



THERMAL DIFFUSION IN H_2 - CH_4 , H_2 - N_2 AND N_2 - CO_2 GAS MIXTURES WITH ADDITION OF THIRD COMPONENT

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Abstract

The thermal diffusion in binary gaseous mixtures while a third component is being added is studied. A modified two-bulb method is used for experimental measurements. The thermal diffusion factor (TDF) measurements are performed for gaseous systems, containing He, Ar, H_2 , N_2 , CO_2 and CH_4 held under atmospheric pressure and at cold- and hot-chamber temperatures of $T_1 = 280K$ and $T_2 = 800K$, respectively. For every gas mixture, measurements are made at different values of the mole fraction of the additive. The dependence of the TDFs on the additive's mole fraction and mass of molecules is studied. To calculate TDF values, a proposed semi-empirical formula is used; calculation results coincide with experimental data within the respective limits of experimental error.

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List of Symbols

f	Geometric factor of setup, $f = V_1 T_2 / V_2 T_1$
p	Gas pressure (MPa)
q_{ij}	Separation factor
T_1, T_2	Gas temperature of cold and hot areas of gas (K)
TDF	Thermal diffusion factor
V_1, V_2	Volumes of cold and hot chambers, respectively (m^3)
x_{ij}^{bin}	Mole fraction of component i in binary i - j mixture before separation
x_i^{mlt}	Mole fraction of component i in multicomponent mixture before separation
x_{iT}^{mlt}	Mole fraction of component i in multicomponent mixture at temperature T in two-bulb apparatus after separation
$x(a)$	Mole fraction of gas a in the mixture
α_{Tij}^{bin}	Thermal diffusion factor in binary mixture of gases i and j
α_{Tij}^{mlt}	Thermal diffusion factor for components i and j in multicomponent gas mixture
$\alpha_T(a-b)^{tm}$	Thermal diffusion factor for gases a and b in ternary gas mixture
Δx_{ij}^{bin}	Mole fraction change of component i in binary i - j mixture after separation
Δx_i^{mlt}	Mole fraction change of component i in multicomponent gas mixture after separation

1. Introduction

The solution of problems of heat and mass transfer is necessary in many areas of science and technology. The development of gas, oil, chemical and other industries requires knowledge of transport properties of substances, which include characteristics of molecular mass transfer, such as diffusion and thermal diffusion [12, 17-19].

Studies of thermal diffusion in ternary gas systems performed in [2-7, 9-11, 13] have shown that addition of the third component to the binary mixture can change the value of thermal diffusion factor (TDF) of initial pair of gases significantly. The TDF can rise or fall two or three times and in some cases, its value can change the sign [4-7] as the mole fraction of the additive is increased.

In studies of thermal diffusion in ternary gas systems, the dependence of TDF on mole fraction of the component being added into binary mixture with fixed composition is usually examined. As some investigations showed [4-7], behavior of the TDF for many gas pairs depends on initial binary mixture composition. As far as we know, there is no systematic investigation of this dependence has been made until now. In the current work, some results of the study of the stated dependence obtained by us are given for a number of gas mixtures.

2. Experimental Technique

Experimental studies were performed with the use of the setup described in [6, 8], which represents a modified two-bulb apparatus. Measurements were made under pressure $p = 0.1\text{MPa}$, at temperatures of cold and hot chambers $T_1 = 280\text{K}$ and $T_2 = 800\text{K}$, respectively. Mixture composition was analyzed using the weight and interferometric methods, as in [6, 8].

In the experiments, gases of high purity were used, specifically, 99.999% for helium and argon, 99.99% for hydrogen and nitrogen, and 99.9% for carbon dioxide and methane.

During the composition mixture analysis after separation, we can get the mixture compositions in the cold and hot chambers separately as well as the difference in mole fractions of each component of the separated mixture between both chambers. Thus, we can calculate the TDF value using the generally accepted equation [14, 18]:

$$\alpha_{Tij}^{mlt} = \frac{\ln q_{ij}}{\ln T_2/T_1} = \frac{\ln \left(\frac{x_{iT_1}^{mlt}}{x_{jT_1}^{mlt}} \right) / \left(\frac{x_{iT_2}^{mlt}}{x_{jT_2}^{mlt}} \right)}{\ln T_2/T_1} \quad (1)$$

as well as the one proposed by us:

$$\alpha_{Tij}^{mlt} = \left(\frac{\Delta x_i^{mlt}}{x_i^{mlt}} - \frac{\Delta x_j^{mlt}}{x_j^{mlt}} \right) / \ln \frac{T_2}{T_1}. \quad (2)$$

Equation (2) was obtained by us [5, 9] expanding the value of $\ln(q_{ij})$ in a series. The value of second term in series expansion depends on geometric factor $f = V_1 T_2 / V_2 T_1$ significantly. However, at fixed cold- and hot-chamber temperatures of T_1 and T_2 , respectively, the value of the factor f is characterized by the ratio of chambers volumes only. However, the two-bulb setup, allowed the volumes of chambers to be easily matched to those, at which the value of factor f is equal to the unity [9]. Thus, the TDF values calculated using equations (1) and (2) should coincide within the limits of the experimental error.

