

crystal volume;  $J_{1\sigma}f(r)dr$ , intensity of mass transfer from carrier phase to  $\sigma$  phase in unit volume per unit time;  $J_{\sigma 1}f(r)dr$ , intensity of mass transfer from  $\sigma$  phase into carrier phase;  $\rho_1$ , mean density of carrier phase,  $\rho_1 = \rho_1^0 \alpha_1$ ;  $\alpha_1$ , volume content of carrier phase,  $\alpha_1 + \int_0^R (r + V_{\sigma}) f(r) dr = 1$ ;  $R$ , volume of largest crystal;  $c_{ki}$ , concentration (mass fraction) of component in  $i$ -th phase;  $v_1$ ,  $v_2(r)$ , velocity of carrier phase and particle of dimension (volume)  $r$ ;  $P$ , pressure;  $f_{12}$ , force of interaction between carrier phase and particle of dimension  $r$ , referred to particle mass;  $u_i$ , specific energy of  $i$ -th phase  $F_i$ , mass force acting on  $i$ -th phase;  $\Sigma$ , surface-tension coefficient;  $q_{i\sigma}$ , heat flux from the  $i$ -th phase to the  $\sigma$  phase;  $i_i$ , enthalpy of the  $i$ -th phase;  $T_i$ , temperature of the  $i$ -th phase;  $\mu_{ki}$ , chemical potential of the component in the  $i$ -th phase;  $\bar{\nabla}q_1$ , heat flux due to heat conduction in the first phase;  $Q_i$ , external heat flux in the  $i$ -th phase;  $S$ ,  $s_i$ , specific entropy of the whole mixture and the  $i$ -th phase, respectively;  $J$ , flux of thermodynamic forces;  $X$ , thermodynamic force;  $R$ , universal gas constant;  $\gamma$ , activity coefficient;  $D$ , diffusion coefficient,  $L_{1\sigma}$ ,  $L_{\sigma 1}$ ,  $L_{2\sigma}$ ,  $L_{\sigma 2}$ , kinetic coefficients;  $S_S$ , surface of the crystal;  $d$ , step height;  $\nu$ , oscillation frequency of atom;  $U_a$ , activation energy of transition between two neighboring equilibrium positions of the molecule at the surface;  $\beta_M$ , mass-transfer coefficient;  $c_S$ , equilibrium concentration at temperature  $T_2$ ;  $a$ , characteristic radius of particle;  $Nu = (\beta_M 2a)/D$ ;  $Re = (\rho_1^0 v_2 2a)/\mu_v$ ;  $\mu_v$ , viscosity coefficient of the solution;  $A$ , constant. Subscripts: 1, carrier phase; 2, disperse phase;  $\sigma$ ,  $\sigma$  phase;  $k$ , component;  $p$ , solvent;  $s$ , state of saturation;  $S$ , surface.

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#### ELEMENTARY KINETIC THEORY OF DIFFUSION IN GASES

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The results of research on the description of diffusion using the elementary kinetic theory are generalized. It is shown that for thermodiffusion and barodiffusion, this theory, bringing to light the physical essence of the phenomenon, leads to the same basic differential equations as the rigorous theory.

Introduction. The elementary kinetic theory first permitted expressing the transport coefficients (diffusion, viscosity, and thermal conductivity) in terms of the molecular characteristics of the gas. But, already with the description of the diffusion of a mixture of two gases, this theory encountered a number of difficulties. Boltzmann [1] obtained equations for the coefficients of diffusion of the separate components of binary mixtures, from which it followed that under isobaric-isothermic conditions each component has its own coefficient of diffusion, which leads to different flows of molecules in opposite directions. This should not occur with diffusion of gases in closed volumes (for example, in a pipe or in two volumes connected by capillaries). In this connection, Boltzmann assumed that the equations he obtained were not correct. Mayer [2] eliminated the contradiction by decreasing the flux of one type of molecule and increasing the flux of the other by an amount so that the two fluxes would equalize. The equations obtained by Mayer resulted in equal diffusion coefficients for components in a binary mixture, which is confirmed experimentally. However, Mayer's equation gave a strong concentration dependence of this coefficient, later called the coefficient of mutual diffusion, which is not observed experimentally. The strong concentration dependence of Mayer's diffusion coefficient was explained by the effect of homogeneous collisions of molecules. Maxwell [3], analyzing Loschmidt's experiments, already used an equation for the coefficient of mutual diffusion which did not contain a term that takes into account the effect of homogeneous collisions on the mean free path length. In all later theories, including also in the rigorous kinetic

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TABLE 1. Comparison of the Measured True Coefficients of Diffusion with the Values Calculated according to (11) at  $T = 298.2^\circ\text{K}$  and  $P = 1$  atm

System 1-2	$\bar{D}_1, \text{cm}^2 \cdot \text{sec}^{-1}$		$\bar{D}_2, \text{cm}^2 \cdot \text{sec}^{-1}$		$\sqrt{\frac{\mu_1}{\mu_2}}$	$\frac{\bar{D}_1}{\bar{D}_2}$
	expt.	theory	expt.	theory		
H <sub>2</sub> -N <sub>2</sub>	1,54	1,34	0,43	0,37	3,74	3,6
H <sub>2</sub> -O <sub>2</sub>	1,29	1,38	0,48	0,38	3,98	3,7
H <sub>2</sub> -Ar	1,49	1,35	0,40	0,35	4,46	3,7
H <sub>2</sub> -CO <sub>2</sub>	1,27	1,17	0,25	0,27	4,60	5,1
He-N <sub>2</sub>	1,19	1,20	0,41	0,36	2,65	2,9
He-O <sub>2</sub>	1,25	1,23	0,44	0,36	2,82	2,8
He-Ar	1,31	1,21	0,40	0,33	3,16	3,3
He-CO <sub>2</sub>	1,09	1,03	0,34	0,22	3,32	3,2

theory, when examining the mutual diffusion, only heterogeneous collisions are taken into account (the effect of homogeneous collisions in these theories is manifested only in higher order approximations).

