CONCENTRATION DEPENDENCE OF THERMODIFFUSION CONSTANT OF H_2—He AND N_2—N_2O MIXTURES

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Experimental data on the thermodiffusion constants of H_2—He and N_2—N_2O mixtures obtained on a two-tank instrument are presented. The experimental results are compared with theoretical results based on the allowance for elastic and inelastic collisions.

Knowledge of the forces of interaction between molecules in gases and gas mixtures is usually obtained through the study of transfer phenomena and their quantitative characteristics: transfer coefficients, especially the coefficient of thermal conductivity, and viscosity, diffusion, and thermodiffusion coefficients. It is assumed that the dependence of the thermodiffusion factor on the type of intermolecular forces is much greater than for the other transfer coefficients. However, up to now the existing data on the thermodiffusion constant cannot be used in full measure to obtain information on the intermolecular interaction. The considerable discrepancies between the experimental data of different investigators and the poor correspondence, and in a number of cases the incompatibility between theory and experiment complicate the practical use of experimental values for the thermodiffusion constant.

Recently the principal attention has been paid to the study of the thermodiffusion constant in mixtures of polyatomic gases, since the existing theories of thermodiffusion for mixtures of polyatomic gases in a majority of cases do not give agreement with experiment. In particular, the greatest disagreement between the theoretically calculated and experimental results is observed for mixtures having an extremal point (maximum or minimum) in the concentration dependence of the thermodiffusion constant [4, 5]. The greatest disagreements among the experimental data of different investigators are also observed for these mixtures. In this sense it is interesting to investigate the mixture H_2—He for which there are quite contradictory experimental data in the literature [6-12].

For example, Barua et al. [11, 12] in a study of the concentration dependence of α_T of this mixture found the appearance of a number of minima which were shifted toward an increase in hydrogen concentration with a decrease in temperature. The depth of the minima varied as a function of the temperature. Barua et al. assumed that inelastic collisions of the molecules affect the thermodiffusion process to a strong degree. Mathur and Watson [7] checked the results of [11, 12] and also found the existence of minima in the concentration dependence in the same temperature range, with this minimum not being so clearly expressed and shifted toward an increase in hydrogen concentration with a decrease in temperature. The minimum disappeared at high temperatures. We should note that exactly the same pattern is observed for the thermal conductivity of the H_2—He mixture [13-16].

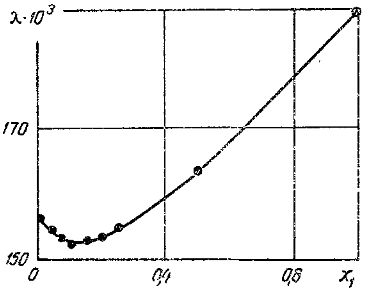

Fig. 1. Dependence of thermal conductivity λ on concentration for H_2—He mixture at T = 328°K [15]. $\lambda \cdot 10^3$, W /m · deg.

The studies of Taylor and Wiesman [6], conducted in the same temperature range as the studies of [11, 12], did not confirm the presence of minima in the concentration dependence of α_T.

Taylor [17] made a further experimental study of the thermodiffusion constant of the H_2—He mixture as a function of the

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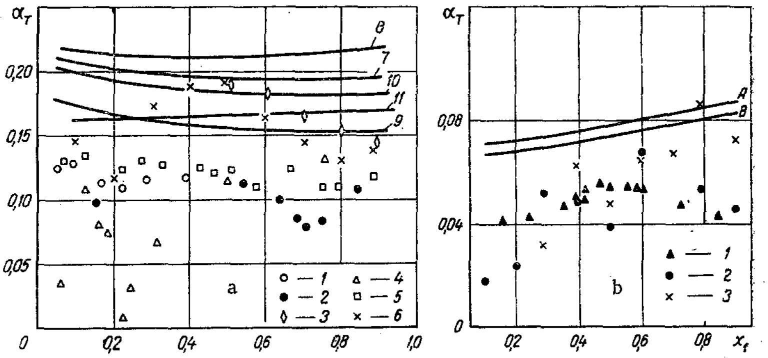

Fig. 2. Dependence of thermodiffusion constant α_T on concentration for H_2—He mixture: a) experimental data: 1) $\bar{T}$ = 320°K; 2) 129.3 [8]; 3) 326 [9]; 4) 335 [11]; 5) T_1 = 293°K, T_2 = 498°K [10]; 6) T_1 = 294.3°K, T_2 = 373°K (our data). Theoretical data with T_1 = 377.6°K, T_2 = 464.2°K: for the Lennard-Jones potential (12-6): 7) α_{T_1}, 8) α_{T_k}; for the (exp-6) potential: 9) α_{T_1} (α = 12), 10) α_{T_1} (α = 15); 11) allowance for inelastic collisions ($\bar{T}$ = 335°K) [11]. For the mixture N_2—N_2O: b) experimental data: 1) T_1 = 283°K, T_2 = 373°K [9]; 2) T_1 = 294.3°K, T_2 = 327°K; 3) T_1 = 294.3°K, T_2 = 370°K (our data). The theoretical data are calculated from the Lennard–Jones potential (12-6) with allowance for dipole (A) and quadrupole (B) moments.

composition at 82°K and compared the results with theoretical values for α_T obtained using quantum-mechanical collision integrals for the potential (exp-6). In this case neither a maximum nor a minimum was discovered in the concentration dependence α_T. We note that the author obtained data earlier on α_T for the same mixture at temperatures of T = 215, 273, and 373°K and no anomalous behavior of the concentration dependence α_T was found. Such a picture is also described in [17], which presents the results of a study of the concentration dependence of α_T at the temperatures T_1 = 293 and 294°K and T_2 = 498, 596.2, 694, and 795.4°K.

