CALCULATION OF THE COEFFICIENT OF THERMAL CONDUCTIVITY OF A CHEMICALLY REACTING GAS MIXTURE OF METHANE AND HYDROGEN IN THE TEMPERATURE RANGE 1000-6000°K

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A method of calculating the coefficient of thermal conductivity of a chemically reacting gas mixture of methane and hydrogen in the temperature range 1000-6000°K is presented. The results of the calculation of the components of the coefficient of thermal conductivity, with the contribution of chemical reactions and dissociation reactions taken into account, are given.

The coefficient of thermal conductivity of a gas mixture, the value of which in the final analysis is determined by the dynamics of intermolecular interaction, can be calculated with the assumption that in the mixture of the gases the molecules of the individual substances take part only in paired collisions [1]. Since this assumption is valid under the conditions of moderate densities, it can to a sufficient degree be regarded as substantiated in the range of temperatures 1000-6000°K and at pressures close to 1 atm. For such calculations we usually use empirical and semiempirical potential functions of various types of intermolecular interactions, the parameters of which are determined from experimental data.

The most convenient and sufficiently satisfactory for the calculations is the Lennard-Jones (12−6) potential [1, 2]:

$$\varphi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{1}$$

The parameters σ and ε characterize the chemical diversity of the colliding molecules and have the dimensions of length (Å) and energy (J), respectively; σ is the distance of the greatest approach of two molecules for which $\varphi(r) = 0$; ε is the maximum energy of attraction of two molecules; and r is the intermolecular distance.

The force constants characterizing the interaction of molecules of different types are determined from empirical combinatorial rules:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \tag{2}$$

$$(\varepsilon/k)_{ij} = [(\varepsilon/k)_i (\varepsilon/k)_j]^{1/2}. \tag{3}$$

The molecular-kinetic theory [1] gives for the coefficient of thermal conductivity of a binary mixture of polyatomic gases, without taking into account the diffusional thermal conductivity, chemical reactions, and dissociation reactions, with an accuracy up to 1%, the following expression:

$$\lambda'_{\text{mix}} = \lambda'_{\text{mix trans}} + \sum_{i\neq j}^{2} \frac{\lambda_i^{\text{int}}}{1 + \dfrac{x_j D_{ii}}{x_i D_{ij}}}. \tag{4}$$

The first term in (4) in the first approximation can be represented by the determinant ratio

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$$[\lambda'_{\text{mix trans}}]_1 = 4\,\frac{\begin{vmatrix} L_{11} & L_{12} & x_1 \\ L_{21} & L_{22} & x_2 \\ x_1 & x_2 & 0 \end{vmatrix}}{\begin{vmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{vmatrix}}\,. \tag{5}$$

The coefficients entering into the expression (5) are given by the expressions

$$L_{ii} = -\frac{4x_i^2}{\lambda_i} - \frac{16T}{25P}\sum_{k\neq i}\frac{x_i x_k\left(\frac{15}{12}M_i^2 + \frac{25}{4}M_k^2 - 3M_k^2 B_{ik}^* + 4A_{ik}^* M_i M_k\right)}{(M_i + M_k)^2 D_{ik}}, \tag{6}$$

$$L_{ij} = \frac{16T}{25P}\cdot\frac{x_i x_j M_i M_j}{(M_i + M_j)^2 D_{ij}}\left(\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^*\right),\quad i\neq j, \tag{7}$$

where D_{ij} is the coefficient of mutual diffusion of the components, A_{ij} and B_{ij} are the functions of the equivalent temperature, x_i are the molar fractions of the components entering into the mixture, and

$$\lambda_i = 0.08328\,\frac{\sqrt{T/M_i}}{\sigma_i^2\Omega_i^{(2,2)}(T_i^*)}\left(\frac{4}{15}\cdot\frac{c_{vi}}{R} + \frac{3}{5}\right), \tag{8}$$

where R is the universal gas constant and c_{vi} is the specific heat in the case of constant pressure.

The expression (8) determines the coefficient of thermal conductivity of a purely monatomic gas, since in addition to the molecular flow of translational energy there is introduced the so-called Eicken correction, which approximately takes into account the energy transfer between the translational and internal (vibrational and rotational) degrees of freedom;

$$\lambda_i^{\text{int}} = 0.08328\,\frac{\sqrt{T/M_i}}{\sigma_i^2\Omega_i^{(2,2)}(T_i^*)}\left(\frac{4}{15}\cdot\frac{c_{vi}}{R} - \frac{2}{5}\right)$$

is the contribution of the internal degrees of freedom of polyatomic molecules to the thermal conductivity of the i-th component. The second term in the expression (4) constitutes the contribution of the internal degrees of freedom to the thermal conductivity of the mixture.