Analyzing the elementary kinetic theory, Jeans [4] came to the conclusion that when molecules collide, the velocities do not change discontinuously, but there is a certain conservation (persistence) of their direction of motion before the collision. By introducing the persistence of velocities, Jeans was able to decrease considerably some of the contradictions between Boltzmann's theory of diffusion and experiment (according to Boltzmann, the magnitude of the ratio obtained for the trace coefficients of diffusion was higher). However, introducing persistence of velocities could not affect the negative attitude toward Boltzmann's theory of diffusion, which is based on the concept of a mean free path length.

After the discovery of the phenomenon of thermodiffusion in gases by Enskog and Chapman, it appeared that the elementary kinetic theory could not describe thermodiffusion (see, for example, [5, 6]) and this theory, being a primitive theory, in the best case describes some transport phenomena only qualitatively. Later, a number of investigators, for example, Fyrt (cited in [7]), Laranjeira [8], and others, obtained, with the help of different mean-free path lengths for transport of particle number and thermal velocity in the elementary kinetic theory, introduced by Jeans [4], equations for the thermodiffusion ratio and thermodiffusion constant which agreed with experiment.

In the last decade, interest has increased in the elementary kinetic theory, which has great heuristic possibilities and provides a clear physical interpretation of phenomena. A number of papers have appeared in which various problems of diffusion, including thermodiffusion, are examined from the point of view of the mean-free path length, while the equivalence between the elementary and rigorous kinetic theories is demonstrated in a paper by Monchik [9].

In this paper, we generalize the results obtained previously and show that the elementary kinetic theory even in its simplest form (i.e., without introducing the concept of different mean-free path lengths) not only describes diffusion in gases, including thermodiffusion and barodiffusion, but also reveals the physical mechanism for phenomena under isothermal and nonisothermal conditions.

**1. Isobaric-Isothermal Diffusion.** In the Maxwell-Boltzmann theory of diffusion, the flux of the number of molecules through a fixed area in a gas, which is stationary as a whole, is calculated based on the principle of local equilibrium and the concept of the mean free path length. Let us examine a binary mixture. Under isobaric-isothermal conditions, the flux of molecules will result only from random thermal motion, while the coefficient of diffusion, defined by Fick's first law, will be a property of the molecular transport and in the elementary kinetic theory equals

$$D_i = \frac{1}{3} \lambda_i v_i, \quad i = 1, 2. \quad (1)$$

Substituting in (1)  $\lambda_i$  and  $v_i$ , we obtain the coefficient of diffusion of the  $i$ -th component in a binary mixture of gases  $i$  and  $j$

$$D_i = \frac{\sqrt{8 kT/\pi m_i}}{3\pi [\sqrt{2} n_i \sigma_i^2 + n_j \sigma_{ij}^2] \sqrt{(m_i + m_j)/m_j}}. \quad (2)$$

Equations (2) for  $D_1$  and  $D_2$  were obtained by Boltzmann [1], and their derivation can be found in a number of handbooks on the theory of gases (see, e.g., [10]).

It follows from (2) that  $D_1 \neq D_2$ , i.e., the flux of molecules of the first gas is not equal to the opposite flux of molecules of the second gas. In experiments with a closed pipe or with two volumes connected by a capillary, identical diffusion coefficients are obtained and the transport of molecules in opposite directions is the same (as follows from the law of conservation of the number of molecules). This forced Boltzmann to assume that his theory of diffusion was inaccurate. Mayer [2] eliminated the contradiction by making the gas fluxes satisfy the condition that they be equal and obtained an identical diffusion coefficient for both components (coefficient of mutual diffusion)

$$D_{12} = D_{21} = \frac{n_1 D_2 + n_2 D_1}{n_1 + n_2} = c_1 D_2 + c_2 D_1. \quad (3)$$

The dependence of the coefficient of mutual diffusion on concentration in the first approximation and a very high, not corresponding to experiment, ratio of the trace coefficients of diffusion, equal to the inverse of the ratio of molecular masses, follow from Mayer's equations (3).

