EXPERIMENTAL STUDY OF THE THERMAL DIFFUSION CONSTANT
OF Kr–N₂O AND NH₃–CO₂ MIXTURES

A. F. Zolotukhina

Some new experimental data regarding the thermal-diffusion constants of Kr–N₂O and NH₃–CO₂ mixtures, obtained in a two-cylinder experimental apparatus, are presented.

Research into the thermal-diffusion separation of binary gas mixtures has shown [1-11] that the greatest difference between theoretical and experimental results in relation to the thermal-diffusion constant occurs for mixtures of polyatomic gases, especially those containing a polar component. The thermal-diffusion constant \( \alpha_T \), being a function of the difference between the masses and sizes of the molecules, depends very substantially on the dynamic characteristics of collisions between these molecules, including the effects of inelastic collisions. However, allowance for the dipole moment and inelastic collisions when calculating the thermal-diffusion constant does not always lead to satisfactory results.

The experimental and theoretical analysis of the thermal-diffusion constants of Kr–N₂O and NH₃–CO₂ mixtures which we shall present in this paper has shown that the theory incorporating the inelastic collisions of molecules agrees less closely with experiment than that which only allows for elastic collisions.

We made an experimental determination of the thermal-diffusion constant with the aid of a two-bulb apparatus, the construction of which was described in [12]. The gas was analyzed by the thermal-conductivity method, using sensitive thermoresistor units of the ST1-19 type. The gases in question had the following purities: Kr–99.97% Kr; N₂O–medically pure; CO₂–99.8% CO₂; NH₃–99.8% NH₃.

Kr–N₂O. The temperature dependence of the thermal-diffusion constant of the Kr–N₂O mixture was studied by Datta et al. [9] for the case \( x_1 = x_2 \) in the temperature range \( T = 362-485 \)°K. Since \( \alpha_T \) falls sharply with falling temperature at 400–363°K, these authors suggest that at a temperature on the order of \( T = 325 \)°K \( \alpha_T \) may assume a zero value, and at lower temperatures it may even change sign.

We studied the thermal-diffusion constant \( \alpha_T \) of the Kr–N₂O mixture at \( T = 309-356 \)°K. In this case \( T_1 = 293.5 \)°K and \( T_2 = 323, 348, 373, 393, 415, 423, 457 \) (Fig. 1). The error of the results was ±4%.

We see from Fig. 1 that the value of \( \alpha_T \) is positive over the whole temperature range studied and increases with rising temperature, first rapidly and then in the range \( T = 348-356 \)°K more slowly. Our experimental results agree with those of [9].

We calculated the thermal-diffusion constant in accordance with the Chapman–Enskog theory, using the Lennard-Jones (12-6) and (12-6-5) potentials [14, 15]. The N₂O molecule has a weak dipole moment, and as indicated in Fig. 1 its influence may be neglected. Earlier calculations [15] showed that the quadrupole moment of this molecule could only make an appreciable contribution to \( \alpha_T \) at low temperatures, at which inversion was encountered.

Allowance for the inelastic collisions was made by the Monchick et al. method [16], based on the quantum-mechanical theory of Wang-Chang and Uhlenbeck [17, 18]. We also used experimental values of the thermal conductivity of pure Kr and N₂O gases taken from [19, 20].

Fig. 1. Thermal-diffusion constant as a function of temperature (°K) for a Kr--N$_2$O mixture ($x_1 = x_3$). Experimental data: 1) author's; 2) [9]. Calculated data: 3) by the Lennard-Jones (12-16) potential; 4) the (12-6-5) potential; 5) $\alpha_{ij}$ allowing for inelastic collisions.

Fig. 2. Concentration dependence of the thermal-diffusion constant $\alpha_T$ for an NH$_3$--CO$_2$ mixture at $T = 330^\circ$K. Points) experimental data. Calculated data: 1) using the (12-6-3) potential [13]; 2) $\alpha_{ij}$ allowing for inelastic collisions.

see on comparing the calculated data with experiment (Fig. 1) that the $\alpha_T$ data obtained after allowing for the inelastic collisions of the molecules be an order of magnitude above the experimental results. The Chapman--Enskog theory gives results agreeing more closely with experiment.

NH$_3$--CO$_2$. For the NH$_3$--CO$_2$ mixture no published data regarding the thermal-diffusion constant are available. It should be noted that very few investigations have yet been carried out for mixtures of NH$_3$ with other gases; NH$_3$ is one of a number of gases in which the molecules have a high dipole moment, so that a study of thermal-diffusion separation in mixtures of NH$_3$ with other gases might produce useful information regarding the effect of the dipole moment on the value of $\alpha_T$.

We studied the concentration dependence of the thermal-diffusion constant of the NH$_3$--CO$_2$ mixture at a mean temperature of $T = 330^\circ$K ($T_1 = 293.5^\circ$K; $T_2 = 373^\circ$K) (Fig. 2). The accuracy of the resultant data was estimated as ±4.6%.

It follows from Fig. 2 that, despite the considerable scatter in the experimental data, the general behavior of the concentration dependence of $\alpha_T$ is characterized by a positive deviation from the linear relationship and does not obey the relationship proposed in [10]. Data calculated by the Chapman--Enskog theory using the (12-6-3) potential [13] fail to describe the experimental results; the same applies to the theory of Monchick et al. [16] allowing for the inelastic collisions of the molecules.

This disagreement between theory and experiment may be associated with the fact that the NH$_3$ is paired with CO$_2$. Experiments [21-24] have shown that the behavior of the thermal-diffusion coefficient $\alpha_T$ of mixtures of CO$_2$ even with certain inert gases (Ar--CO$_2$, Ne--CO$_2$, Xe--CO$_2$) exhibits a number of singularities which have never yet received a proper physical explanation.

As in the case of the Kr--N$_2$O mixture, the theory allowing for inelastic collisions between the molecules in the NH$_3$--CO$_2$ mixture disagrees more seriously with experiment than the Chapman--Enskog theory.

LITERATURE CITED

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