Mechanodiffusion of a moderately low-density binary gas mixture under Couette flow conditions

V. V. Vysotskiĭ and S. P. Bakanov

Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow
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Experimental observations of mechanodiffusion of a moderately low-density binary gas mixture under Couette flow conditions confirmed earlier theoretical predictions [S. P.Bakanov, B. V. Deryagin, and V. I. Roldugin, Inzh.-Fiz. Zh. **41**(1), 40 (1981); S. P. Bakanov and V. I. Roldugin, Kolloidn. Zh. **51**, 12 (1989)]. The experimental results confirmed the physical ideas underlying the theory. The effect can be used to separate gas mixtures and isotopes.

INTRODUCTION

A new effect called mechanodiffusion was predicted in Refs. 1 and 2. This effect may be described as follows: if a slightly rarefied binary gas mixture is in a slit channel formed by physically different surfaces a and b moving relative to one another at a velocity $\mathbf{u}$ and if the accommodation coefficients of the tangential momentum of molecules ε_{ik} are different for these surfaces ($i = a,b$; $k = 1,2$), an equilibrium difference between the concentrations of the components of the mixture proportional to u should be established.

This effect is due to diffusive creeping of the gas mixture similar to the thermal creep of an inhomogeneously heated gas. The latter is entirely due to thermal polarization of bodies in a stream of a slightly rarefied one-component gas, first pointed out in Ref. 3. The predictions of the theory of Ref. 3 were confirmed experimentally by subsequent investigations.[4]

It would undoubtedly be of interest to observe experimentally the effect of mechanodiffusion in a binary gas mixture because this would provide the next step in the understanding of the processes that occur near the interface between the phases. Moreover, such observations would provide another proof (in addition to the results reported in Ref. 4) of the conclusion, which was questioned earlier (see, for example, Ref. 5) that the concepts and methods of thermodynamics of irreversible processes can be used to describe the phenomena that occur in Knudsen layers. The mechanodiffusion effect is important also from the point of view of practical applications as the basis of a new method for the separation of gas mixtures.

The present paper reports an experimental observation of the mechanodiffusion effect in a binary gas mixture under Couette flow conditions.

1. THEORY

The velocity of diffusive creep can be described by an expression of the form

$$v_{DS}^{(i)} = -K_{DS}^{(i)} D_{12} \nabla c, \tag{1}$$

where D_{12} is the mutual diffusion coefficient of the components of the mixture; c is the concentration of one of the components (specifically the first); $K_{DS}^{(i)}$ is the diffusive creep coefficient which is a function of the property of components of the mixture, and also of the nature of the interaction between molecules in the mixture and the ith surface. As a rule, we have $\varepsilon_{ik} \approx 1$ (almost diffuse reflection), so that we can quite accurately assume that

$$K_{DS}^{(i)} = \tilde{K}_{DS} + \alpha \frac{\varepsilon_{i1} - \varepsilon_{i2}}{\varepsilon} = \tilde{K}_{DS} + \alpha \frac{\Delta\varepsilon_i}{\varepsilon}, \tag{2}$$

where $\tilde{K}_{DS}$ and α are functions of just the properties of the components of the mixture, and $\varepsilon \approx 1$ is an average value of the coefficients ε_{ik}.

In the range of low Knudsen numbers $\mathrm{Kn} = \lambda / h \ll 1$ (λ is the mean free path of molecules in the mixture and h is the gap between the surfaces forming the flow channel) and for a constant pressure p the equilibrium value of the drop in the concentrations of the components of the mixture inside the channel established by simultaneous mechanodiffusion and ordinary diffusion processes is given by the expression[2]

$$\Delta c = (K_{DS}^{(a)} - K_{DS}^{(b)}) \frac{u\eta L c(1-c)}{ph^2}, \tag{3}$$

where L is the length of the channel (along the direction of u) and η is the dynamic viscosity of the mixture. The coefficients $K_{DS}^{(a)}$ and $K_{DS}^{(b)}$ represent the creep of the mixture along the surfaces a and b. Therefore, under these conditions a concentration drop appears in the case (and only in that case) when the difference $K_{DS}^{(a)} - K_{DS}^{(b)}$ is nonzero. This in turn implies that the effect can occur only for $\Delta\varepsilon_z \neq \Delta\varepsilon_b$, i.e., it is related to the difference between the nature of the interaction of molecules in a mixture and the surfaces of the channel, and (in the final analysis) is due to the properties of these surfaces (for a given gas mixture).

