EFFECT OF NONLINEARITY OF GAS MIXTURES ON THE PROCESS OF THEIR PARTITION BY THERMAL DIFFUSION

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Under consideration is the effect of nonideality of the components in a gas mixture on the process of their separation by thermal diffusion. It is demonstrated that in the expressions for the heat flux and the mass flux, the thermodiffusion ratio and the characteristic of diffusional thermal conductivity the effect of nonideality appears in the heat of mixing.

The temperature gradient in a nonisothermal system consisting of several components effects, according to experimental evidence, a transport of material by causing a "separation" of components in the originally homogeneous mixture, i.e., causing the space distribution of their concentrations to become nonuniform. This phenomenon is called thermal diffusion.

Although many studies on this subject have been published in Soviet and foreign technical literature, the mechanism of thermal diffusion in gas mixtures still remains not entirely understood, even in regard to mixtures of monatomic gases.

The phenomenon of thermal diffusion ranks specially among other transport phenomena such as heat conduction and diffusion [1], being called a second-order effect on account of its strong dependence on the nature of intermolecular interactions and, furthermore, hypothetically vanishing in mixtures of ideal gases [2].

We will examine available mathematical models of the thermal diffusion process: three variants of the elementary molecular-kinetic theory, a rigorous molecular-kinetic theory, and two variants of the thermodynamic theory.

The elementary molecular-kinetic theory describes the transport of any substance with a Maxwell velocity distribution of molecules in a steady-state system, i.e., in an ideal gas (ideal mixture). On the other hand, this theory also operates with a concept which pertains to the model of a molecule as a solid sphere and, accordingly, admits the concept of the mean free path for molecules so that the given gas (gas mixture) ceases to be ideal. In this way the mathematical model of the transport process based on the elementary molecular-kinetic theory contains certain contradictions.

The concept of an ideal gas has great significance in any study of the transport processes. An ideal gas is an array of mathematical (imaginary) points of infinitesimally small dimensions. There are no interaction forces between such molecules, which makes an ideal gas a mathematical abstraction.

An ideal gas can be regarded as an array of particles whose interaction energy is small in comparison with their kinetic energy. The interaction energy is small here not because of the weak force interaction between molecules but because of the relatively infrequent interaction events, and yet these events establish a thermodynamic equilibrium in the gas.

The degree of rarefaction of a gas is characterized by the parameter $\varepsilon = nr_0^3$, where r_0 denotes the diameter of molecules, and thus interaction occurs when the distance between their centers decreases to r_0.

When $\varepsilon \ll 1$, then the gas is said to be rarefied. An ideal gas is the extreme case of a rarefied gas. Interaction of molecules in it does not contribute anything at all to the thermodynamic functions. In the expressions for the thermodynamic functions there appear

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additional terms proportional to the density parameter ε for a rarefied gas which drop out for an ideal gas.

The kinetic theory of transport characteristics accounts basically for the occurrence of collisions but not for their nature so that the kinetic characteristics are determined primarily by the presence of certain forces acting between molecules and only secondarily by the nature of those forces [3].

There are three variants of the elementary molecular-kinetic theory of thermal diffusion: the Fürth theory [4], the Laranjeira theory [5-7], and the Whalley–Winter theory [8]. All three theories describe the steady-state thermal diffusion, being based on the condition that $\nabla p = 0$. The end result of these theories is the relation

$$\bar{u}_1 - \bar{u}_2 = -\frac{1}{x_1 x_2}\left(D_{12}\frac{\partial x_1}{\partial z} + D_1^T \frac{1}{T}\frac{\partial T}{\partial z}\right) = -\frac{D_{12}}{x_1 x_2}\left(\frac{\partial x_1}{\partial z} + \kappa_T \frac{1}{T}\frac{\partial T}{\partial z}\right),$$

while the thermodiffusion ratio is defined as

$$\bar{l}'_i = a\bar{l}_i,$$

$$\kappa_T = -\left(1 - \frac{a}{2}\right)\frac{a_1 x_1 - a_2 x_2}{b_1 x_1^2 + b_2 x_2^2 + b_{12} x_1 x_2}\, x_1 x_2;$$

according to the Fürth theory,

$$\bar{l}'_i = (1 + a)\,\bar{l}_i,$$

$$\kappa_T = \frac{1 - a}{2}\,\frac{x_2 S_2 - x_1 S_1}{x_1^2 Q_1 + x_2^2 Q_2 + x_1 x_2 Q_{12}}\, x_1 x_2;$$

according to the Laranjeira theory, and

$$\bar{l}'_i = a\bar{l}_i,$$

$$\kappa_T = \left(1 - \frac{a}{2}\right)\frac{a_1 x_1 - a_2 x_2}{b_1 x_1^2 + b_2 x_2^2 + b_{12} x_1 x_2}\, x_1 x_2$$

according to the Whalley–Winter theory.

