.61	14.49	66.90	14.52	14.93	2.82	13.99	−3.65	13.81	−4.9
30.19	38.48	31.33	20.09	19..65	−2.19	19.35	−3.7	19.03	−5.3
45.37	15.67	38.96	22.81	21.58	−5.4	29.91	−8.3	20.46	−10.3
59.84	13.01	27.15	27.54	26.22	−4.79	25.99	−5.6	25.41	−7.7
79.19	15.69	71.52	13,92	13.92	−2.65	12.98	−4.2	12.86	−5.2

We now consider the dependence of the parameters B_1 and B_2 in (8) on the temperature. The dependence of the thermal conductivity of a pure gas on the temperature T may be represented as [1, 9, 10]

$$\lambda_i \sim T^{\gamma_i}, \tag{9}$$

where $\gamma_i = 0.5 + \alpha_i$, $\alpha_i \ll 0.5$. Hence it follows that the function F_2 determined from experimental data at a single temperature T_0 is valid in a rather wide temperature range since the arguments are only ratios of pure transfer coefficients. Proceeding from (9), we may say that the width of this range ΔT is proportional to the absolute temperature T_0 at which F_2 is determined. Indeed, the ratio of thermal conductivities of pure components may be represented as

$$\lambda_1(T)/\lambda_3(T) = \lambda_1(T_0)\left\{1 + (\alpha_1 - \alpha_3)(T - T_0)/T_0\right\}/\lambda_3(T_0). \tag{10}$$

When $\Delta T = T - T_0$ is such that

$$(\alpha_1 - \alpha_3)\,\Delta T/T_0 < 1,$$

the function F_2 may be considered as independent of temperature. In the solid sphere approximation widely used in the kinetic theory of gases [1, 9], $\alpha_i = 0$.

Results and Discussion. The Padé approximant method allows concentration dependences of transfer coefficients to be described by simple and rather accurate formulas (8), as it has been demonstrated for two mixtures on the example of the thermal conductivity of a ternary mixture. It is important that the coefficients B_1 and B_2 determined from experimental data at the specified temperature T_0 are almost the same in the wide temperature range

$\Delta T/T_0 < 0.3 - 0.4$.

It is also significant that the choice of the states of the ternary mixture in which the coefficients B_1 and B_2 are determined exerts only a slight influence on the accuracy of calculations. This probably depends on the fulfillment of conditions (4)-(6) and the Padé approximant properties [7]. Of interest is one more circumstance. For instance, for a gas mixture (*A*, *B*, *C*) the properties of the transfer coefficient of the binary mixtures (*A*, *B*)

and (B, C) are often known [5, 11]. As our calculations have shown, when experimental data on just binary mixtures are employed, for determination of B_1 and B_2 in (8), we obtain a rather accurate calculation formula valid in a wide temperature range, though the accuracy attained is lower than that of calculations using thermal conductivity of the ternary mixture itself. When a single experimental value is available for a ternary mixture, then choosing, as a second experimental point, known data on one of the binary mixtures (A, B) or (C, B), we may attain almost the same accuracy as in the case of using data on just the ternary mixture. This circumstance makes the suggested approach especially valuable in practice since a sufficiently large body of data on binary mixtures is available by now.

Using the similarity to the viscosity coefficient shown in the kinetic theory of gases [1], we may employ our approach with confidence to describe the concentration dependence of viscosity coefficients of ternary gaseous mixtures.

NOTATION

λ, thermal conductivity of the ternary mixture; T_0, temperature of the mixture whose experimental data are used to determine the parameters in the Padé approximant; λ_i, thermal conductivity of the mixture component at the temperature T_0; λ_{exp} and λ_{calc}, experimental and calculated thermal conductivity of the ternary mixture, respectively; $\delta_1 = (\lambda_{calc}-\lambda_{exp})/\lambda_{exp}$, relative error of the calculation using two experimental thermal conductivities; δ_2, relative error of the calculation based on one experimental value for the ternary mixture and one value for the binary mixture; δ_3, relative error of the calculation based on two thermal conductivity values of the binary mixtures composed of the gases forming the ternary mixture.

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