CALCULATION OF THE THERMAL DIFFUSION FACTOR
OF INERT GAS MIXTURES

A. F. Zolotukhina

UDC 536.539.1

We discuss a semiempirical relation for the thermal diffusion factor of inert gas mixtures. In contrast to earlier relations of this kind, our formula does not involve correction constants. The results of the calculations are compared with the experimental data.

In our previous papers [1, 2] we obtained various relations for the thermal diffusion factor α_T for inert gas mixtures in the framework of the theory of corresponding states. These equations involved a set of correction quantities (n, k) dependent on temperature and concentration. The complexity of determining these quantities in different temperature and concentration regions makes the practical application of these relations difficult. In the present paper we obtain an approximation formula based on a systematization of the experimental data for α_T according to the method of [3]. The approximation formula obtained here does not contain correction constants.

Results obtained by various methods were included in the set of experimental data comprising the systematization, which was larger by 200-250 points than the preceding systematization. The average deviation between the data of the different authors was ±2—12%, in comparison with experimental errors in the range ±1—10%.

In order to simplify the analysis of the data, we excluded α_T data showing an anomalous temperature dependence. In particular, we did not include low-temperature α_T data for Ar—Kr and Ar—Ne mixtures, which suggests a positive minimum.

The reduced variables α_T^* and T^* were determined as in [3] with the help of the parameters $\alpha_{T.hs}$ and ε/k. The values of ε/k were taken from [4]. The collisional diameters for the hard sphere model needed in the calculation of $\alpha_{T.hs}$ were determined from viscosity data obtained at 273 K [5]. The potential parameters used in the calculations are given in Table 1. The potential parameters for a mixture were calculated with the help of the combination rules:

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} , \quad \varepsilon_{12} = (\varepsilon_1 \cdot \varepsilon_2)^{1/2} .$$

The temperature interval corresponding to the measured values of α_T of inert gas mixtures is 150-500 K. At higher temperatures (up to 750-873 K) only the data of Taylor, et al. are available [6, 7] and at temperatures 2000-4000 K only the data of [8] for He—Ar mixtures with He as a small (up to 4.5%) impurity are available.

It was possible to obtain reduced temperatures in the temperature region 2000 K and higher for He—Ar mixtures with the help of the values of εk given in Table 1. Calculations show that the values of ε/k for He and Ar obtained according to the method of [4] from the viscosity data of [5] differ only slightly from the values of ε/k given in Table 1 in the

TABLE 1. Potential Parameters ε/k
[4] and σ_{hs} Used in the Calcula-
tions

Gas	$\varepsilon/k,^{*)}K$	$\sigma_{h.s.},\, \overset{\circ}{A}$
He	10,22	2,18
Ne	35,7	2,60
	27,5	
Ar	124,2	3,64
	116,0	
Kr	190	4,16
Xe	229	4,86

*The upper values of ε/k for Ne and
Ar correspond to the temperature
region 80-300 K and the lower values
correspond to 300-1000 K.

temperature region 1500-2500 K. For example, we obtain values of ε/k of 10.2 and 11.4 K
for He in the temperature regions 1500-2000 K and 2000-2500 K, respectively. The corres-
ponding results for Ar are 116.5 and 112.0 K.

The reduced quantities α_T^* were fit by the method of least squares to the following
polynomial in T^*

$$\ln(\alpha_T^*)^{-1} = \sum_{i=1}^{n} C_i (\ln T^*)^{i-1} .$$ (1)

Calculations show that a fourth-order polynomial best describes the temperature dependence
of $(\alpha_T^*)^{-1}$ in logarithmic coordinates. From (1) we obtain the following expression for α_T

$$\alpha_T = \alpha_{T.hs} \left\{ \exp \left[\sum_{i=1}^{n} C_i (\ln T^*)^{i-1} \right] \right\}^{-1} ,$$ (2)

where $\alpha_{T.hs}$ is calculated from the relations given in [4].

As in [1-3], we assume a linear dependence of the reciprocal of α_T on concentration.
The method of least squares was used to fit the calculated values of $\alpha_{T.hs}$ for inert gas
mixtures to the polynomial $\alpha_{T.hs}^{-1} = a + bx_1$ (Table 2), where x_1 is the concentration of
the light component of the mixture.

The thermal diffusion factor was calculated from the formula

$$\alpha_T = (a + bx_1)^{-1}/\exp[2,87802 - 2,75969\ln T^* + 1,19411(\ln T^*)^2 -$$
$$- 0,220411(\ln T^*)^3 + 0,0149076(\ln T^*)^4].$$ (3)

As an example, we show in Fig. 1a the temperature dependence of α_T calculated from (3) for
equimolar concentrations of inert gas mixtures. Figure 2 shows the deviations between the
calculated values and the experimental data.