Tables 1-4 present the values of the TDF α_{Tij}^{tm} calculated using both mentioned equations for the mixtures H_2 - CH_4 , H_2 - N_2 and N_2 - CO_2 with the additives of H_2 , He, N_2 , Ar and CO_2 .

Table 1. Experimental values of thermal diffusion factor of pair of gases H₂-CH₄, $\alpha_T(\text{H}_2\text{-CH}_4)^{tm}$, at different mole fractions of additives N₂ and CO₂ calculated using equations (1) and (2) at temperatures of cold and hot chambers of $T_1 = 280\text{ K}$, $T_2 = 800\text{ K}$, respectively, under pressure $p = 0.1\text{ MPa}$, $f = 0.95$

x_i	$x(\text{H}_2)/x(\text{CH}_4) = 0.2501$		x_i	$x(\text{H}_2)/x(\text{CH}_4) = 3.998$	
	Using eq. (1)	Using eq. (2)		Using eq. (1)	Using eq. (2)
Dependence of $\alpha_T(\text{H}_2\text{-CH}_4)^{tm}$ on $x(\text{N}_2)$					
0.000	0.21	0.20	0.000	0.52	0.51
0.060	0.19	0.20	0.071	0.51	0.50
0.247	0.20	0.20	0.195	0.46	0.45
0.381	0.17	0.18	0.331	0.42	0.40
0.521	0.17	0.17	0.515	0.33	0.33
0.654	0.16	0.15	0.621	0.27	0.28
0.789	0.11	0.12	0.731	0.22	0.21
0.932	0.09	0.10	0.937	0.13	0.12
Dependence of $\alpha_T(\text{H}_2\text{-CH}_4)^{tm}$ on $x(\text{CO}_2)$					
0.000	0.20	0.20	0.000	0.52	0.51
0.059	0.19	0.21	0.069	0.51	0.51
0.235	0.19	0.19	0.212	0.48	0.47
0.361	0.17	0.18	0.355	0.41	0.40
0.510	0.17	0.17	0.539	0.34	0.33
0.632	0.15	0.14	0.652	0.27	0.26
0.775	0.12	0.13	0.786	0.20	0.21
0.942	0.10	0.11	0.946	0.12	0.13

Table 2. Same as Table 1 but for the pairs of gases $\text{N}_2\text{-CO}_2$ and $\text{H}_2\text{-N}_2$ for the additives He and Ar, respectively

x_i	$x(\text{N}_2)/x(\text{CO}_2) = 1.000$		x_i	$x(\text{H}_2)/x(\text{N}_2) = 0.9995$	
	Using eq. (1)	Using eq. (2)		Using eq. (1)	Using eq. (2)
Dependence of $\alpha_T(\text{N}_2\text{-CO}_2)^{im}$ on $x(\text{He})$			Dependence of $\alpha_T(\text{H}_2\text{-N}_2)^{im}$ on $x(\text{Ar})$		
0.000	0.058	0.056	0.000	0.28	0.27
0.091	0.063	0.062	0.062	0.29	0.28
0.213	0.057	0.059	0.201	0.26	0.27
0.41	0.060	0.062	0.344	0.24	0.26
0.521	0.075	0.072	0.511	0.24	0.24
0.597	0.079	0.077	0.690	0.21	0.20
0.753	0.123	0.119	0.797	0.18	0.19
0.897	0.156	0.161	0.919	0.17	0.17