Jeans [4], analyzing the mechanism of collisions between molecules in elementary kinetic theory, came to the conclusion that in a collision, the velocities do not change suddenly, but there is some conservation of velocities (persistence of velocities) and that, therefore, the mean-free path lengths will be equal

$$\lambda^{-1} = \pi [\sqrt{2} n_i \sigma_i^2 (1 - \omega_{ii}) + n_j \sigma_{ij}^2 (1 - \omega_{ij}) \sqrt{(m_i + m_j)/m_j}], \quad (4)$$

where

$$\omega_{ij} = \frac{1}{2} M_i + \frac{1}{2} M_i^2 M_j^{-\frac{1}{2}} \ln [(M_j^{\frac{1}{2}} + 1)/M_i^{\frac{1}{2}}]; \quad M_i = m_i/(m_i + m_j); \quad (5)$$

$$\omega_{ii} = 0,406.$$

Taking into account the dependence of  $\lambda$  on  $v$  and substituting (4) into (1), we obtain [11]

$$D_i = \frac{1,051 \sqrt{8 kT/\pi m_i}}{3\pi [\sqrt{2} n_i \sigma_i^2 (1 - \omega_{ii}) + n_j \sigma_{ij}^2 (1 - \omega_{ij}) \sqrt{(m_i + m_j)/m_j}]} \quad (6)$$

Separating out the coefficient of self-diffusion in (6), we obtain

$$D_i = \frac{D_{ii}}{(1 - \alpha_{ij}) c_i + \alpha_{ij}}, \quad (7)$$

where

$$D_{ii} = \frac{0,3754}{n \sigma_i^2} \sqrt{\frac{kT}{\pi m_i}}; \quad (8)$$

$$\alpha_{ij} = \frac{1 - \omega_{ij}}{1 - \omega_{ii}} \left( \frac{\sigma_{ij}}{\sigma_{ii}} \right)^2 \sqrt{(m_i + m_j)/2m_j}. \quad (9)$$

The coefficient of self-diffusion (8), obtained within the framework of Boltzmann's diffusion theory, coincides with the coefficient of self-diffusion, obtained in a rigorous kinetic theory for models of solid elastic spheres [5].

It should be noted that the coefficients  $D_1$  and  $D_2$  in gases were identified for a long time with the coefficients of self-diffusion, while Mayer's equation (3) was very often written in a distorted form (see, e.g., [12, 13]).

In 1943, Kramers and Kistemaker [14] discovered that in the process of diffusion, a pressure difference arises at the ends of the capillary connecting two volumes with the diffusing gases. This effect, later referred to as the diffusion baroeffect [15], demonstrated that the process of diffusion in a closed apparatus is complicated: a transport of a component by hydrodynamic flow of the gas mixture is superposed on the intrinsic diffusion transport. In this connection, the coefficient of diffusion measured by Loschmidt's method or the two-container method is a characteristic of the total mass transport: transport by random thermal motion of molecules and hydrodynamic flow of a mixture, arising with the diffusion process. The initial isobaric nature of the conditions is destroyed by the diffusion process itself so that the given methods, in the form in which they exist, are fundamentally inadequate for measuring  $D_1$  and  $D_2$ .

The coefficients of diffusion under strict isobaric conditions (the deviation from isobaric conditions is much less than the magnitude of the baroeffect) were measured [16] by a stationary flow-through method, the essence of which is as follows. Nonpulsating gas flows with constant bulk velocity move along two pipes. The pipes are connected by a capillary (or by a collection of capillaries with identical diameters in order to increase the diffusion flow), along which gases diffuse in opposite directions. After the diffusion, the mixture of gases is analyzed and the diffusion coefficient is calculated according to Fick's first law. The same pressure is maintained at the ends of the capillary by a special method. The coefficient of diffusion measured in this case will be isobaric and integral, i.e., measured over a certain range of concentrations. In order to compare the measured integral coefficient of diffusion  $D_i$  with the computed value, it is necessary to find, using well-known rules, the mean value, for the given range of concentrations, of the diffusion coefficient, i.e.,

$$\bar{D}_i = \frac{1}{c_i^t - c_i^0} \int_{c_i^0}^{c_i^t} D_i(c_i) dc_i. \quad (10)$$

Substituting into (10) the expression for  $D_i$  from (7), we obtain after integration

$$\bar{D}_i = \frac{0,3754 \sqrt{kT/\pi m_i}}{(c_i^t - c_i^0)(1 - \alpha_{ij})} \ln \frac{(1 - \alpha_{ij})c_i^t + \alpha_{ij}}{(1 - \alpha_{ij})c_i^0 + \alpha_{ij}}. \quad (11)$$

Table 1 shows a comparison of the measured [17] isobaric-isothermal (true) diffusion coefficients of some binary mixtures, sealed to normal pressure, with the values calculated using Eq. (11). The error in the measurements for the light component was 1-5% and 6-10% for the heavy component. The effective diameters of the molecules were calculated from data on self-diffusion and viscosity.

As can be seen from Table 1, the best agreement with experiment is observed for diffusion coefficients for the light component and the worst agreement is for the heavy component, which is explained by a number of reasons (the rough approximation of the hard sphere model, nonadditivity of effective diameters, low accuracy in measuring self-diffusion). The true diffusion coefficients differ considerably from the self-diffusion coefficients, while their ratio is close to the square root of the ratio of the molecular masses (see the last two columns of the table).

In [18], the true diffusion coefficients were measured by a quasistationary two-vessel method with the help of a ballast gas (a gas, whose diffusion properties are similar to those of one of the diffusing gases) in order to determine the quantity of the component transported by the hydrodynamic flow of the mixture during the diffusion process. Values of the coefficients of diffusion, agreeing (within the limits of error of the experiment) with those measured by the stationary method, were obtained for the systems He-Ar and He-CO<sub>2</sub>.

Naturally, the technique for measuring the true diffusion coefficients is far from perfect, which is indicated by the comparatively large errors in the measurements, but from the data obtained, it is clearly evident that they can by no means be identified with the coefficients of self-diffusion either in the physical sense or in magnitude.