The calculated results of Kestin et al. [9] are also shown in Fig. 1a. These results
encompass a large temperature region and agree quite closely with most of the experimental
α_T data for inert gas mixtures. for temperatures of 300 K and above the data of [9] agree
with the values calculated from (3) to within ±2-10%. For the mixtures He—Ne, He—Ar, and
Ne—Ar the agreement extends to all temperatures. In the temperature region 50-300 K, the
slope of the temperature dependence calculated from (3) for mixtures of He and Ne with Kr
and Xe is steeper than that of [9]. For the mixtures Ar—Kr, Ar—Xe, and Kr—Xe the results
of [9] indicate the presence of a positive minimum in this temperature region, whereas the
values calculated from (3) approach a zero value of α_T for temperatures below 50 K. Calcu-
lations in the Chapman—Enskog theory using the Lennard—Jones (12-6) potential (not plotted
in Fig. 1a) showed that for inert gas mixtures the quantity α_T changes sign in the temper-
ature region below 200 K, except for mixtures containing He.

We note that experimental data for α_T are not available in the literature for most inert
gas mixtures in the temperature region below 150 K. In the case of Ar—Kr mixtures, the
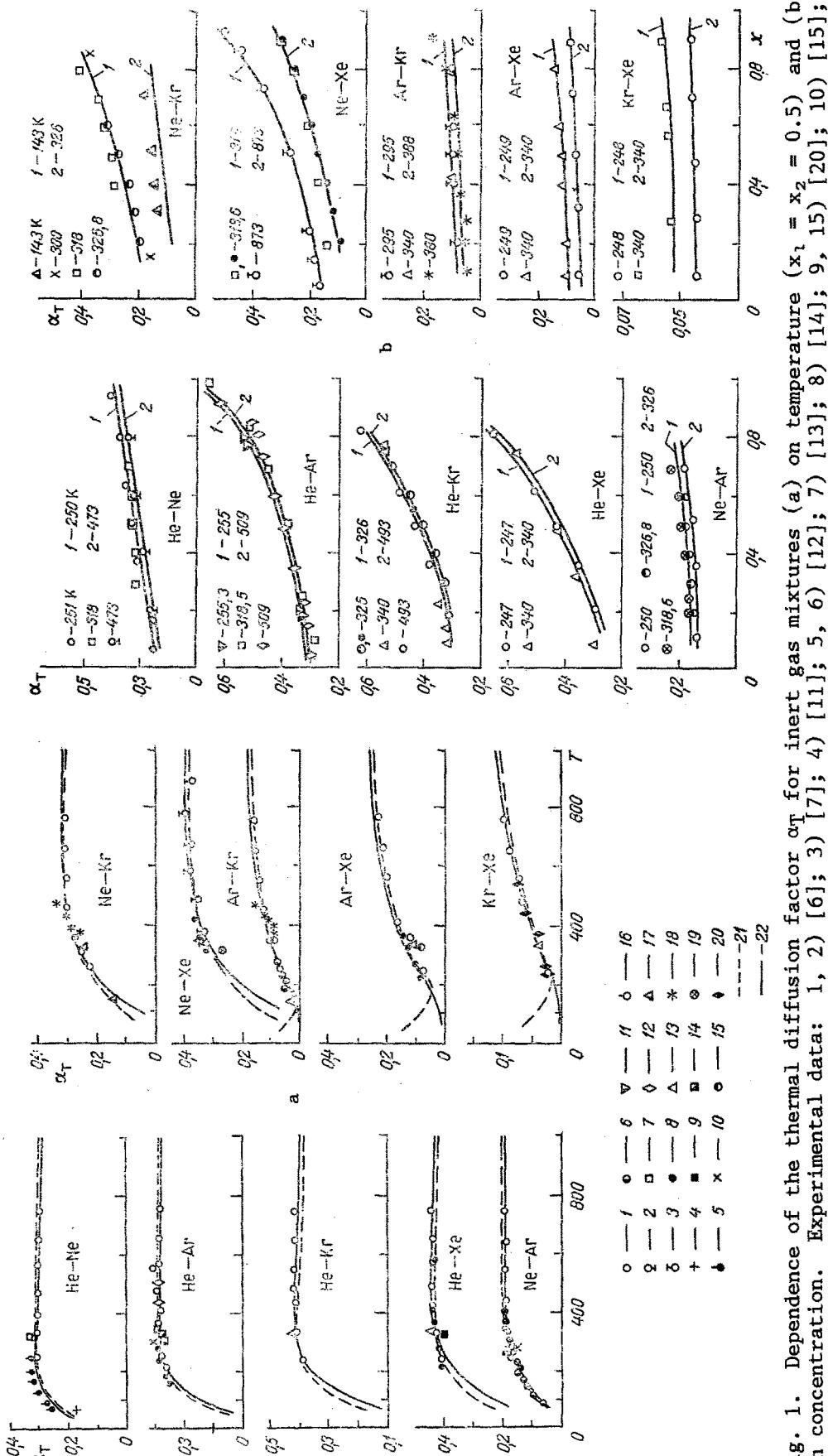
Fig. 1. Dependence of the thermal diffusion factor α_T for inert gas mixtures (a) on temperature ($x_1 = x_2 = 0.5$) and (b) on concentration. Experimental data: 1, 2) [6]; 3) [7]; 4) [11]; 5, 6) [12]; 7) [13]; 8) [14]; 9, 15) [20]; 10) [15]; 11) [16]; 12) [17]; 13) [18]; 14) [19]; 16) [21]; 17) [22]; 18) [23]; 19) [24]; 20) [25]; calculated data: a) 21 [9]; 22) obtained from equation (3); b) 1-2 from equation (3). T, °K.