In the development of the experimental method it has become clear that the simplest way of ensuring the Couette flow of a gas mixture is to place it inside the gap between two coaxial cylinders with large radii R_a, $R_b \gg R_a - R_b = h$, which are rotating in opposite directions. The working channels can be established by dividing the space between the cylinders along the cylinder generators using one or more suitable partitions. However, this gives rise to a number of new effects that influence the concentration drop Δc.

The most important of the new phenomena is the curvature effect.[6] We are speaking here of the influence of the curvature of the surface on the diffusion glide of the mixture. At low values of λ / R (R is the radius of curvature of the surface, which in our case is represented by the radii of the cylinders) this influence is governed by a correction of the type

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$$\bar{K}_{DS}=K_{DS}^{(0)}\left(1+\beta\frac{\lambda}{R}\right)=K_{DS}^{(0)}\left(1+\beta\frac{h}{R}\text{Kn}\right).$$

Here, $K_{DS}^{(0)}$ is understood to be the coefficient of the diffusion glide along a plane surface. The coefficient β is a function of the properties of the components of the mixture. The sign of the curvature (i.e., whether the curvature is convex or concave in the case under discussion) is of considerable importance. Therefore, in the case of two cylinders the difference due to the curvature is

$$K_{DS}^{(a)}-K_{DS}^{(b)}\approx 2K_{DS}^{(0)}\beta(h/R)\text{Kn}.$$

The second effect can appear if in the course of our experiments the condition that the pressure in the mixture be constant along the channel (in the azimuthal direction) breaks down. When the cylinders are rotated in the opposite directions, this constancy is retained as long as the linear velocity of the working surfaces of the cylinders are equal, i.e., as long as

$$\Delta u=u_a-u_b=\omega_a R_a-\omega_b R_b=0,$$

where ω_i are the angular velocities of rotation of the cylinders. In the opposite case a pressure drop appears along the channel and this drop is proportional to the difference given above:

$$\Delta p=\gamma\frac{\eta L}{h^2}\Delta u$$

(γ is a coefficient depending on the channel geometry and on the experimental conditions); consequently, we can expect barodiffusion[7] of the components of the mixture and this effect gives rise to an additional term in Eq. (3) which is of the $k_p(\Delta p/p)c(1-c)$ type, where k_p is the barodiffusion coefficient. Depending on the signs of k_p and Δu, such barodiffusion can increase or reduce the effect under investigation.

There is a further effect which can influence the experimental results. It is associated with the presence of two opposite fluxes of the mixture inside the channel, which are created by rotation of the cylinders in opposite directions. One part of the mixture, which is in the inner zone of the gap between the cylinders is moving, for example, in the clockwise direction, whereas the other is moving in the opposite direction. If the composition of the mixture in the direction of rotation is variable, then such flow should favor (in addition to ordinary diffusion) equalization of the concentration along the channel because of convective motion of the components of the mixture out of the zone with a higher concentration to one where the concentration is lower. However, diffusion of this mixture across the channel, which reduces the difference between the concentrations in the opposite fluxes discussed above, also automatically reduces the influence of this effect. If

$$\frac{u}{L}\frac{h^2}{D_{12}}\approx\frac{h}{L}\text{Re}\ll 1$$

(Re is the Reynolds number), we can ignore convective mixing.

Summarizing our analysis, we can write down the expression for the equilibrium value of the concentration drop in the form

$$\Delta c=\Delta c_\varepsilon+\Delta c_R+\Delta c_p,$$

where

$$\Delta c_\varepsilon=\alpha(\Delta\varepsilon_a-\Delta\varepsilon_b)u\varphi\propto\text{Kn},$$

$$\Delta c_R=2K_{DS}^{(0)}\beta(h/R_a)\text{Kn}\,u\varphi\propto\text{Kn}^2,$$

$$\Delta c_p=k_p\gamma\Delta u\varphi\propto\text{Kn},\quad \varphi=\eta Lc(1-c)/ph^2.$$