Within the framework of these three variants of the elementary molecular-kinetic theory there follows a direct relation between the thermodiffusion ratio and the characteristic of the intermolecular interaction process.

In an analysis of the fundamental premises of these theories, there arises the same one question throughout: what intermolecular interactions can occur in an ideal gas of solid spheres? A gas of solid spheres is ideal when $T \to \infty$, $\lim\limits_{T\to\infty} B(T) = -\lim\limits_{T\to\infty} 2\pi\bar{N}\int\limits_0^\infty \left(e^{-\varphi(r)/kT} - 1\right) r^2 dr \to 0$, but then $n \to 0$ and this is a Knudsen gas, a gas in which no thermal diffusion occurs. This statement agrees with the fundamental premises of the Chapman theory [9], according to which in a mixture of gases in the steady state under constant pressure there is no concentration gradient in the direction of the temperature gradient.

It has been demonstrated in an earlier study [10] that it is not possible to construct an elementary molecular-kinetic theory of thermal diffusion using the concept of only one length of the mean free path for molecules. According to that study, the expression for the flux of particles of the first kind is

$$I_1 = -\frac{n_1 D_{12}}{T}\left(\frac{\partial n_1}{\partial T}\,\frac{T}{n_1} + \frac{1}{2}\right)\frac{\partial T}{\partial z} = 0,$$

which corresponds to the steady state of a Knudsen gas, for which $p/\sqrt{T}$ = const and $(T/n_1\, \partial n_1/\partial T + 1/2) = 0$.

It is noteworthy that the impossibility of rigorously constructing an elementary molecular-kinetic theory of thermal diffusion for ideal mixtures has, evidently, led other authors [4-8] to the necessity of introducing two lengths of the mean free path for molecules.

In the rigorous molecular-kinetic theory of gases there is widely used the concept of two lengths of the mean free path for molecules [11], inasmuch as it is necessary to satisfy the correct value of the Prandtl number (this value being two-thirds for rarefied monoatomic gases). A description of the transport phenomena on the basis of the BCH model (Byrd—Curtiss—Hirschfelder [13]) equation using only one length of the mean free path for molecules leads, however, to the incorrect value 1.0 of the Prandtl number. In the rigorous molecular-kinetic theory one postulates that

$$\overline{l}_i = \frac{2}{5}\sqrt{\pi}\,\frac{\lambda_{i\,\mathrm{trans}}}{p}\left(\frac{m_i T}{2k}\right)^{1/2},\quad \overline{l}_i' = \sqrt{\pi}\,\frac{\eta_i}{p}\left(\frac{kT}{2m_i}\right)^{1/2},$$

so that $\overline{l}_i = 1.5\overline{l}_i'$. This makes it evident that the condition $\overline{l}_i' = a\overline{l}_i$ does not yield information about the nature of intermolecular interactions.

The end result of the rigorous molecular-kinetic theory is that the thermodiffusion constant for rarefied gas mixtures, just like other transport coefficients, can be expressed through a set of collision integrals which depend on the intermolecular interaction potential [12, 13]:

$$\mathbf{J}_i = n_i m_i \overline{\mathbf{V}}_i = \frac{n^2}{\rho}\sum_{j=1}^{\nu} m_i m_j D_{ij}\mathbf{d}_j - D_i^{\mathrm{T}}\,\frac{\partial \ln T}{\partial \mathbf{r}},\quad \overline{\mathbf{V}}_i - \overline{\mathbf{V}}_j = -\frac{n^2}{n_i n_j}\,D_{ij}\left\{\frac{\partial}{\partial \mathbf{r}}\left(\frac{n_i}{n}\right) + \kappa_{\mathrm{T}}\,\frac{\partial}{\partial \mathbf{r}}\,\ln T\right\}.$$

In the steady state

$$\frac{\partial}{\partial \mathbf{r}}\,(n_1/n) = -\kappa_{\mathrm{T}}\,\frac{\partial}{\partial \mathbf{r}}\,\ln T$$

and

$$\frac{T_{12}^* d\kappa_{\mathrm{T}}^*}{\kappa_{\mathrm{T}}^* dT_{12}^*} \approx \frac{6T_{12}^* dC_{12}^*}{(6C_{12}^* - 5)\,dT_{12}^*} \approx 2\,\frac{T_{12}^*}{(1 + 2\,d\ln\Omega_{12}^{(1,1)*}/d\ln T_{12}^*)}\,\frac{d^2 \ln \Omega^{(1,1)*}}{d(\ln T_{12}^*)^2},$$

where $K_T^* = K_T/K_{T,\mathrm{sol.sph.}}$

According to another study [14], at low temperatures the thermal diffusion of rarefied gas mixtures is much more sensitive to intermolecular forces than to other transport characteristics.