To obtain correct data it is necessary to estimate the contribution of the diffusional thermal conductivity in the overall heat flux [3]. For a binary mixture this contribution is given by the relation [4]

$$\frac{k}{2n}\sum\frac{n_i n_j}{D_{ij}}\left(\frac{D_i^{\mathrm{T}}}{m_i n_i} - \frac{D_j^{\mathrm{T}}}{m_j n_j}\right)^2 = \alpha_{\mathrm{T}} k_{\mathrm{T}}\frac{pD_{12}}{T}, \tag{9}$$

where k_T is the thermodiffusion ratio, and α_T is a thermodiffusion constant ($k_T = \alpha_T x_1 x_2$).

Thus, the coefficient of thermal conductivity of the gas mixture without taking into account the chemical reactions and dissociation is made up of the three components:

$$\lambda_3 = \lambda_{\text{mix trans}} + \lambda_{\text{mix}}^{\text{int}} + \lambda_{D^{\mathrm{T}}}, \tag{10}$$

where $\lambda_{\text{mix trans}}$ is the coefficient of thermal conductivity of the mixture of monatomic gases; $\lambda_{\text{mix}}^{\text{int}}$ is the contribution of the internal degrees of freedom of polyatomic molecules to the thermal conductivity of the mixture; and λ_{DT} is the contribution of the diffusional thermal conductivity to the thermal conductivity of the mixture.

In the calculation carried out we used the data obtained by us earlier on the content of components in the solution as a function of the concentrations of the initial products. For each temperature we singled out two components which dominated in content. The molar fractions of the remaining components were distributed equally between the dominant components (Table 1).

The constants of forces of interaction of the components for the Lennard-Jones (12–6) potential are taken from [1]; the collision integrals for this potential are taken from [2].

A program for the computation of λ_3 of the binary mixture has been set up in FORTRAN for a Minsk-32 computer. The results of the calculations have been presented in Fig. 1a-d.

In a nonisothermal mixture of chemically reacting gases, side by side with molecular and diffusional thermal conductivity, a considerable amount of heat is transferred by diffusion in the form of chemical enthalpy. For example, in the gas heat can be transferred when a molecule dissociates in a high-temperature region

TABLE 1. Molar Fractions of Components of Gas Mixture Taken into Account in the Calculation of the Coefficient of Thermal Conductivity

T, °K	Mixture			
	90vol.% H_2 10vol.% CH_4	80vol.% H_2 20vol.% CH_4	70vol.% H_2 30vol.% CH_4	50vol.% H_2 50vol.% CH_4
1000	H — 0,900 CH_4 — 0,100	H_2 — 0,800 CH_4 — 0,200	H_2 — 0,700 CH_4 — 0,300	H_2 — 0,500 CH_4 — 0,500
1500	H_2 — 0,923 CH_4 — 0,077	H_2 — 0,873 CH_4 — 0,126	H_2 — 0,839 CH_4 — 0,161	H_2 — 0,791 CH_4 — 0,209
2000	H_2 — 0,954 C_2H_2 — 0,046	H_2 — 0,916 C_2H_2 — 0,084	H_2 — 0,884 C_2H_2 — 0,116	H_2 — 0,832 C_2H_2 — 0,167
2500	H_2 — 0,943 C_2H_2 — 0,057	H_2 — 0,907 C_2H_2 — 0,093	H_2 — 0,866 C_2H_2 — 0,134	H_2 — 0,826 C_2H_2 — 0,174
3000	H_2 — 0,837 H — 0,163	H_2 — 0,822 H — 0,178	H_2 — 0,810 H — 0,190	H_2 — 0,790 H — 0,210
3500	H_2 — 0,552 H — 0,448	H_2 — 0,546 H — 0,454	H_2 — 0,541 H — 0,459	H_2 — 0,534 H — 0,467
4000	H_2 — 0,238 H — 0,762	H_2 — 0,241 H — 0,759	H_2 — 0,243 H — 0,757	H_2 — 0,247 H — 0,753
4500	H_2 — 0,128 H — 0,872	H_2 — 0,130 H — 0,870	H_2 — 0,145 H — 0,855	H_2 — 0,148 H — 0,852
5000	H — 0,906 C — 0,094	H — 0,898 C — 0,102	H — 0,879 C — 0,121	H — 0,872 H — 0,128
5500	H — 0,905 C — 0,095	H — 0,898 C — 0,102	H — 0,879 C — 0,121	H — 0,872 C — 0,128
6000	H — 0,905 C — 0,095	H — 0,900 C — 0,100	H — 0,880 C — 0,120	H — 0,874 C — 0,126