Introducing the notation

$$u=R_a\left(\omega_a+\frac{R_b}{R_a}\omega_b\right)=R_a\omega,\quad \Delta u=R_a\left(\omega_a-\frac{R_b}{R_a}\omega_b\right)=R_a\Delta\omega,$$

we can rewrite the above expression in the form

$$\Delta c=A(\text{Kn})R_a\omega+B(\text{Kn})R_a\Delta\omega, \qquad (4)$$

where

$$A(\text{Kn})=[\alpha(\Delta\varepsilon_a-\Delta\varepsilon_b)+2K_{DS}^{(0)}\beta(h/R_a)\text{Kn}]\varphi,$$

$$B(\text{Kn})=k_p\gamma\varphi.$$

2. EXPERIMENTAL METHOD

The Couette flow in our experiment occurred in an annular channel between two coaxial cylinders rotating in opposite directions about a vertical axis. The space between the cylinders was separated by vertical partitions into three identical sections. The investigated mixture was passed through these channels in the downward direction. The bottom plane of each section had escape apertures. The change in the composition of the mixture was determined at the exit.

We can easily see that since the second term in Eq. (4) depends linearly on $\Delta\omega$, plotting the experimental linear dependence of Δc on $\Delta\omega$ yields the value of $A(\text{Kn})$ at the point of intersection of this straight line with the ordinate, i.e., we can find the effects of mechanodiffusion in its pure form. If the working surfaces of the cylinders are physically different, then Δc is governed by two terms, Δc_ε and Δc_R. Since these terms can generally have opposite signs, it follows that the resultant mechanodiffusion effect can sometimes vanish. It is therefore desirable to establish the contribution of one of them under the conditions when the contribution of the other is close to zero *a priori*. In our case such a situation is realized if the cylinders are made from the same material and their surfaces are treated in the same manner.

Figure 1 shows schematically the apparatus we used. The cylinders were inside a vacuum chamber and were driven by two electric motors using a magnetic coupling. A vacuum system based on a two-rotor mechanical pump ensured that the lowest pressure in the chamber was $\sim 10^{-2}$ Pa. Formation of a flux of the investigated mixture with a given degree of rarefaction took place when a valve 3 was closed and involved continuous supply of the mixture to the chamber and its removal via apertures 8. The monitoring and measurements of the volume flux of each component of the mixture were carried out at the entry of the chamber using needle leak valves and liquid flow meters. The pressure of the mixture in the chamber was measured using an oil cup manometer and a PMT-2 sensor.

Equal parts of the mixture, one of which was enriched and the other depleted of one of the components, were admitted through an appropriate set of three apertures 8 locat-

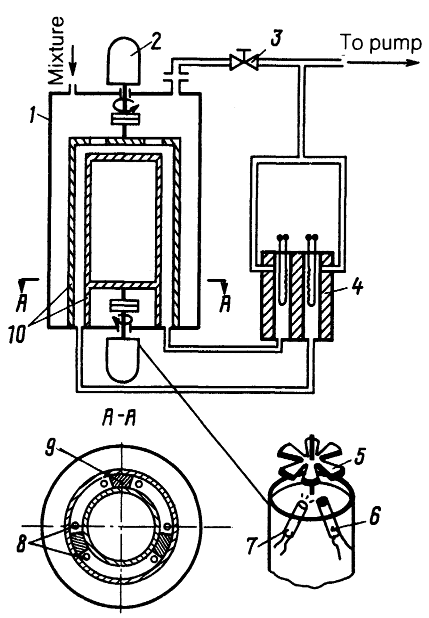

FIG. 1. Schematic diagram of the apparatus: 1) vacuum chamber; 2) electric motor; 3) vacuum valve; 4) katharometer; 5) "asterisk"; 6) photodiode; 7) incandescent lamp; 8) escape aperture; 9) partitions; 10) working cylinders.

ed on both sides of partitions 9, and was circulated through chambers of a differential detector based on the thermal conductivity (katharometer).[8] The sensitive elements of this katharometer (tungsten helices) were parts of adjoining arms of a Wheatstone bridge circuit. The other two arms were sets of resistors of the R-4831 type. The measuring diagonal of the bridge included a photogalvanometric amplifier with a pointer microvoltmeter at the output. The bridge was balanced when the cylinders were at rest. Rotation of the cylinders altered the concentration of the mixture by Δc in the chambers; this was detected because it gave rise to a bridge unbalance, so that an unbalanced voltage ΔV appeared at the entry to the amplifier. Using the known[9] expressions for the currents flowing through the components of such a bridge circuit in the presence of a constant bridge supply current $I=$ const, we obtained $\Delta V = 1/4 I \Delta r$, where $\Delta r = kr\Delta T$ is the change in the electrical resistance r of the sensitive elements of the katharometer as a result of a change in their temperature by ΔT, due to a change in the composition of the mixture in the detection chambers, and $k \approx 5\times 10^{-3}$ K^{-1} is the temperature coefficient of the resistance of tungsten. Obviously,