The theory of "free flight," which makes it possible to describe the process of separation by thermal diffusion, has been developed in two studies [15, 16] and the velocity distribution of molecules has been defined there by the function

$$f_i^{(1)} = -\tau_i^{(0)} f_i^{(0)}(W_i^2 - 5/2)\,\mathbf{W}_i\left(\frac{m_i}{2kT}\right)^{-1/2}\nabla \ln T,$$

with $\mathbf{W}_i = \sqrt{m_i/2kT}\mathbf{V}_i$. The difference between diffusion rates is

$$\overline{\mathbf{V}}_i - \overline{\mathbf{V}}_j = -\frac{8}{3}\,\frac{kT}{\sqrt{\pi}}\left\{\frac{1}{m_i}\int_0^\infty \frac{W_i^4}{\nu_i^{-1}(W_i)}\,(W_i^2 - 5/2)\,\times\right.$$

$$\left.\times\exp(-W_i^2)\,dW_i - \frac{1}{m_j}\int_0^\infty \frac{W_j^4}{\nu_j^{-1}(W_j)}\,(W_j^2 - 5/2)\exp(-W_j^2)\,dW_j\right\}\nabla \ln T = -D_i^{\mathrm{T}}\nabla T,$$

where ν_i is the frequency of collisions between molecules

$$\nu_i = \int_0^\infty \frac{W_i^4}{\nu_i^{-1}(W_i)}\,(W_i^2 - 5/2)\exp(-W_i^2)\,dW_i,\quad D_i^{\mathrm{T}} = \frac{8}{3}\,\frac{k}{\sqrt{\pi}}\left(\frac{\nu_1^{-1}}{m_1} - \frac{\nu_2^{-1}}{m_2}\right).$$

In another study [16] the function characterizing the velocity distribution of molecules or rather, more precisely, the function $\Delta f_i/|\nabla \ln T|$, $\Delta f_i = f_i^{(1)} - f_i^{(0)}$ is shown graphically. The two wings of such a distribution function are treated in that study [16] as two molecule fluxes moving in opposite directions along the temperature gradient and thus separating by thermal diffusion. It is to be noted, nowever, that $\Delta f_i/|\nabla \ln T|$ does not represent a molecule flux and that the existence of a "negative" wing of this distribution function ($f_i^{(1)} < f_i^{(0)}$

indicates a change in the velocity distribution of molecules in the gas mixture having occurred as a consequence of the temperature gradient and in turn giving rise to the molecule flux.

In phenomenological thermodynamics of irreversible processes, one deals with nonequilibrium transport processes. An advantage of this method is the possibility of deriving relations which characterize the fundamental laws without using the concept of the intermolecular interaction potential.

The source of entropy in irreversible heat- and mass-transport processes can be described by the expression [13]

$$\sigma = -\frac{1}{T}\sum_i (\mathbf{J}_i \cdot \mathbf{\Lambda}_i) - \frac{1}{T^2}\left(\mathbf{J}_q \cdot \frac{\partial T}{\partial \mathbf{r}}\right),$$

where

$$\mathbf{\Lambda}_i = \frac{1}{m_i}\frac{\partial \mu_i}{\partial \mathbf{r}} + \frac{\bar{s}_i}{m_i}\frac{\partial T}{\partial \mathbf{r}} = \frac{1}{m_i}\sum_{\substack{j=1\\ j\neq i}}\left(\frac{\partial \mu_i}{\partial n_j}\right)_{\substack{T,p,x_k\\ k\neq i,j}}\frac{\partial x_j}{\partial \mathbf{r}} + \frac{\bar{v}_i}{m_i}\frac{\partial p}{\partial \mathbf{r}};$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,x_j} = -\bar{s}_i,\ \left(\frac{\partial \mu_i}{\partial p}\right)_{T,x_i} = \bar{v}_i;$$

and $\bar{v}_i$ is the molar volume. The expressions for heat and mass fluxes can be written in the form

$$\mathbf{J}_q = -\lambda_0\frac{\partial T}{\partial \mathbf{r}} - p\sum_{j=1}^{\nu}\frac{D_j^{\mathrm{T}}}{n_j m_j}\mathbf{d}_j, \tag{1}$$

$$\mathbf{J}_i = \frac{D_i^{\mathrm{T}}}{T}\frac{\partial T}{\partial \mathbf{r}} + \frac{n^2}{\rho}\sum_{j=1}^{\nu} m_i m_j D_{ij}\mathbf{d}_j, \tag{2}$$