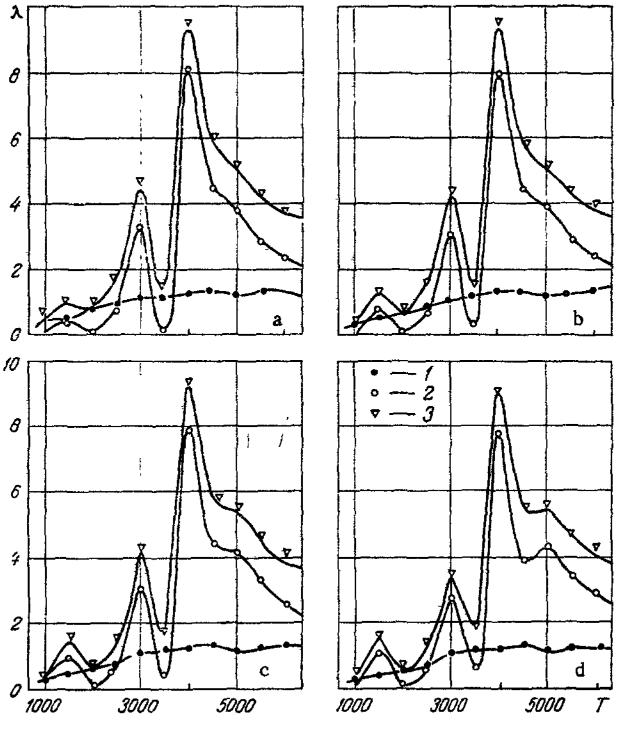

Fig. 1. Dependence of the components of the coefficient of thermal conductivity of gas mixture —(90 vol. % H_2 + 10 vol. % CH_4) (a), (80 vol. % H_2 +20 vol. % CH_4) (b), (70 vol. % H_2 +30 vol. % CH_4) (c), and (50 vol. % H_2 +50 vol. % CH_4) (d) — on the temperature, taking into account two components which predominate in content [1) λ_3; 2) λ_R; 3) λ_Σ]. Pressure, 1 atm; λ, W/m·°K; T, °K.

TABLE 2. Components and Possible Chemical Reactions of a Gas Mixture of Methane and Hydrogen Taken into Account When Calculating the Coefficient of Thermal Conductivity

T, °K	Mixture components		Chemical reactions
1500	$1 - H_2$ $2 - CH_4$	$3 - C_2H_2$ $4 - C_2H_4$	$2\ CH_4 \rightleftarrows C_2H_4 + 2\ H_2$ $C_2H_4 \rightleftarrows C_2H_2 + H_2$
2000	$1 - H_2$ $2 - CH_4$	$3 - C_2H_2$ $4 - C_2H_4$	$2\ CH_4 \rightleftarrows C_2H_4 + 2\ H_2$ $C_2H_4 \rightleftarrows C_2H_2 + H_2$
2500	$1 - H_2$ $2 - C_2H_2$	$3 - C_2H_4$ $4 - H$	$C_2H_4 \rightleftarrows C_2H_2 + H_2$ $H_2 \rightleftarrows 2\ H$
3000	$1 - H_2$ $2 - C_2H_2$	$3 - H$ $4 - C_2H$	$C_2H_2 \rightleftarrows C_2H + H$ $H_2 \rightleftarrows 2\ H$
3500	$1 - H_2$ $2 - C_2H_2$	$3 - H$ $4 - C_2H$	$C_2H_2 \rightleftarrows C_2H + H$ $H_2 \rightleftarrows 2\ H$
4000	$1 - H_2$ $2 - H$	$3 - C_2H$ $4 - C$	$C_2H \rightleftarrows 2\ C + H$ $H_2 \rightleftarrows 2\ H$
4500	$1 - H_2$ $2 - H$	$3 - C_2H$ $4 - C$	$C_2H \rightleftarrows 2\ C + H$ $H_2 \rightleftarrows 2\ H$
5000	$1 - H$ $2 - H_2$		$H_2 \rightleftarrows 2\ H$
5500	$1 - H_2$ $2 - H$		$H_2 \rightleftarrows 2\ H$
6000	$1 - H_2$ $2 - H$		$H_2 \rightleftarrows 2\ H$

and then diffuses in the direction of a lower temperature region, where the concentration of dissociated molecules is less. In the low-temperature region recombination takes place, as a result of which heat is emitted, this heat being absorbed in the high-temperature region [5].