Table 3. Same as Table 1 but for the pair of gases $\text{N}_2\text{-CO}_2$ and for the additives H_2 and He

x_i	$x(\text{N}_2)/x(\text{CO}_2) = 0.2499$		x_i	$x(\text{N}_2)/x(\text{CO}_2) = 4.002$	
	Using eq. (1)	Using eq. (2)		Using eq. (1)	Using eq. (2)
Dependence of $\alpha_T(\text{N}_2\text{-CO}_2)^{im}$ on $x(\text{H}_2)$					
0.000	0.054	0.056	0.000	0.066	0.067
0.058	0.052	0.051	0.077	0.064	0.064
0.222	0.039	0.038	0.221	0.073	0.071
0.386	0.015	0.015	0.346	0.099	0.097
0.514	-0.014	-0.013	0.515	0.141	0.138
0.649	-0.003	-0.004	0.657	0.192	0.195
0.789	0.033	0.031	0.773	0.219	0.214
0.930	0.145	0.141	0.921	0.235	0.240
Dependence of $\alpha_T(\text{N}_2\text{-CO}_2)^{im}$ on $x(\text{He})$					
0.000	0.055	0.056	0.000	0.065	0.067
0.061	0.048	0.047	0.084	0.075	0.073
0.184	0.040	0.042	0.235	0.092	0.091
0.356	0.007	0.006	0.387	0.132	0.130
0.487	-0.007	-0.008	0.513	0.149	0.147
0.634	-0.010	-0.009	0.621	0.177	0.181
0.783	0.043	0.045	0.814	0.225	0.221
0.924	0.109	0.106	0.946	0.232	0.228

Table 4. Same as Table 1 but for the pair of gases H₂-N₂ and for the additives Ar and CO₂

x_i	$x(\text{H}_2)/x(\text{N}_2) = 0.2501$		x_i	$x(\text{H}_2)/x(\text{N}_2) = 4.002$	
	Using eq. (1)	Using eq. (2)		Using eq. (1)	Using eq. (2)
Dependence of $\alpha_T(\text{H}_2\text{-N}_2)^{im}$ on $x(\text{Ar})$					
0.000	0.21	0.22	0.000	0.34	0.36
0.060	0.24	0.24	0.070	0.35	0.36
0.212	0.22	0.22	0.211	0.36	0.35
0.355	0.21	0.22	0.357	0.33	0.32
0.500	0.20	0.21	0.499	0.28	0.29
0.685	0.18	0.19	0.655	0.24	0.25
0.812	0.17	0.18	0.782	0.21	0.22
0.921	0.16	0.16	0.936	0.17	0.18
Dependence of $\alpha_T(\text{H}_2\text{-N}_2)^{im}$ on $x(\text{CO}_2)$					
0.000	0.23	0.22	0.000	0.35	0.36
0.073	0.25	0.24	0.069	0.38	0.37
0.193	0.23	0.22	0.216	0.36	0.36
0.312	0.21	0.21	0.332	0.33	0.33
0.500	0.19	0.20	0.511	0.29	0.29
0.710	0.17	0.18	0.697	0.25	0.24
0.821	0.16	0.16	0.808	0.19	0.20
0.937	0.14	0.15	0.938	0.15	0.16

As it can be seen from the tables, the TDFs, obtained from the results of measurements of gas mixture composition in cold and hot chambers using equation (1), clearly agree with those calculated using the components' mole fraction changes between chambers with the help of equation (2). The observed agreement lies within the experimental error limits.

Using our method of the mixture composition analysis, the accuracy of calculation of the TDFs using equation (2) turned out slightly better compared to equation (1). Therefore, in general, we measured directly the mole fraction changes of the mixture components during experiments and then calculated the TDF values using equation (2).

The experimental errors of defining the TDFs for the studied gas systems are listed in Table 5.

Table 5. Errors of defining the thermal diffusion value α_{Tij}^{tm} in experimental study of thermal diffusion separation in ternary gas mixtures at temperatures of cold and hot chambers of $T_1 = 280\text{ K}$, $T_2 = 800\text{ K}$, respectively, under pressure $p = 0.1\text{ MPa}$, for confidence probability 0.95. Experimental errors of defining the value α_{Tij}^{tm} using equations (1) and (2) are given in first and second lines of each cell, respectively

Gas system	Additive				
	H ₂	He	N ₂	Ar	CO ₂
H ₂ -CH ₄	-	-	8.9%	-	8.8%
			5.8%		5.7%
N ₂ -CO ₂	9.1%	6.1%	-	-	-
	6.0%	4.7%			
H ₂ -N ₂	-	-	-	9.2%	8.1%
				6.2%	5.2%

3. Results of Measurement and Calculation

To investigate the dependence of the TDF value on initial binary mixture composition and mole fraction of the third component, following gas binary systems have been chosen: H₂-CH₄, N₂-CO₂ and H₂-N₂. For each system, we have prepared three mixtures with ratios of components' mole fractions approximately equal to 0.250, 1.00 and 4.00.