where

$$\mathbf{d}_j = \frac{n_j}{p}\sum_i \frac{\partial \mu_j}{\partial \ln x_j}\frac{\partial \ln x_j}{\partial \mathbf{r}} + \left(n_j\bar{v}_j - \frac{n_j m_j}{\rho}\right)\frac{\partial \ln p}{\partial \mathbf{r}}, \tag{3}$$

with

$$\mathbf{d}_j = \frac{\partial x_j}{\partial \mathbf{r}} + (x_j - c_j)\frac{\partial \ln p}{\partial \mathbf{r}},\ c_j = \frac{n_j m_j}{\rho},$$

for mixtures of ideal gases and

$$\mathbf{d}_j = \frac{nkT}{p}\left(1 + \frac{\partial \ln f_j}{\partial \ln x_j}\right)\frac{\partial x_j}{\partial \mathbf{r}} + \left[x_j\frac{nkT}{p}(1 + \ln f_j) - c_j\right]\frac{\partial \ln p}{\partial \mathbf{r}} \tag{4}$$

for mixtures of real gases or, since $\partial \log f_j/\partial T = -H_j/RT^2$ (H_j denoting the partial molar heat of mixing for the j-th component [17, 18]), in the steady state

$$\mathbf{d}_j = \frac{nkT}{p}\left(1 + \frac{H_j x_j}{RT\kappa_{\mathrm{T}j}}\right)\frac{\partial x_j}{\partial \mathbf{r}}. \tag{5}$$

For a mixture of real gases, therefore, the expressions for heat and mass fluxes contain the heat of mixing for each of its components.

Let us consider a steady nonequilibrium state of a binary gas mixture inside a closed vessel with given concentration and temperature distributions at the walls [2]. The referred heat flux is

$$\mathbf{J}_q' = \mathbf{J}_q - \frac{\partial \bar{h}}{\partial c_1}\mathbf{J}_1, \tag{6}$$

where J_q denotes the heat flux in a system of coordinates moving at the mean-mass velocity and h denotes the specific enthalpy of the mixture.

For a binary mixture we have

$$\sigma = -\mathbf{J}_1 \nabla \left(\frac{\mu_1 - \mu_2}{T} \right) - \mathbf{J}_q \frac{\nabla T}{T^2}, \tag{7}$$

where σ denotes the local entropy output and expression (7) can be rewritten as

$$\sigma = \mathbf{J}_1' (-\nabla c_1) + \mathbf{J}_q' \nabla (1/T), \tag{8}$$

so that the relations

$$\mathbf{J}_1' = \frac{1}{T} \frac{\partial^2 \overline{g}}{\partial c_1^2} \mathbf{J}_1, \quad \mathbf{J}_q' = \mathbf{J}_q - \mathbf{J}_1 \frac{\partial \overline{h}}{\partial c_1}, \tag{9}$$

$$\mathbf{J}_q = \mathbf{J}_1 c_1 \frac{\partial \overline{\mu}_1}{\partial c_1} \alpha_T + \mathbf{J}_1 \frac{\partial \overline{h}}{\partial c_1} - \lambda_\infty \nabla T \tag{10}$$

and

$$\mathbf{J}_1 = -\rho D_{12} \left(\alpha_T c_1 c_2 \frac{\nabla T}{T} + \nabla c_1 \right), \tag{11}$$

$$\mathbf{J}_q = \mathbf{J}_1 \left(\alpha_T c_1 c_2 \frac{\partial^2 \overline{g}}{\partial c_1^2} + \frac{\partial \overline{h}}{\partial c_1} \right) - \lambda_\infty \nabla T. \tag{12}$$

will hold true.

Let us evaluate the gradients of concentration and temperature in the case of steady-state thermal diffusion $J_1 = 0$ and a diffusion thermoeffect $J_q' = 0$:

$$\nabla c_1 = -\alpha_T c_1 c_2 \frac{\nabla T}{T}, \quad \mathbf{J}_q' = \mathbf{J}_1 \alpha_T c_1 c_2 \frac{\partial^2 \overline{g}}{\partial c_1^2} - \lambda_\infty \nabla T = 0, \tag{13}$$

$$\alpha_T \frac{\nabla c_1}{\nabla T} = -\alpha_T^2 c_1 c_2 \frac{1}{T} - \frac{\lambda_\infty}{\rho D_{12}} (c_1 c_2 \partial^2 \overline{g} / \partial c_1^2)^{-1}. \tag{14}$$

The first term on the right-hand side of expression (14) is always smaller than the second term and can, on account of the smallness of α_T, be disregarded [2]. Then

$$\frac{\nabla T}{\nabla c_1} \approx -\alpha_T c_1 c_2 \frac{\partial^2 \overline{g}}{\partial c_1^2} \frac{\rho D_{12}}{\lambda_\infty} \tag{15}$$

or in molar fractions

$$\frac{\nabla T}{\nabla x_1} \approx -\alpha_T x_1 x_2 \frac{\partial^2 g}{\partial x_1^2} \frac{n D_{12}}{\lambda_\infty}.$$