$$\Delta T = \frac{\Delta \bar{\varkappa}}{\bar{\varkappa}}(T_1 - T_2) = \frac{\varkappa_1 - \varkappa_2}{\bar{\varkappa}}(T_1 - T_2)\frac{\Delta c}{2},$$

where $\varkappa_1$ and $\varkappa_2$ are the thermal conductivities of the components of the mixture; $\bar{\varkappa} = c\varkappa_1 + (1-c)\varkappa_2$; $T_1 - T_2$ is the difference between the temperatures of the sensitive element and the body of the katharometer. We finally obtain

$$\Delta V = \frac{1}{8} Irk \frac{\varkappa_1 - \varkappa_2}{\bar{\varkappa}}(T_1 - T_2)\Delta c. \qquad (5)$$

In recording the frequencies of rotation of the cylinders we placed on the axis of each them an "asterisk" 5 below which we located FD-3 photodiode and an NM-6.3 incandescent lamp. When the motor was operating, the scattering of a light flux by the sectors of the star system during the passage above the lamp created electrical pulses at the photodiode output and these, after amplification with a wide-band U7-1 amplifier, were recorded with an RChZ-07-0002 electronic frequency meter.

We investigated a 50% helium–argon mixture. This mixture was selected primarily because of the considerable difference between the thermal conductivities of Ar and He, which ensured a sufficient sensitivity of the detector [see Eq. (5)].

The average radius of the cylinders was $\bar{R} = 75$ mm and the height was $H = 250$ mm; the width of the channel was $h = 6$ mm and the relative angular velocity of the rotating cylinders was $\omega = 40$–100 s^{-1}. The rate of flow was of the order of 0.1 cm^3/s; the other parameters were $I \approx 35\times 10^{-3}$ A, $r \approx 100\ \Omega$, and $T_1 - T_2 \approx 140$ °C.

3. EXPERIMENTAL RESULTS

In the course of our experiments we measured ΔV for different values of $\Delta\omega$ and a fixed Knudsen number Kn, which was governed by the pressure inside the chamber. This was followed by similar measurements under conditions represented by other Knudsen numbers. We carried out two series of such experiments. In the first series we found the contribution made to the mechanodiffusion only by Δc_R, while in the second series we found the overall contribution $\Delta c_R + \Delta c_a$. This was achieved as follows: in the first series of measurements both cylinders were made of stainless steel and the working surfaces had an approximately the same grade of finish; in the second series the inner cylinder was made of Dural and the outer cylinder was made of stainless steel and, moreover, the grade of finish of the two surfaces was different.

The experimental dependences $\Delta V^* = \Delta V / R_a\omega$, and $\Delta\omega^* = \Delta\omega/\omega$ are plotted in Figs. 2a and 2b, respectively. The straight lines in these figures represent the results of an analysis of the experimental data by the least-squares method.

We also carried out a series of experiments on each of the gases, Ar and He, using stainless steel cylinders. These experiments were done at the same pressure corresponding to the Knudsen number Kn$\approx$0.175 for the mixture. The results of these experiments were analyzed by the least-squares method and are included in Fig. 2a, where the dashed line represents Ar and the chain line represents He.

Bearing in mind that $\Delta c_R \propto$ Kn^2 and $\Delta c_\varepsilon \propto$ Kn, and using Eq. (5), we found the value of A(Kn) from the dependences in Fig. 2 and then plotted the corresponding dependences A/Kn $= a + b$ Kn by estimating the contribution of each of these effects. The dependences obtained are plotted in Fig. 3. An analysis by the least-squares method yielded the following linear regressions:

$$A/\mathrm{Kn} = (-0{,}01 + 1{,}2\,\mathrm{Kn})\cdot 10^{-8}, \quad \sigma = 10^{-8};$$

$$A/\mathrm{Kn} = (0{,}11 + 1{,}3\,\mathrm{Kn})\cdot 10^{-8}, \quad \sigma = 1{,}5\cdot 10^{-8}.$$

Hence, we obtained the values $K_{DS}^{(0)}\beta \approx -0.1$ and $\alpha(\Delta\varepsilon_a - \Delta\varepsilon_b) \approx 10^{-3}$.