Earlier, in [5], the impact of addition of the third component to equimolar binary mixture on the TDF value was studied for the listed systems. At that, one of the mentioned gases: H₂, CH₄, N₂ or CO₂ was used as an additive. In the current work, the results of that study were used for analysis of influence of the third component on the TDF behavior depending on binary mixture composition. Moreover, for some pairs of gases, the impact of addition of noble gases such as He and Ar on the TDF value depending on initial binary mixture composition was studied, too.

As it is well known [14-16], the values of thermal diffusion characteristics depend significantly on masses of molecules participating in thermal diffusion separation. That is why, as far as possible in our study, as an additional component, we used a lighter gas or a heavier one compared to both gases of initial binary system. The results of this study are presented in Tables 1-4 and on Figures 1-3.

Earlier, in [3], we proposed the method of calculation of the TDF for a given pair of gases in the ternary gas system using the TDFs for the corresponding binary gas mixtures:

$$\alpha_{Tij}^{trn} = \alpha_{Tij}^{bin} + x_k^{trn} (\alpha_{Tik}^{bin} - \alpha_{Tjk}^{bin} - \alpha_{Tij}^{bin}). \quad (3)$$

Equation (3) can be obtained with the use of the equations for calculation of the TDF value α_{Tij}^{trn} in the ternary systems presented in [5, 6]. Equation (3) can also be derived from the equation given in [20], if we suppose that the values α_{Tij}^{bin} are the TDFs of binary gas systems, provided that cold- and hot-chamber temperatures in experiments coincide for binary and ternary mixtures, and the corresponding ratios of mole fractions of *i*th and *j*th components are equal:

$$x_{ij}^{bin} / x_{ji}^{bin} = x_i^{trn} / x_j^{trn}.$$

For all the studied gas mixtures, we calculated the TDF values of α_{Tij}^{trn} , using equation (3), too. Corresponding values of α_{Tij}^{bin} have been calculated, using data presented by us for binary gas mixtures in [1, 5-7].

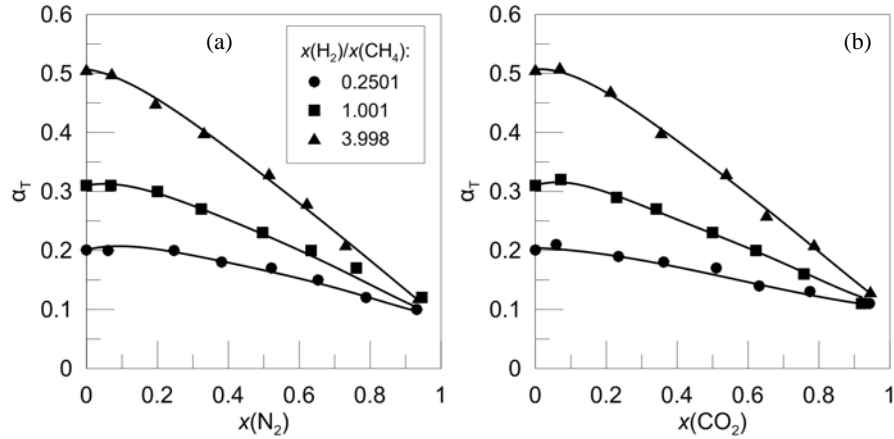


Figure 1. Dependence of the thermal diffusion factor of pair of gases $\text{H}_2\text{-CH}_4$ on mole fraction of third component at different mixture compositions. Experimental values are marked by symbols; curves were calculated using equation (3) for the following gases as an additional component: (a) N_2 ; (b) CO_2 .

Figure 1 shows the dependence of the TDF for the system $\text{H}_2\text{-CH}_4$, $\alpha_T(\text{H}_2\text{-CH}_4)^{trm}$, on the mole fraction of a heavier additive for three ratios of the mole fractions of components of mixtures $\text{H}_2\text{-CH}_4$. The calculated values are presented on the figure as solid curves. Gases N_2 and CO_2 were used as additional components supplemented to initial binary mixtures. The experimental values of $\alpha_T(\text{H}_2\text{-CH}_4)^{trm}$ for the mole fractions ratio $x(\text{H}_2)/x(\text{CH}_4) = 1.001$ with additives of N_2 and CO_2 have been taken from [5]. As it can be seen from Figure 1, addition of a heavier component to a binary mixture of two lighter gases leads to decrease of the TDF value as additive's mole fraction increases.