Taylor [17] assumes that inelastic collisions make a relative contribution to the thermodiffusion of no more than 10% at low temperatures and no more than 1% above 200°K. The experimental data agree well with the theory using quantum mechanical collision integrals.

We made a study of the concentration dependence of the thermodiffusion constant of the H_2—He mixture at T = 330.57°K (T_1 = 294.3°K, T_2 = 373°K). The gases studied were He of high purity, containing 99.993% He, and H_2 containing 98.9% H_2. The study was conducted on a two-tank instrument for which a description was given in [18]. Since the analysis of the gas composition was conducted by the method of thermal conductivity it was necessary that the concentration dependence of the thermal conductivity of this mixture not have anomalies (maximum or minimum) in the concentration range of interest to us. This question was also touched on by the authors of [8], who suggested that works on the study of the concentration dependence of the thermodiffusion constant of H_2—He in which the analysis of the mixture was carried out by the katharometer method should be excluded from consideration. However, as seen from Fig. 1, in which the concentration dependence of the thermal conductivity of the mixture H_2—He at $\bar{T}$ = 328°K [15] is presented, the presence of a minimum is observed mainly in the region of 0-0.2 H_2. In our opinion, therefore, at such temperatures the method of analysis by thermal conductivity is fully applicable for the study of the concentration dependence of α_T of the H_2—He mixture in the concentration region of 0.1-0.8 H_2.

The results of our studies in comparison with the data of other authors are presented in Fig. 2a. Both the theoretical results obtained from strict kinetic theory using different potential functions and data allowing for the inelastic collisions of the molecules are given here. It is seen that not one of the theoretical curves presented can describe the anomalous behavior of the concentration dependence of the thermodiffusion constant of the H_2—He mixture.

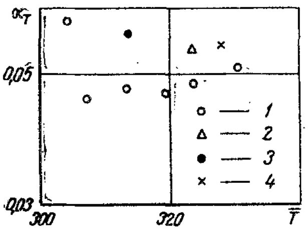

Fig. 3. Dependence of thermodiffusion constant on temperature for N_2—N_2O mixture (x_1 = 0.45): 1) [21]; 2) [20]; 3, 4) our data. $\bar{T}$, °K.

It should be noted, however, that in the H_2—He mixture the light molecule (H_2) has a greater effective-collision diameter than the heavy molecule (He) and therefore it is possible that the existence of a minimum at certain temperatures may be the result of the presence of a "mass effect" and a "size effect" [4].

Mixture of N_2 and N_2O. Initial gases: the N_2 was 99% N_2 and the N_2O was medicinally pure.

While anomalies of approximately the same nature in the concentration dependence of the thermal conductivity and the thermodiffusion constant are observed for the H_2—He mixture, one cannot say the same for the N_2—N_2O mixture. According to [19] the dependence of the thermal conductivity on the concentration for the N_2—N_2O mixture has a negative deviation from the linear law $\lambda_1 = \lambda_1 x_1 + \lambda_2 x_2$, whereas the concentration dependence of the thermodiffusion constant α_T is characterized in general by a positive deviation (Fig. 2b). As seen from Fig. 2b, the concentration dependence of α_T for the N_2—N_2O mixture at a temperature of $\bar{T}$ = 310.2°K which we studied shows the presence of a maximum. With an increase in temperature the maximum is shifted toward an increase in the content of the light component in the mixture. In particular, at $\bar{T}$ = 329°K the concentration dependence of α_T has the form of an increasing convex curve. The data of the authors of [20] at $\bar{T}$ = 323°K, according to which the concentration dependence of α_T has a maximum at x_1 = 0.5, are also presented in Fig. 2b. However, the theoretically calculated values of α_T with allowance for dipole (A) and quadrupole (B) moments do not give even qualitative correspondence with experiment.

The temperature dependence of the thermodiffusion constant is presented in Fig. 3. It is interesting to note that according to the data of [21] the temperature dependence of α_T has the form of a concave curve, i.e., with an increase in temperature α_T first decreases and then increases. The data interpolated from our measurements and the measurements of [20] for a concentration x_1 = 0.45 also show a decrease in α_T with an increase in temperature. Such a dependence is not satisfied for other concentrations, however. The quantity and scatter of the experimental data on the concentration dependence of the thermodiffusion constant at this stage do not allow one to bring out any regularity in the behavior of the temperature dependence of α_T for different concentrations.

The maximum error in the experimental data is estimated as follows: 4.6% for the H_2—He mixture; 6.0% for N_2—N_2O.

It should be noted that the use of commercial gas as one of the components of the mixture may somewhat alter the true nature of the behavior of α_T with the composition (especially at extremal concentrations of the components of the mixture). However, according to Fig. 2a, where this change should be more clearly revealed, better agreement with the experimental data of other authors is observed at the extremal concentrations ($x_1 \to 0.1$, $x_1 \to 0.9$).

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