In [19, 20], equations were obtained for the true coefficients of diffusion using Chapman's method for different intermolecular interaction potentials and different orders of approximation. Calculations using these equations gave results that agreed with experiment. For the hard sphere model, these equations describe the experiments just as does Boltzmann's theory.

We note that after the discovery of Kirkendal's effect in 1946, a theory of diffusion was created in solid-state physics, in which the diffusion of each component is characterized by its own coefficient of diffusion (partial), through which the coefficients of mutual diffusion are expressed by Darken's equation, which coincides in form and in physical sense with Eq. (3), obtained by Mayer  $\approx 70$  years before Darken (see, e.g., [21]).

**2. Mutual Diffusion.** The term mutual diffusion is usually used to refer to diffusion of a single gas in another in a closed volume. In this case, the diffusion of both gases is characterized by a single coefficient: the coefficient of mutual diffusion (CMD). It was assumed that in the process of mutual diffusion the initial isobaric conditions are maintained. It was experimentally shown by Kramers and Kistemaker that isobaric conditions are destroyed. The magnitude of the pressure difference, arising at the ends of the diffusion capillary with a diameter of the order of a single millimeter at atmospheric pressure, is  $10^{-6}$ - $10^{-7}$  atm. Such a small change in the uniformity of the pressure, as a rule, was not considered, since it is assumed a fortiori that it does not lead to appreciable changes in the magnitude of the diffusion flux. This point of view turned out

to be erroneous, since **direct measurements** have shown [22] that the amount of gas transported by the hydrodynamic flow arising in the diffusion process is of the same order of magnitude as the transport by the diffusion process itself. In this connection, CMD appears as a characteristic of the total mass transport: transport of molecules by random thermal motion and hydrodynamic flow.

In the elementary kinetic theory, under different assumptions, many equations were obtained for the CMD (some of these are presented in [23]). The most rigorous equation is Mayer's equation (3), which was rejected without any serious experimental verification of this equation, since the coefficients  $D_1$  and  $D_2$ , which were often identified with the coefficient of self-diffusion, were not measured.

After the experiments of Kramers and Kistemaker [14], the physical picture of the mutual diffusion of two gases in a closed volume can be represented as follows. Initially (i.e., the time at which the barrier separating the gases is removed), due to the difference, under the isobaric-isothermal conditions, in the thermal velocities of the molecules, the flux of molecules of one kind will not be equal to the flux of molecules of the other kind. In one gas, the number density of molecules increases (compared to equilibrium before diffusion), while in the other it decreases. A pressure difference, which could result in the appearance of a hydrodynamic flow of the gas mixture, arises between the diffusing gases. The hydrodynamic flux of the mixture will decrease the transport of a single component and increase the transport of the other. A quasistationary state will appear in which the total transport of a single component in one direction will equal the transport of the other component in the opposite direction. The observed transport of a component will represent the sum of the diffusion and hydrodynamic flows, i.e.,

$$\mathbf{j}_1 = \mathbf{j}_1(D) + \mathbf{j}_1(\Delta p) = -D_1 \nabla n_1 + n_1 \mathbf{V} \equiv -D_{12} \nabla n_1, \quad (12)$$

$$\mathbf{j}_2 = \mathbf{j}_2(D) + \mathbf{j}_2(\Delta p) = -D_2 \nabla n_2 + n_2 \mathbf{V} \equiv -D_{21} \nabla n_2. \quad (13)$$

The fluxes (12) and (13) satisfy the law of conservation of the number of particles in a closed volume

$$\mathbf{j}_1 + \mathbf{j}_2 = 0. \quad (14)$$

Solving (12) and (13) simultaneously under the condition (14) and assuming that due to the weak breakdown of isobaric conditions

$$n_1 + n_2 = n = \text{const}, \quad \nabla n_1 + \nabla n_2 = 0, \quad (15)$$

we obtain

$$\mathbf{V} = \frac{D_1 - D_2}{n_1 + n_2} \nabla n_1. \quad (16)$$

Substituting the hydrodynamic flow velocity (16) into Eqs. (12) and (13), we prove the equality of the coefficients of diffusion  $D_{12}$  and  $D_{21}$  and obtain Mayer's equation (3).

The first verification of Mayer's equation by an independent measurement of all three diffusion coefficients was carried out [24]. It turned out that within the limits of error of the measurements (6-10%) the left side equals the right.

In order to check Eqs. (3) rigorously, it is necessary to obtain first the integral expression, since the experiment gives an average over the concentration value of the diffusion coefficient. Substituting Eq. (3) into (10) with the true coefficients taken from (7) and integrating, we obtain [25]

$$\begin{aligned} \bar{D}_{12} = & \frac{D_{11}}{1 - \alpha_{12}} \left\{ [(1 - \alpha_{12})(c_1^L - c_1^0)]^{-1} \ln \frac{(1 - \alpha_{12}) c_1^L + \alpha_{12}}{(1 - \alpha_{12}) c_1^0 + \alpha_{12}} - 1 \right\} + \\ & + \frac{D_{22}}{1 - \alpha_{21}} \left\{ [(1 - \alpha_{21})(c_2^L - c_2^0)]^{-1} \ln \frac{(1 - \alpha_{21}) c_2^L + \alpha_{21}}{(1 - \alpha_{21}) c_2^0 + \alpha_{21}} - 1 \right\}. \end{aligned} \quad (17)$$

In (17),  $D_{ij}$  and  $\alpha_{ij}$  are defined by expressions (8) and (9), respectively.