The slopes of the straight lines in Fig. 2 represented the magnitude of the effect associated, on the one hand, with the

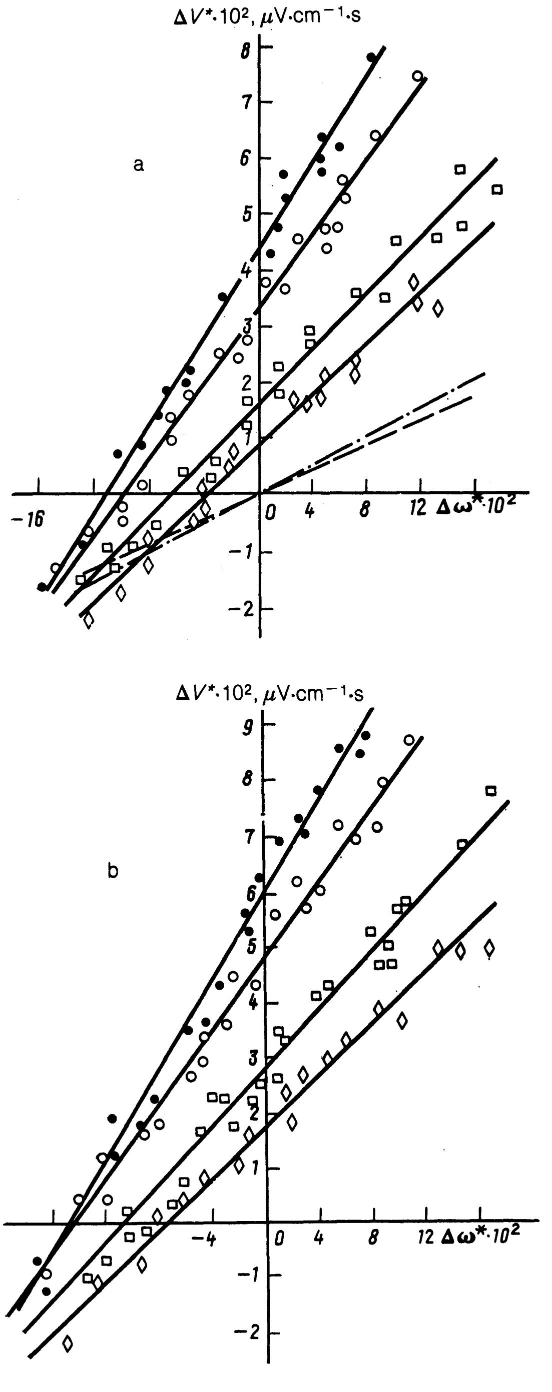

FIG. 2. Experimental results: a) both cylinders made of stainless steel; b) inner cylinder made of Dural and outer cylinder made of stainless steel; ◇) Kn = 0.135; □) 0.175; ○) 0.25; ●) 0.28.

difference between the pressures in the detection chambers of the katharometer because of the pressure drop at the ends of the working channels when $\Delta\omega \neq 0$ (this was the reason for the slopes of the experimental straight lines for Ar and He) and, on the other, with the barodiffusion of the components of the mixture caused by this pressure drop. By analogy with Eq. (5), we can show that

$$\Delta V = {}^1/_8 Irk(T_1 - T_2)\Delta p'/p,$$

where $\Delta p'$ is the difference between the pressures in the detection chambers of the katharometer. Subtracting the average slopes of the experimental dependences for pure Ar and He from the corresponding values for the mixture and bearing in mind that the katharometer sensitivity was inversely proportional to the pressure, we obtained values of $B(\mathrm{Kn}) \propto \mathrm{Kn}$. We plotted this dependence in Fig. 4 using the average of the measurements carried out in the two series.