The authors of [5] proposed a method of calculating the thermal conductivity of a mixture consisting of μ components, in which ν reactions simultaneously take place. The expression of Brokaw [6], obtained in an approximation of the local chemical equilibrium, has the form

$$\lambda_R = -\frac{1}{RT}\cdot\frac{\begin{vmatrix} A_{11} & \ldots & A_{1\nu} & \Delta H_1 \\ \cdot & \cdot & \cdot & \cdot \\ A_{\nu 1} & \ldots & A_{\nu\nu} & \Delta H_\nu \\ \Delta H_1 & \ldots & \Delta H_\nu & 0 \end{vmatrix}}{\begin{vmatrix} A_{11} & \ldots & A_{1\nu} \\ A_{\nu 1} & \ldots & A_{\nu\nu} \end{vmatrix}}, \tag{11}$$

where the elements of the determinants are

$$A_{ij} = A_{ji} = \sum_{k=1}^{\mu-1}\sum_{l=k+1}^{\mu}\frac{RT}{D_{kl}p}\,\frac{(n_{ik}x_l - n_{il}x_k)(n_{jk}x_l - n_{jl}x_k)}{x_k x_l}, \tag{12}$$

$$A_{ii} = \sum_{k=1}^{\mu-1}\sum_{l=k+1}^{\mu}\frac{RT}{D_{kl}p}\,\frac{(n_{ik}x_l - n_{il}x_k)^2}{x_k x_l}. \tag{13}$$

In the expressions (11)-(13), p is the pressure of the mixture; n_{ik} and n_{jl} are the stoichiometric coefficients of the components k and l taking part in the reactions i and j, respectively; and ΔH_i is the thermal effect of the i-th reaction, which is computed according to the well-known relation [7].

The expression (11) is valid for mixtures including any number of reacting components and chemical reactions. The latter can be connected if they have one or several identical reagents; however, from this system we have to exclude reactions which can be obtained as linear combinations of the rest [8].

Since the reactions which make a substantial contribution to λ_R are unknown beforehand, for each temperature interval we carried out a selection of basic components and possible reactions. Here it turned out to be sufficient to take into account up to four components (with $x_i > 10^{-3}$) and up to two reactions for each of the temperature intervals (Table 2).

Heats of the chemical reactions at different temperatures ΔH (J) are presented in Table 3.

TABLE 3. Chemical Reactions and Heat Values of Chemical Reactions Taken into Account When Calculating the Coefficient of Thermal Conductivity of a Gas Mixture of Methane and Hydrogen

T, °K	Chemical reactions	Heat of chemical reactions
1500	$2\ CH_4 \rightleftarrows C_2H_4 + 2\ H_2$ $C_2H_4 \rightleftarrows C_2H_2 + H_2$	220448 189277
2000	$2\ CH_4 \rightleftarrows C_2H_4 + 2\ H_2$ $C_2H_4 \rightleftarrows C_2H_2 + H_2$	220276 190307
2500	$C_2H_4 \rightleftarrows C_2H_2 + H_2$ $H_2 \rightleftarrows 2\ H$	166710 453033
3000	$H_2 \rightleftarrows 2\ H$ $C_2H_2 \rightleftarrows C_2H + H$	459765 356966
3500	$H_2 \rightleftarrows 2\ H$ $C_2H_2 \rightleftarrows C_2H + H$	461494 358156
4000	$H_2 \rightleftarrows 2\ H$ $C_2H \rightleftarrows 2\ C + H$	463228 925149
4500	$H_2 \rightleftarrows 2\ H$ $C_2H \rightleftarrows 2\ C + H$	464249 927485
5000	$H_2 \rightleftarrows 2\ H$	464124
5500	$H_2 \rightleftarrows 2\ H$	464576
6000	$H_2 \rightleftarrows 2\ H$	465024

The results of the calculation of the components of the coefficient of thermal conductivity of the gas mixture, taking into account the contribution of chemical reactions and dissociation, are presented in Fig. 1a-d.

As is seen from the figure, the decisive contribution to the total thermal conductivity is made by chemical reactions and dissociation reactions.

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