Equation (17) was checked according to data in the literature for 12 binary gas systems over a wide temperature range in [26]. The average deviation of the CMD computed using (17) from the measured values did not exceed 1-2%, which lies within the range of the experimental error.

The explanation of the concentration dependence of CMD has a long and confused history. The experimental data are often contradictory, since the CMD depends weakly on concentration. In order to study this

dependence, it is necessary to have methods that permit measuring the local coefficients. Care must be exercised in extracting the concentration dependence from measurements of integral coefficients, e.g., by a two-vessel method, since the reverse problem (finding the local coefficient according to the integral diffusion coefficient) is not fundamentally a unique problem. Measuring the concentration distribution along the diffusion path, local diffusion coefficients for different concentrations were obtained in [27, 28] for some pairs of gases. An appreciable dependence of the CMD of systems investigated in [27, 28] is revealed only for low concentrations of the heavy components.

The ratio of the trace diffusion coefficients, i.e., when the concentration of the diffusing component is low, is of special interest. In Boltzmann's theory of diffusion, the trace coefficient is completely defined physically: trace coefficients are characterized by diffusion under conditions when collisions between different types of molecules play an important role, while collisions between molecules of the same kind can be neglected. The ratio of the trace coefficients in the Chapman-Enskog theory of diffusion [5] is smaller than in Boltzmann's theory [4, 11]. Experiments for four systems, containing helium as one of the components, showed [11] that the measured ratio is closer to that computed using Boltzmann's theory. This is explained primarily by the fact that in the Chapman-Enskog theory collisions between like molecules do not affect the mutual diffusion in the first approximation.

A general analysis of the concentration dependence of the CMD leads to the conclusion that Boltzmann's theory correctly describes the concentration dependence of the CMD as well.

**3. Diffusion Baroeffect.** The diffusion baroeffect, viz., the appearance of a pressure difference at the ends of a diffusion path, was predicted by Boltzmann [1], but observed experimentally much later [14]. There are two points of view on the nature of the diffusion baroeffect (see, e.g., [29]). According to one point of view, the baroeffect appears due to differences between the diffusion velocities of components, which lead to an increase in the number density of particles in one volume and to a decrease in the other. The pressure difference that arises leads to a volume flow (the analog of the Kirkendall effect [21]) with velocity (16). According to the second point of view, the baroeffect is explained by a mean mass velocity that differs from zero with the mutual diffusion of two gases. The baroeffect is studied in a number of papers [15, 30, 31].

If it is assumed that there is a Poiseuille's flow in the capillary connecting the vessels with the diffusing gases, then we obtain the differential equation for finding the magnitude of the baroeffect  $\Delta p$  [32] by equating the velocity (16) with the velocity of this flow:

$$\nabla p = -\frac{8\eta}{r^2} (D_1 - D_2) \nabla c_1. \quad (18)$$

Using the relation between the true coefficients of diffusion of the binary mixture in CMD, obtained in [33],

$$D_i = \frac{\sqrt{m_j} D_{12}}{c_i \sqrt{m_i} + c_j \sqrt{m_j}}, \quad (19)$$

we rewrite (18) in the form

$$\nabla p = -\frac{8\eta(\sqrt{m_2} - \sqrt{m_1}) D_{12}}{r^2(\sqrt{m_2} - \sqrt{m_1})c_1 - \sqrt{m_2}} \nabla c_1. \quad (20)$$

Integrating (20) over the entire diffusion path from  $c_1^0$  to  $c_1^L$  and assuming that the CMD is constant in magnitude, we obtain

$$\Delta p = p^L - p^0 = \frac{8\eta D_{12}}{r^2} \ln \frac{(\sqrt{m_2} - \sqrt{m_1})c_1^L - \sqrt{m_2}}{(\sqrt{m_2} - \sqrt{m_1})c_1^0 - \sqrt{m_2}}. \quad (21)$$

Most experiments on studying the baroeffect are carried out under conditions when the volumes, separated by the capillary, contain pure gases, i.e., when  $c_1^0 = 1$ ,  $c_1^L = 0$ . Under these conditions, (21) takes the form

$$\Delta p = p^L - p^0 = (4\eta D_{12}/r^2) / \ln(m_2/m_1). \quad (22)$$

Equations (21) and (22) have been confirmed by experiments on the study of the concentration dependence of the magnitude of the baroeffect for a number of binary mixtures [34].

**4. Diffusion in Multicomponent Mixtures.** In the elementary kinetic theory, the density of the diffusion flux of the  $i$ -th component under isobaric-isothermal conditions depends on the concentration gradient of only

this component, while the coefficient of diffusion (the true coefficient of diffusion) is determined by Eq. (1). Substituting into (1) the value of the mean-free path length of molecules of the component in the mixture, we obtain

$$D_i = 1.051 \sqrt{8 kT/\pi m_i/3} \pi \sum_j (1 - \omega_{ij}) n_j \sigma_{ij}^2 \sqrt{(m_i + m_j)/m_j}. \quad (23)$$

If the diffusion occurs in a closed volume, then there arises a diffusion baroeffect, which is explained by the equality of the characteristic diffusion fluxes [35]. A hydrodynamic flow of the mixture of gases appears and the component flux observed in this case will represent the sum of the characteristic diffusion and hydrodynamic transport:

$$\mathbf{j}_i = -D_i \nabla c_i + c_i \mathbf{V}, \quad (24)$$

which greatly complicates the interpretation of the result.