It has been demonstrated in another study [2] that in mixtures of ideal gases there occurs no thermal diffusion and no diffusion thermoeffect, i.e., that both phenomena characterize the nonideality of the mixture components. We will examine the proof of this statement more closely. On the basis of expression (6) for the referred heat flux, one can say that in a steady state

$$\operatorname{div} \mathbf{J}_q' = -\mathbf{J}_1 \nabla \frac{\partial \overline{h}}{\partial c_1}. \tag{16}$$

When the given system under consideration comprises an infinitesimally small volume element, then function h will be a constant within its boundaries. With the steady-state boundary conditions for the temperature or the concentration stipulated, one can find the steady state where $\nabla(\partial \overline{h}/\partial c_1) = 0$ and then also div $J'_q = 0$. With the constraint $\nabla(\partial \overline{h}/\partial c_1) = 0$ imposed, it is possible to find the only value of the ratio $\nabla T/\nabla c_1$ at which div $J'_q = 0$, viz.,

$$\nabla T / \nabla c_1 = -\frac{\partial^2 \overline{h} / \partial c_1^2}{\partial^2 \overline{h} / \partial T \partial c_1}. \tag{17}$$

This constraint corresponds to the case of the concentration given at all points on the boundary surface and the temperature given at any one point whatever, i.e., the quantity $(\partial \overline{h}/\partial c_1)_0$ given at that point. It is possible to find a temperature distribution over the other points on the surface which will make $\partial \overline{h}/\partial c_1$ at all those points the same as at that starting point: $\partial \overline{h}/\partial c_1 = (\partial \overline{h}/\partial c_1)_0$.

In any small element it is thus possible to stipulate boundary conditions for the temperature or the concentration so that the relations

$$\mathbf{J}_q' = 0,\ \operatorname{div}\mathbf{J}_q' = 0,\ \operatorname{div}\mathbf{J}_i = 0,\ \operatorname{div}\mathbf{J}_q = 0,$$

$$\sum_{i=1}^{n-1}\mathbf{J}_i\left(\frac{\partial^2\bar{h}}{\partial c_i\partial T}\ \nabla T + \sum_{\kappa=1}^{n-1}\frac{\partial^2\bar{h}}{\partial c_i\partial c_\kappa}\ \nabla c_\kappa\right) = 0.$$

will hold true inside the element in a steady state.

According to the last two of these relations, the two equalities

$$\mathbf{J}_q' = \mathbf{J}_1\alpha_T c_1 c_2\frac{\partial^2\bar{g}}{\partial c_1^2} - \lambda_\infty\nabla T = 0, \qquad \operatorname{div}\mathbf{J}_q' = 0.$$

hold true simultaneously in a steady state.

It can be demonstrated that in such a steady state there holds true the equality

$$\mathbf{J}_q = \frac{\partial\bar{h}}{\partial c_1}\ \mathbf{J}_1.$$

Applying now the condition of stationarity div $J_q = 0$, we obtain relation (17).

The relations $J'_q = \mathbf{J}_1\alpha_T c_1 c_2\ \partial^2\bar{g}/\partial c_1^2 - \lambda_\infty\nabla T$ and $\mathbf{J}_1 = -\rho D_{12}(\alpha_T c_1 c_2\ \nabla T/T + \nabla c_1)$ yield

$$\alpha_T\left(\frac{\nabla c_1}{\nabla T} + \alpha_T c_1 c_2\frac{1}{T}\right) = -\frac{\lambda_\infty}{\rho D_{12}}\cdot\left(c_1 c_2\frac{\partial^2\bar{g}}{\partial c_1^2}\right)^{-1}. \tag{18}$$

From expressions (17) and (18) we obtain

$$\alpha_T\ \frac{\partial^2\bar{h}/\partial c_1\partial T}{\partial^2\bar{h}/\partial c_1^2} = \alpha_T^2\, c_1 c_2\ \frac{1}{T} + \frac{\lambda_\infty}{\rho D_{12}}\ (c_1 c_2\partial^2\bar{g}/\partial c_1^2)^{-1},$$