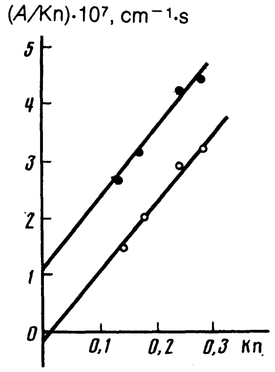

FIG. 3. Dependence of the mechanodiffusion rate on Kn: ○) both cylinders made of stainless steel; ●) inner cylinders made of Dural and the outer cylinder made of stainless steel.

It had been established experimentally that $\Delta p' \approx 0.05\Delta p$. Using the experimental dependence of ΔV^* on $\Delta\omega^*$ for the pure gas, we could derive the relationships between Δp and $\Delta\omega$, i.e., we could determine the value of the coefficient γ (Sec. 1), which amounted to ≈ 0.1. Bearing this point in mind and knowing the slope of the dependence plotted in Fig. 4, we found $k_p \approx 0.2$.

It should be pointed out that the numerical values of the coefficients we obtained should be regarded only as rough estimates.

4. DISCUSSION OF RESULTS

Our experimental results showed that the passage of an Ar–He mixture through the space between two coaxial cylinders rotating in opposite directions resulted in separation of the components of the mixture. This separation was due to the difference between the signs of curvature of the cylinder surfaces, the different physical nature of the surfaces, and in the $\Delta\omega \neq 0$ case also due to barodiffusion. The values of the quantities k_p, $K_{DS}^{(0)}\beta$, and $\alpha(\Delta\varepsilon_a - \Delta\varepsilon_b)$, associated with these effects were determined.

The straight lines plotted in Figs. 2a and 2b confirmed

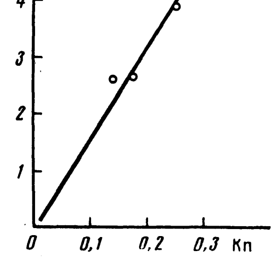

FIG. 4. Dependence of barodiffusion rate on Kn.

the linear nature of the dependence of the mechanodiffusion effect on the velocity of rotation of the centers. The dependences of A and B on Kn plotted in Figs. 3 and 4 were in agreement with the theoretical predictions.

We found no published experimental data at all on $K_{DS}^{(0)}\beta$ and $\alpha(\Delta\varepsilon_a - \Delta\varepsilon_b)$. The expression for $K_{DS}^{(0)}\beta$ derived in Ref. 6 is valid if the values of the masses m_k and diameters d_k of molecules of the components of the mixture are similar. It is clear from general considerations that we have $\beta \sim 1$. According to the results of Ref. 1, if

$$2m_1/(m_1+m_2)=1{,}9, \quad 2d_1/(d_1+d_2)=1{,}8, \quad \varepsilon=1,$$

which were the conditions close to those in our experiments, we should have $K_{DS}^{(0)} = -0.26$. Therefore, the value of $K_{DS}^{(0)}\beta$ estimated from the experimental results is physically reasonable. A comparison of $\alpha(\Delta\varepsilon_a - \Delta\varepsilon_b)$ with the results of calculations of K_{DS} for several values of m_k, d_k, and ε_{ik} given in Ref. 2 including the values of ε_{ik} taken from the published literature (see, for example, Refs. 10–12) showed that this value was again reasonable. The sign and order of magnitude of k_p were in agreement with the experimental value obtained for an Ar–He mixture in Ref. 13.

The presence of a gap ~ 0.5 mm wide between the surfaces of the rotating cylinders and the partitions (Fig. 1), and also between the lower ends and the base of the chamber, reduced the degree of separation because of escape of the mixture. Consequently, the values of the coefficients given above were somewhat underestimated.

CONCLUSIONS

The experimental results reported above, namely the nature of the dependence of the measure effect on ω, $\Delta\omega$, and on the Knudsen number, as well as the physically reasonable values of the quantities $K_{DS}^{(0)}\beta$, k_p, and $\alpha(\Delta\varepsilon_a - \Delta\varepsilon_b)$, deduced from these dependences, can be regarded—in our opinion—as proof of the existence of the theoretically predicted mechanodiffusion effect in a slightly rarefied binary gas mixture.

Moreover, the value of $\alpha(\Delta\varepsilon_a - \Delta\varepsilon_b)$ found in this investigation should be of interest from the point of view of studies of the interaction of gas molecules with surfaces. To the best of our knowledge, adequately sensitive differential methods for the detection of the differences between the accommodation properties of the surfaces has not yet been developed.

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