Analyzing diffusion in multicomponent mixtures, Toor [36] came to the conclusion that in these mixtures, there appear characteristics which are not characteristic of diffusion in binary mixtures. Toor's effects are easily explained by different ratio of the terms in (24) [22]. The diffusion barrier (the component is not in equilibrium, but its transport velocity equals zero) corresponds to equal absolute magnitudes of oppositely directed transport of characteristic diffusion and hydrodynamic flow. In the case of osmotic diffusion, the transport of the component, with its gradient equal to zero, occurs by hydrodynamic flow. And, finally, the most paradoxical case, viz., antidiffusion (transport of the component along its concentration gradient), corresponds to diffusion conditions when transport by hydrodynamic flow is greater than the transport by diffusion.

It follows also from (24) that in a closed volume transport of a given component is determined by the gradients of  $(n - 1)$  of the components, which is demonstrated by eliminating the velocity  $\mathbf{V}$  with the help of the closure condition (14), extended to multicomponent diffusion, and taking into account the fact that the sum of the relative concentrations equals unity.

The measurement of the true diffusion coefficients of multicomponent mixtures presents great methodological and experimental difficulties. The true diffusion coefficients, measured [37] for a single particular case using the ballast gas method, for a triple system consisting of helium-argon-carbon dioxide coincided, within the limits of error of the experiment ( $\sim 6-10\%$ ), with the computed values.

In the description of multicomponent diffusion, effective diffusion coefficients are often used (see, e.g., [38]), formally defined by Fick's first law

$$\mathbf{j}_i = -D_i^{\text{eff}} \nabla c_i. \quad (25)$$

The effective diffusion coefficient (EDC) is a function of composition and concentration gradients of all components. The EDC are measured by the usual methods, used for measuring CMD, and are complicated functions of them [39]. The EDC describe the experimental results on nonstationary diffusion well [40, 41].

The physical meaning of EDC is clearly revealed by Boltzmann's theory. Comparing (24) and (25), eliminating  $\mathbf{V}$ , and assuming that the diffusion is one-dimensional, we obtain [42]

$$\bar{D}_i^{\text{eff}} = D_i - c_i \sum_j D_j (c_j^L - c_j^0)/(c_i^L - c_i^0). \quad (26)$$

The true diffusion coefficient is always positive, so that sign of EDC is determined by the relation between the first and second terms in Eqs. (24) and (26). If the transport by hydrodynamic flow is greater than molecular transport, then the resulting transport will occur along the concentration gradient, i.e., it will be an antidiffusion transport. In this case, the EDC will be negative. When both types of transport balance one another, then the EDC will equal zero and the total transport will equal zero for a nonzero concentration gradient (diffusion barrier). For a uniformly distributed component (its concentration gradient equals zero), its transport (osmotic diffusion) will occur by hydrodynamic flow, arising due to pressure differences formed with the diffusion of other components.

**5. Diffusion Under Nonisothermal Conditions.** We shall examine one-dimensional diffusion under nonisothermal conditions with constant pressure along the diffusion path. Let the temperature increase in the positive direction along the abscissa axis, which is perpendicular to the area  $dS$  being examined. We shall denote physical quantities characterizing the gas to the left of the surface by a single prime above the variable, to the right of the surface by two primes, and on the surface itself without any marks.

We shall examine a single-component gas. The resulting flow of molecules over time  $d\tau$  will equal

$$dN = dN' - dN'' = \frac{1}{6} (n'v' - n''v'') dSd\tau. \quad (27)$$

Taking into account the fact that  $p = nkT$  and  $v = \sqrt{8kT/\pi m}$ , we rewrite (27) in the form

$$dN = \frac{p}{6} \sqrt{\frac{8}{\pi km}} \left( \frac{1}{\sqrt{T'}} - \frac{1}{\sqrt{T''}} \right) dSd\tau. \quad (28)$$

The temperatures  $T'$  and  $T''$  are expressed in terms of the temperature  $T$  in elementary kinetic theory as follows:

$$T' = T - \lambda \frac{dT}{dx}, \quad T'' = T + \lambda \frac{dT}{dx}. \quad (29)$$

Substituting (29) into (28), we obtain

$$dN = \frac{p}{6} \sqrt{\frac{8}{\pi km}} \frac{1}{\sqrt{T}} \left[ \frac{1}{\sqrt{1 - \frac{\lambda}{T} \frac{dT}{dx}}} - \frac{1}{\sqrt{1 + \frac{\lambda}{T} \frac{dT}{dx}}} \right]. \quad (30)$$

The second term under the square root sign in (30) is much less than unity. Extracting the root approximately, transforming to  $n$  and  $v$  and keeping in mind (1), we obtain

$$dN = \frac{1}{6} nv\lambda \frac{d \ln T}{dx} dSd\tau = \frac{1}{2} D_{11} n \frac{d \ln T}{dx} dSd\tau = D_{11}^T n \frac{d \ln T}{dx} dSd\tau. \quad (31)$$

It is evident from (31) that in a single-component gas under nonisothermal conditions, there is diffusion transport of molecules in the direction of the temperature gradient. In analogy with self-diffusion, this transport, discovered experimentally in [43, 17], was called thermoself-diffusion. It is evident from (31) that in the approximation being examined, the coefficient of thermoself-diffusion equals one-half the self-diffusion coefficient.

The diffusion flow of molecules out of the cold region of gas into the hot region leads to the appearance of a thermodiffusion baroeffect [43, 17].