In molar fractions

$$\frac{\partial^2 h}{\partial x_1^2} = \frac{\alpha_T\left(\dfrac{\Delta M}{\bar{M}}\ c_p + \partial c_p/\partial x_1\right)}{\alpha_T^2 x_1 x_2\ \dfrac{1}{T} + \dfrac{\lambda_\infty}{nD_{12}}\ (x_1 x_2\partial^2 g/\partial x_1^2)^{-1}} \tag{19}$$

or

$$\frac{\partial^2 h}{\partial x_1^2} \approx \alpha_T\varkappa x_1 x_2\ \frac{\partial^2 g}{\partial x_1^2}, \tag{20}$$

inasmuch as

$$\alpha_T x_1 x_2\ \frac{1}{T} \ll \frac{\lambda_\infty/nD_{12}}{x_1 x_2\partial^2 g/\partial x_1^2},$$

where

$$\varkappa = \frac{nD_{12}}{\lambda_\infty}\left(\frac{\Delta M}{\bar{M}}\ c_p + \frac{\partial c_p}{\partial x_1}\right).$$

For an ideal mixture we rewrite relation (20) as

$$\frac{\partial^2 h}{\partial x_1^2} \approx \alpha_T\,\frac{pD_{12}}{\lambda_\infty}\ \frac{\Delta M}{\bar{M}}\ c_p x_1 x_2,$$

Since $\rho D_{12}/\lambda_\infty = \overset{\infty}{\lambda}_D T\cdot T/\lambda_\infty\kappa_T\alpha_T$, hence $\partial^2 h/\partial x_1^2 \approx h\Delta M/\alpha_T\bar{M}\ \lambda_D^\infty T/\lambda_\infty$, with $\overset{\infty}{\lambda}_D T = \lambda_0 - \lambda_\infty$ and finally

$$\frac{\partial^2 h}{\partial x_1^2} \approx \frac{h\ \dfrac{\Delta M}{\bar{M}}\ \lambda_{DT}^\infty/\lambda_\infty}{\alpha_T}. \tag{21}$$

We note that expressions (21) and (20) do not have the same form.

Thus, relation (20), which is used in support of the statement that thermal diffusion ceases in mixtures of ideal gases, has not been expressed before [2] in a complete form with the $\varkappa$-term inversely porportional to the product $\alpha_T\kappa_T$.

In another study [19] has been presented the phenomenological theory of steady thermal diffusion in multicomponent liquid mixtures. Defining the thermodiffusion constant in the form $\nabla \ln x_K/x_i = -\alpha_{Ki} \nabla \ln T$ and using the relation $\nabla^T \mu_K = -Q_K^* \nabla \ln T$, where $\nabla^T = \nabla - \nabla T(\partial/\partial T)_{n_i}$, the author [19] has demonstrated that

$$\alpha_{12} = \frac{v_2 Q_1^* - v_1 Q_2^*}{vkT\,(1 + \partial \ln f_1/\partial \ln x_1)}, \tag{22}$$

where $\sum\limits_{i=1} n_i Q_i^* = T\,(\partial p/\partial T)_{n_i}$.

As an end result of that study [19] has been obtained the expression

$$\alpha_{\kappa i} = \alpha_0 \frac{m_\kappa - m_i}{2m}, \text{ where } \alpha_0 = \frac{1}{3}\left(\frac{v\beta}{k\beta'} - 1\right).$$

for isotope mixtures. The relation $\alpha_0 = 1/3(v\beta/k\beta' - 1)$ indicates that thermal diffusion ceases in ideal mixtures. This incorrect conclusion is a consequence of the Gibbs–Duhem equation having been written incorrectly as $\sum\limits_{i=1}^{M} n_i \nabla^T \mu_i = \nabla^T$ [19] instead of $\sum\limits_{i=1}^{M} n_i \nabla^T \mu_i = 0$, , since $\nabla p = \partial p/\partial T\ \nabla T = 0$ and $\partial p/\partial T = 0$.

Also the relation for the heat of transport is incorrect, therefore, it should be $\sum\limits_{i=1}^{M} n_i Q_i^* = 0.$

We note that relation (22) characterizes thermal diffusion in a rarefied gas [20] and cannot be used for describing the thermal diffusion in liquids.

In another study [10] has been determined the effect of nonideality of the mixture components on the thermodiffusion ratio. It has been shown, specifically, that this effect can be expressed as†

$$\kappa_T^E = \kappa_{T_i} - \kappa_T^* = x_i \frac{n\,(b_0 - 2B) + (1 + 2nB)\dfrac{\partial \ln n_i/n_i^*}{\partial \ln T} + B'_{n_i}\left(1 + \dfrac{\partial \ln n_i^*}{\partial \ln T}\right)}{1 + 2nB + B'_{n_i}}, \tag{23}$$

where $B'_{n_i} = n_i\, \partial B(T, x_i)/\partial x_i$.

The quantity K_T^E characterizes the thermal shift of concentration due to the thermodynamic excess function $h^E = -nkT(b_0 - 2B)$. We will now show that this thermal shift of concentration is associated with the heat of mixing of the mixture components.