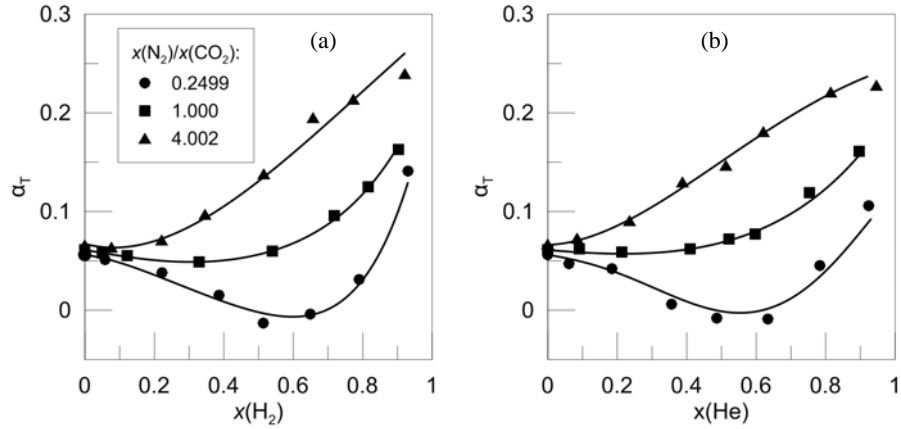


Figure 2. Same as for Figure 1 but for pair of gases N₂-CO₂ and for the following gases as an additional component: (a) H₂; (b) He.

Figure 2 presents the dependence of $\alpha_T(\text{N}_2\text{-CO}_2)^{trn}$ on mole fraction of a lighter additive of H₂ and He, separately. The corresponding values of $\alpha_T(\text{N}_2\text{-CO}_2)^{trn}$ at $x(\text{N}_2)/x(\text{CO}_2) = 1.000$ for different mole fractions of H₂ have been taken from [5]. Here we can see that the dependence of $\alpha_T(\text{N}_2\text{-CO}_2)^{trn}$ on the mole fraction of a lighter additive is more complex. The TDF value can rise, fall, or take negative values and then rise again as mole fraction of additive increases.

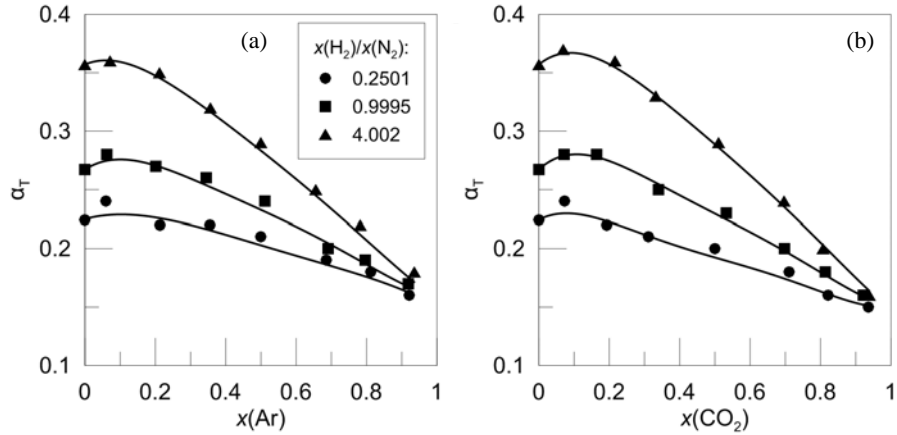


Figure 3. Same as for Figure 1 but for pair of gases $\text{H}_2\text{-N}_2$ and for the following gases as an additional component: (a) Ar; (b) CO_2 .

Figure 3 visualizes the dependence of the TDFs for the binary gas mixtures $\text{H}_2\text{-N}_2$ on the mole fraction of an additive. For this system, heavier gases, compared to gases of initial binary system, were taken as additives making ternary mixtures. The values of α_{Tij}^{tm} for equimolar binary mixture with additive of CO_2 have been taken from [5]. As it can be seen from figures, adding a heavier component to these binary mixtures leads to the decrease of the TDF value with the increase in the additive's mole fraction.

4. Conclusion

No unambiguous conclusion about impact of mass of additive's molecules on the TDF can be derived based upon the results of the current study. However, we can state that adding a heavier component to a binary mixture will decrease the TDF value in most cases. In contrast, an impact of a lighter additive has a complex character, as it depends on the composition of the initial binary mixture and the mole fraction of the additive.

From the results of the study performed, it becomes clear, that to define the dependence of the TDF for binary mixtures on mole fraction of the third

component, a deeper analysis is required. Probably, taking into account not only masses of components' molecules, but also intermolecular potential parameters, would clarify this dependence.

In addition, it should be noted that the proposed method for calculating the TDF value in ternary gas mixtures gives results that agree with the experimental data for the mixtures of different compositions within the experimental error.

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