Let us examine a mixture of gases under isobaric conditions. In analogy to (27), we write

$$dN_i = dN_i' - dN_i'' = \frac{1}{6} (n_i' v_i' - n_i'' v_i'') dSd\tau. \quad (32)$$

Carrying out the same operations with (32) as with (27), we obtain

$$dN_i = \frac{1}{6} n_i \lambda_i v_i \frac{d \ln T}{dx} dSd\tau = \frac{1}{2} D_i n_i \frac{d \ln T}{dx} dSd\tau = D_i^T n_i \frac{d \ln T}{dx} dSd\tau. \quad (33)$$

It is evident from (33) that each component of the mixture under isobaric conditions will diffuse along the temperature gradient with a partial thermodiffusion coefficient equal to one-half the true diffusion coefficient.

Let us find the magnitude of the thermodiffusion separation in the binary mixture in the two-vessel apparatus, often used in thermodiffusion studies. In the stationary state, the resulting transport of each component equals zero, since the thermodiffusion flow is balanced by the reverse transport resulting from hydrodynamic flow, arising as a result of the formation of the thermodiffusion baroeffect, and by the concentration diffusion flow, arising due to the appearance of a concentration difference in the presence of thermodiffusion, i.e.,

$$j_1^T = n_1 D_1^T \nabla \ln T + n_1 \mathbf{V} - n D_{12} \nabla c_1 = 0, \quad (34)$$

$$j_2^T = n_2 D_2^T \nabla \ln T + n_2 \mathbf{V} - n D_{12} \nabla c_2 = 0. \quad (35)$$



Taking into account the fact that the concentration diffusion flows are equal in magnitude, but opposite in direction, we obtain from (34) and (35)

$$\mathbf{V} = - \frac{n_1 D_1^T + n_2 D_2^T}{n_1 + n_2} \nabla \ln T. \quad (36)$$

Substituting (36) into (34) or into (35), we obtain a differential equation for determining the shift in concentration with thermodiffusion

$$dc_1 = \frac{n_1 n_2}{n^2} \frac{D_1^T - D_2^T}{D_{12}} d \ln T. \quad (37)$$

Assuming that the ratio  $(D_1^T - D_2^T)/D_{12}$  is constant and integrating (37), we obtain

$$\Delta c_1 = c_1^{\text{hot}} - c_1^{\text{cold}} = c_1 c_2 \alpha_T \ln (T_{\text{hot}}/T_{\text{cold}}). \quad (38)$$

Equation (38) coincides with the well-known equation in [34], if we assume that the thermodiffusion constant is given by

$$\alpha_T = \frac{D_1^T - D_2^T}{D_{12}} = \frac{D_1 - D_2}{2 D_{12}}. \quad (39)$$

Let us find the difference in the average velocities of components in the binary mixture, owing to the non-isothermal conditions. Under isobaric conditions, the average velocity of a component coincides with the diffusion velocity, so that

$$\mathbf{j}_1^T = D_1^T \nabla \ln T \equiv n_1 \bar{\mathbf{v}}_1, \quad \mathbf{j}_2^T = D_2^T \nabla \ln T \equiv n_2 \bar{\mathbf{v}}_2. \quad (40)$$

The following equation follows from (40) under the condition (39):

$$\bar{\mathbf{v}}_1 - \bar{\mathbf{v}}_2 = \alpha_T D_{12} \nabla \ln T, \quad (41)$$

which agrees with the well-known equation in [5, 44].

Thus, the elementary kinetic theory leads to the same basic equations (Eqs. (38) and (41)) as the rigorous kinetic theory. However, in describing certain aspects of the phenomenon, differences arise between these theories. The basic difference reduces to the fact that in the elementary kinetic theory thermodiffusion exists in a single-component gas as well (thermoself-diffusion), while a displacement in concentrations in a binary mixture arises due to the difference in the thermodiffusion velocities. In the elementary kinetic theory, thermodiffusion will also exist when the velocity difference (41) vanishes. In this case,  $D_1 = D_2$ ,  $\alpha_T = 0$ , and there is no displacement of the concentration (components move with identical velocities). According to a rigorous kinetic theory, when the velocity difference (41) vanishes, there is no thermodiffusion. In the elementary kinetic theory, the thermodiffusion flux under isobaric conditions is always directed along the temperature gradient, since the flux of molecules, owing to the random thermal motion, out of the cold region is greater than out of the hot region [43, 17].

6. Barodiffusion. For a single-component gas under isothermal conditions, it follows from (27) that

$$dN = - \frac{1}{3} \lambda v \frac{dn}{dx} dS d\tau = - D_{11} n \frac{d \ln p}{dx} dS d\tau. \quad (42)$$

It is evident from (42) that in a single component gas there will exist a diffusion transport of molecules in the direction of decreasing pressure: baroself-diffusion. For the  $i$ -th component of the mixture, under isothermal conditions, we obtain from (32)

$$\mathbf{j}_i^p = - D_i \nabla n_i = - D_i n_i \nabla \ln p_i \quad (43)$$

It follows from (43) that each component of the mixture has a diffusion velocity directed opposite to the gradient in its own partial pressure, which in general may not coincide with the gradient in the total pressure.