TABLE 2. Coefficients of the Polynomial $\alpha_T \cdot \bar{hs}^{-1} = a + bx_1$ for Inert Gas Mixtures

Gas mixture	a	b	Gas mixture	a	b
He—Ne	2,2306	—0,8683	Ar—Kr	3,3531	—0,8196
He—Ar	2,0967	—1,337	Ar—Xe	2,5327	—1,0913
He—Kr	2,0432	—1,4619	Ne—Kr	2,3617	—1,3230
He—Xe	2,0287	—1,5754	Ne—Xe	2,1849	—1,4684
Ar—Ne	3,5308	—1,4795	Kr—Xe	4,8915	—1,1780

TABLE 3. Comparison between the Experimental and Calculated Values of α_T for Inert Gas Mixtures with Trace Concentrations of One of the Components, and Also Mixtures of Isotopes

Gas mixture	T, K	Concentration of the light component	$\alpha_{T.c}$	$\alpha_{T.e}$	$\frac{\alpha_{T.c}-\alpha_{T.e}}{\alpha_{T.c}} \times 100\%$	Literature source of the experimental data
Ne—Xe	311	0,987	0,580	0,601	—3,6	[26]
		0,01	0,204	0,225	—10,3	
	300	Xe→0	0,59	0,57	+3,4	[27]
	500		0,73	0,65	+11,0	
	700		0,77	0,68	+11,7	
Ar—Xe	300	Xe→0	0,141	0,15	—6,4	[27]
	500		0,256	0,26	—1,6	
	700		0,319	0,31	+2,8	
^{3}He—^{4}He	203	0,104	0,0716	0,0724	—1,1	[28]
		0,293	0,0720	0,0680	+5,6	
		0,701	0,0733	0,0745	—1,6	
		0,893	0,0739	0,0719	+2,7	
	136	0,5	0,0729	0,0696	+4,5	[29]
	234		0,0708	0,0657	+7,2	
	312		0,0696	0,0651	+6,5	
^{20}Ne—^{22}Ne	214	0,101	0,0231	0,0225	+2,6	[30]
	215	0,500	0,0232	0,0220	+5,1	
		0,901	0,0234	0,0226	+3,4	
	274	0,502	0,0243	0,0229	+5,8	[30]
	473	0,502	0,0247	0,0255	—3,1	[30]
	573		0,0244	0,0257	—5,3	
^{36}Ar—^{40}Ar	216	0,103	0,0091	0,0090	+1,1	[30]
		0,5	0,0092	0,0086	+6,5	
	373	0,510	0,0188	0,0167	+11,1	[31]
	473	0,504	0,0219	0,0211	+3,7	
	573	0,527	0,0240	0,0238	+0,8	
	673	0,527	0,0254	0,0258	—1,6	
	773	0,5	0,0269	0,0270	—0,4	
	873	0,510	0,0268	0,0282	—5,2	
^{78}Kr—^{86}Kr	250	0,544	0,0052	0,0055	—5,8	[31]
	350		0,0094	0,0104	—10,6	
	450		0,0130	0,0133	—2,3	
	550		0,0160	0,0162	—1,3	
	650		0,0183	0,0179	+2,2	
	750	0,545	0,0200	0,0207	—3,5	
	850	0,542	0,0214	0,0221	—3,3	
^{124}Xe—^{136}Xe	242	0,054	0,0026	0,0025	+3,8	[32]
	348	0,134	0,0062	0,0062	0	
	448	0,188	0,0091	0,0087	+4,4	
	640	0,273	0,0139	0,0126	+9,3	
	747	0,333	0,0158	0,0154	+2,5	
	850	0,348	0,0174	0,0161	+7,5	

absence of a positive minimum in the values calculated from (3) is not unexpected, since as mentioned above, low-temperature (below the condensation point of Kr) experimental data for this mixture were not included in the systematization of the data used in the analysis. In connection with this, the use of (3) for inert gas mixtures not containing He must be restricted to temperatures above 200 K; below this temperature the errors in the calculated values of α_T will obviously be significant.