Using the methods of thermodynamics of irreversible processes, we obtain an expression for the thermodiffusion constant for binary mixtures of real gases in a steady state. Since the particle flux is zero, we have

$$\frac{\partial \mu_1}{\partial x_1} \nabla x_1 + (U_1^* - h_1)\frac{\nabla T}{T} = 0,$$

and from there

$$\frac{\nabla x_1}{\nabla T} = -\frac{U_1^* - h_1}{T \partial \mu_1/\partial x_1} = -\frac{Q_1^*}{T \partial \mu_1/\partial x_1}, \tag{24}$$

where Q_1^* is the heat of transport for the first component.

Upon introduction of the thermodiffusion constant α_T, the relation $\nabla x_1/x_1 = -\alpha_{T_1} - \nabla T/T$ yields

$$\alpha_{T_1} = \frac{Q_1^*}{\partial \mu_1/\partial \ln x_1}. \tag{25}$$

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†For simplicity, the equation of state was considered in the form $pv = kT(1 + B(T, x_i)/v)$.

For a mixture of real gases this expression can be written as

$$\alpha_{\mathrm{T}_1}=\frac{Q_1^*}{kT\left(1+\dfrac{\partial \ln f_1}{\partial \ln x_1}\right)}=\frac{Q_1^*}{kT\left(1+\dfrac{H_1}{RT^2}\;\dfrac{T}{\alpha_{\mathrm{T}_1}}\right)}, \tag{26}$$

where $(\partial \ln f_i/\partial T)_{x_i} = -H_i/RT^2$. Furthermore,

$$\alpha_{\mathrm{T}_1}=\frac{Q_1^*+H_1/\tilde{N}}{kT}. \tag{27}$$

According to expression (27) the thermodiffusion constant for a real mixture depends on the heat of transport Q_1^* and on the heat of mixing H_1 for the first component. For an ideal mixture

$$\alpha_{\mathrm{T}}^*=Q_1^*/kT. \tag{28}$$

Relations (27) and (28) yield

$$H_1=(\alpha_{\mathrm{T}_1}-\alpha_{\mathrm{T}}^*)\cdot RT=\alpha_{\mathrm{T}}^E\cdot RT. \tag{29}$$

The preceding analysis completely supports Dickel's hypothesis [10] that the thermal separation effect in a gas mixture consists of two components: thermal diffusion, which produces a concentration gradient in the gas mixture, and thermal concentration shift in mixtures of real gases attributable to thermodynamic excess functions.

According to Dickel's classification, therefore, thermal diffusion is an effect observed in ideal mixtures only.

Using the methods of thermodynamics of irreversible processes, we will now obtain an expression for the thermodiffusion constant for mixtures of real gases in a nonsteady state.

In a nonsteady state the particle flux is

$$\frac{\partial\mu_1}{\partial x_1}\;\nabla x_1+Q_1^*\;\frac{\nabla T}{T}=x_1\;\frac{\partial\mu_1}{\partial x_1}\;\frac{\nabla p}{p}, \tag{30}$$

from where

$$T\;\frac{\nabla x_1}{\nabla T}=-\frac{Q_1^*}{\partial\mu_1/\partial x_1}+\frac{x_1\nabla p/p}{\nabla T/T}.$$

Upon introduction of the thermodiffusion constant β_{T}, the relation $\nabla x_1/x_1 = -\beta_{\mathrm{T}_1}, \nabla T/T+\nabla p/p$, yields

$$\beta_{\mathrm{T}_1}=\frac{Q_1^*}{\partial\mu_1/\partial \ln x_1}=\frac{Q_1^*+(H_1/\tilde{N})}{kT}. \tag{31}$$

For an ideal mixture

$$\beta_{\mathrm{T}}^*=\frac{Q_1^*}{kT}\quad\text{and}\quad Q_1^*=\beta_{\mathrm{T}}^*\cdot kT. \tag{32}$$

Then $H_1 = (\beta_{\mathrm{T}_1}-\beta_{\mathrm{T}}^*)\cdot RT = \beta_{\mathrm{T}}^E\cdot RT$ and the thermodiffusion ratio in a nonsteady state is inserted into expression (21).

Thus, the thermal shift of concentration in a nonsteady state is, indeed, associated with the heat of mixing of the mixture components.

In conclusion, let us examine how nonideality of the mixture components affects the contribution of diffusional heat conduction to conductive heat transfer.