Let us examine a binary mixture for which  $n_1 = n_2 = n/2$  and, therefore,  $p_1 = p_2 = p/2$ . In this case, the difference in the velocities of components will equal

$$\bar{\mathbf{v}}_1 - \bar{\mathbf{v}}_2 = - (D_1 - D_2) \nabla \ln p = - \alpha_p D_{12} \nabla \ln p, \quad (44)$$

where the barodiffusion constant is

$$\alpha_p = (D_1 - D_2)/D_{12}. \quad (45)$$

For this binary mixture, the barodiffusion constant is twice as great as the thermodiffusion constant, which is evident from (45) and (39).

Equation (44) coincides with the analogous equation in strict kinetic theory and was obtained previously [45] within the scope of Boltzmann's theory of diffusion by another method.

Transport phenomena are usually examined in the center of mass system. In this case, (44) must contain the difference of the partial diffusion coefficients in the center of mass system, transforming which in terms of CMD [34], we obtain the equation

$$\bar{v}_1 - \bar{v}_2 = \frac{n(m_2 - m_1)}{n_1 m_1 + n_2 m_2} D_{12} \nabla \ln p, \quad (46)$$

which agrees with the analogous equation in [5, 44].

It is evident from (43) and (44) that in elementary kinetic theory, barodiffusion of components will also occur in the case when the difference of velocities (44) vanishes, but in this case, there will be no barodiffusion separation.

**Conclusions.** The elementary kinetic theory, even in its simplest form, explains from a unified point of view diffusion, arising due to nonuniformity of the composition, temperature, or pressure, revealing the physical mechanism of this molecular transport. According to this theory, diffusion transport also exists in a single-component gas: self-diffusion, thermostself-diffusion, and barostself-diffusion. The theory explains simply and clearly the appearance of baroeffects with diffusion in closed volumes: diffusion and thermodiffusion, as well as the characteristics of multicomponent diffusion.

An important characteristic of diffusion transport is the isobaric-isothermal diffusion coefficient (the true diffusion coefficient), in terms of which all other transport characteristics are actually expressed.

Refining the elementary kinetic theory and comparing it with experimental results will show in greater detail its weak and strong points.

#### NOTATION

$p$ , overall pressure;  $p_i$ , partial pressure;  $\tau$ , time;  $S$ , area;  $T$ , temperature;  $v$ , arithmetic mean velocity;  $\bar{v}_i$ , average velocity of a component;  $j_i$ , flux density of the molecules;  $j_i^T$ , thermodiffusion flux density of molecules;  $j_i^D$ , barodiffusion flux density of molecules;  $D_i$ , true diffusion coefficient;  $D_i^T$ , partial coefficient of thermodiffusion;  $D_i^{\text{eff}}$ , effective diffusion coefficient;  $D_{11}$ , self-diffusion coefficient;  $D_{11}^T$ , coefficient of thermostself-diffusion;  $D_{12}$ , coefficient of mutual diffusion;  $m$ , mass of the molecules;  $n$ , number density of molecules;  $\sigma$ , effective diameter;  $\lambda$ , mean-free path length;  $c$ , relative number density of molecules;  $\eta$ , coefficient of viscosity;  $r$ , radius of a capillary;  $N$ , resulting flux of molecules;  $k$ , Boltzmann's constant;  $\alpha_T$ , thermodiffusion constant;  $\alpha_p$ , barodiffusion constant. The lower index  $i$  indicates that the variable corresponds to the  $i$ -th component; a bar above a coefficient indicates the average value of the coefficient.

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## THE DRYING MECHANISM FOR PEAT MODIFIED BY SURFACTANTS

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A study has been made of the effects of surfactants SA of various types on the drying kinetics and structuring in peat.

It is becoming increasingly important to manage the drying of rheologically complicated dispersed materials. However, at present there are no new theoretical approaches that would enable one to use physical methods to modify the drying of peat systems considerably. Researches based on physicochemical methods of altering the peat appear promising [1-6] because surface phenomena and capillary effects are dominant for these semicollodial macromolecular systems, and they largely determine the structuring and the mass transfer. A peat system has the properties of a polyelectrolyte [2] as well as a high specific surface, and it is very sensitive to various compounds, particularly surfactants, which differ from other compounds in acting simultaneously on the properties of the liquid and solid phases. One cannot consider the mass transfer and structuring separately for a system that deforms on drying. This applies also to materials modified by SA, as the properties are very different from those of the initial ones.

There are many papers [7-11] on the drying mechanisms for chemically modified peat systems, which represent the comprehensive studies on the structuring and mass transfer. Therefore, in what follows we consider only the effects of SA on the drying mechanism.

The apparatus described in [9] was used to examine the mechanism of radiative-convective drying of peat modified by SA; the material was lower sedge peat with a nominal specific surface of 320 m<sup>2</sup>/kg. The modification was produced by SA of various types, in particular sulfonol anionic ones, E-4 cationic ones, neonol nonionic ones, etc. [12]. The SA were introduced into the peat by spraying as 0.01-0.2% aqueous solutions at a rate of 0.01-0.5% on the basis of the dry material. After careful mixing into the peat, flat specimens of diameter 100 mm and thickness 20 mm were formed. A constant temperature of 30°C was maintained in the apparatus, along with a constant speed of 0.33 m/sec air and a constant humidity of 0.86, while the radiation flux was constant at 0.3 kcal/m<sup>2</sup>·sec.

Radioactive tracers were used to examine the internal mass transfer during the drying [13]; we used Na<sub>2</sub>SO<sub>4</sub>(S<sup>35</sup>). The production of the water-content pattern was examined by dividing the specimens into layers and

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