The concentration dependence of α_T calculated from (3) is shown in Fig. 1b, along with the experimental data of a number of different authors. This figure demonstrates the non-agreement between the data of the different authors.

TABLE 4. Coefficients of the Polynomial for $\alpha_{T.hs}$ for Mixtures of Isotopes ($\alpha_{T.hs}^{-1}$ = $cx_1 + d$)

Mixture of isotopes	c	d
^{3}He—^{4}He	—0,31133	7,81264
^{20}Ne—^{20}Ne	—0,20846	22,5202
^{36}Ar—^{40}Ar	—0,30005	20,4507
^{78}Kr—^{83}Kr	—0,30091	22,04219
^{124}Xe—^{136}Xe	—0,29854	23,2837
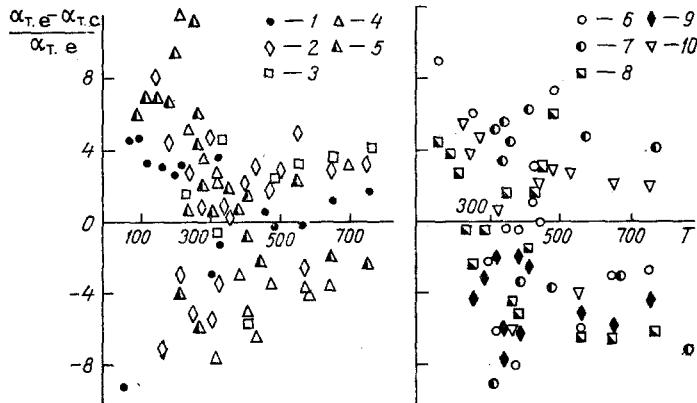
Fig. 2. Deviations of the experimental values of α_T (in percent) obtained by different authors from the values calculated using (3) for inert gas mixtures: 1) He—Ne; 2) He—Ar; 3) He—Kr; 4) He—Xe; 5) Ne—Ar; 6) Ne—Kr; 7) Ne—Xe; 8) Ar—Kr; 9) Ar—Xe; 10) Kr—Xe.

Table 3 compares the calculated values of α_T with experimental data from mixtures with trace concentrations of one of the components (these mixtures were not used in the systematization of the experimental data discussed above) and also for mixtures of inert gas isotopes. As in the case of inert gas mixtures, the values of $\alpha_{T.hs}$ needed in the calculation of α_T for mixtures of isotopes were determined from the relations given in [4].

The coefficients of the polynomial $\alpha_{T.hs}^{-1} = cx_1 + d$ are given in Table 4, where x_1 is the concentration of the light component.

We note that the strongest concentration dependence of α_T occurs for He^3—He^4 mixtures. To a good apprximation, the value of $\alpha_{T.hs}$ for concentration 0.5 can be used for the other mixtures of isotopes.

The following simple formula is often used to calculate $\alpha_{T.hs}$ for mixtures of heavy isotopes [10]:

$$\alpha_{T.hs} = 0,89\,(M_2 - M_1)/(M_2 + M_1), \qquad (4)$$

where M_1 and M_2 are the molecular masses of the isotopes (the subscript 1 refers to the light component of the mixture). In a number of papers [30-32 and others] the quantity $\alpha_{T.hs}$ was set equal to the relative mass difference $(M_2-M_1)/(M_2 + M_1)$. Use of (4) for $\alpha_{T.hs}$ leads to an underestimation of the thermal diffusion factor by about 2-4%, while use of the relative mass difference for $\alpha_{T.hs}$ leads to an overestimation by about 5%. (The calculated values of α_T of Table 3 for mixtures of isotopes were used in the comparison.)

It follows from comparing the calculated values of α_T with the experimental data (see Figs. 1, 2 and Table 3) that to within experimental error the relation (3) can be used to calculate the thermal diffusion factor of inert gas mixtures and also mixtures of inert gas isotopes in temperature and concentration values of α_T are not required in order to calculate the thermal diffusion factor using (3).

NOTATION

$\alpha_T^* = \alpha_{T.e}/\alpha_{T.hs}$, reduced value of the thermal diffusion fctor; $\alpha_{T.e}$, $\alpha_{T.hs}$, experimental value of the thermal diffusion factor and the theoretical value calculated for hard spheres; $T^* = kT/\varepsilon$, reduced temperature; ε/k, parameter of the intermolecular interaction potential function in K.

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