In the case of a full heat flux [10]

$$\lambda_{D^{\mathrm{T}}}^{\infty}=\frac{nD_{ij}}{T}\left(\alpha_{\mathrm{T}}\;\frac{\partial\mu_i}{\partial \ln x_i}+\frac{\partial h}{\partial x_i}\right)\kappa_{\mathrm{T}}=\frac{nD_{ij}}{T}\;\kappa_{\mathrm{T}}\left[\alpha_{\mathrm{T}}\left(kT+\frac{H_i x_i}{\tilde{N}\kappa_{\mathrm{T}_i}}\right)+\frac{\partial h}{\partial x_i}\right],\; k_{\mathrm{T}_i}=-T\,\frac{\partial x_i}{\partial T}. \tag{33}$$

In the case of a reduced heat flux

$$\lambda_{D^{\mathrm{T}}}^{\infty}=\frac{nD_{ij}}{T}\;\left(kT+\frac{H_i}{\tilde{N}}\;\;\frac{x_i}{\kappa_{\mathrm{T}_i}}\right)\alpha_{\mathrm{T}}\kappa_{\mathrm{T}},\quad k_{\mathrm{T}}=\frac{\rho D_i^T}{n^2 m_i m_j D_{ij}}. \tag{34}$$

Accordingly, the effect of nonideality of the mixture components is manifested in the heat of mixing of the components.

NOTATION

p, pressure; ρ, density; $\bar{l}_i$, length of the mean free path for molecules during transport of particles; l'_i, length of the mean free path for particles during a transfer of the mean velocity; n, molecule concentration; M, molecular weight; I, particle flux; J, mass flux; m, mass of a molecule; t, time; D_{ij}, coefficient of interdiffusion for a binary mixture; D_i^T coefficient of thermal diffusion; K_T, thermodiffusion ratio; α_T, thermodiffusion constant; x_i, molar fraction of the i-th component in the mixture $\varphi(r)$, intermolecular interaction potential; r, intermolecular distance; $\Omega^{(l,s)*}$, collision integrals; T, temperature; T*, referred temperature; R, universal gas constant; k, Boltzmann constant; $\tilde{N}$, Avogadro's number; v, mean velocity of molecules; $\bar{V}$, diffusion rate; $\lambda_{i,\mathrm{trans}}$, thermal conductivity associated with translatory degrees of freedom; $f_i(r, v, t)$, velocity distribution function of molecules; η, viscosity; μ_i, chemical potential of the i-th component; c_i, mass fraction; λ_0, thermal conductivity at the initial instant of time; λ_∞, thermal conductivity in the steady state; $\lambda_D{}^T$, diffusional component of thermal conductivity; g and h, molar thermodynamic functions; g and $\bar{h}$, specific thermodynamic functions; c_p, specific heat; J_q, heat flux; J'_q, reduced heat flux; B, second virial coefficient; U*, transport energy; β, coefficient of thermal expansion; β', coefficient of isothermal compression; and f_i, activity coefficient for the i-th mixture component.

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EFFECT OF FEEDPOINT LOCATION FOR A BINARY MIXTURE ON THE EFFICIENCY OF SEPARATION IN A THERMAL-DIFFUSION COLUMN

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We show that there exists an optimal position of the feedpoint of a column at which the separation efficiency is maximum and for which, at the same time, the energy consumption is a minimum.

Rozen [1] was the first to solve the problem of the effect produced by the position of the feedpoint of the initial binary mixture on the separation efficiency in column apparatuses. However, the method used for this was worked out in terms of the theory of rectification, which had no real physical analogs in the theory of thermal-diffusion equipment. (For example, finding the points of intersection of the operating lines in the liquid—vapor equilibrium diagram.)

In connection with the development of a technology for the thermal-diffusion separation of petroleum products, it became necessary to solve the above-mentioned problem of finding the optimum coordinate of the feedpoint of the mixture being separated for a thermal-diffusion column, shown schematically in Fig. 1. The upper part of the column (I) is the concentrating part, while the lower is the stripping part (II). The input to the column is at the cross section whose dimensionless coordinate is y_0. For each part of the column, in accordance with [2], we can write the transfer equation in the form

$$\tau' = H\left[c'(1-c') - \frac{dc'}{dy} + \varkappa_e c'\right],$$

$$\tau'' = H\left[c''(1-c'') - \frac{dc''}{dy} - \varkappa_i c''\right].$$

The simultaneous solution of this system of equations leads, since it is nonlinear, to results which are cumbersome and inconvenient for analysis [3], and for this reason it is desirable to resort to linearization of the quadratic term in the form

$$c(1-c) = a + bc, \tag{1}$$

which is entirely applicable to the solution of some separation problems. Then, taking account of (1), the above system takes the form

$$\begin{aligned} \tau' &= H\left[a + (b + \varkappa_e)c' - \frac{dc'}{dy}\right], \\ \tau'' &= H\left[a + (b - \varkappa_i)c'' - \frac{dc''}{dy}\right]. \end{aligned} \tag{2}$$

Since we are considering the stationary state, we know that $d\tau/dy = 0$, and from (2) we obtain the system

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