CALCULATION OF DIFFUSION COEFFICIENTS FOR DENSE GASES

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Calculated values of mutual gas diffusion coefficients are compared to values measured by the laser interferometry method.

The study of diffusion of dense gases is complicated by the effects of change in volume upon mixing. In closed type experimental apparatus these effects lead to development of additional convective flows, so that it is difficult to establish what reference frame is suitable for the diffusion tube [1, 2]. These effects are decreased in experiments involving diffusion of a minor impurity with use of laser interferometry [3, 4], which latter provides information on the concentration fields in the diffusion cuvette from the time of admission of the impurity to complete equalization of the mixture inhomogeneity. To eliminate methodological errors the diffusion coefficient is found by processing interferograms which reflect only that stage of the transient process which to the required accuracy can be described by the conventional diffusion equation given zero mean numerical velocity [5].

Data obtained by this method show that the concentration and pressure dependences are interrelated and that a power dependence of the mutual diffusion coefficient upon pressure is applicable only for coefficients referring to one and the same concentration value. The present study will offer results which indicate that expressions for the diffusion coefficients obtained by solution of the Boltzmann—Lorentz—Enskog equation [7] properly reflect the interrelation of pressure and concentration dependences.

The molecular flux of the component α in an inhomogeneous s-component mixture has the form [6, 7]:

$$\mathbf{\Gamma}_\alpha = \mathbf{W} n_\alpha - n_\alpha D_\alpha \nabla \ln x_\alpha - n_\alpha D_\alpha \nabla \ln p + n_\alpha D_\alpha \nabla \ln z + n_\alpha D_\alpha^T \nabla \ln T, \qquad (1)$$

in which the reversible component of the flux is characterized by a convection velocity **W** and the irreversible by diffusion and thermodiffusion coefficients D_α, D_α^T and the gradients of the corresponding macroparameters.

For solid spherical molecules the effective diameters of which are temperature-dependent, the diffusion coefficients D_α can be calculated conveniently with the following expression [6-8]:

$$D_\alpha = 1{,}025 azT^{\frac{3}{2}} \left\{ p \sum_{\beta=1}^{s} Y_{\alpha\beta} x_\beta M_{\beta\alpha}^{-\frac{1}{16}} \alpha_{\alpha\beta} \right\}^{-1}, \qquad (2)$$

where

$$\alpha_{\alpha\beta} = \sigma_{\alpha\beta}^2 \sqrt{2\mu_\alpha \mu_\beta/(\mu_\alpha + \mu_\beta)};$$

$$Y_{\alpha\beta} = 1 + \frac{\pi}{6} \sum_{\gamma=1}^{s} n_\gamma \sigma_{\gamma\gamma}^3 + \frac{\pi}{2} \frac{\sigma_{\alpha\alpha}\sigma_{\beta\beta}}{\sigma_{\alpha\alpha} + \sigma_{\beta\beta}} \sum_{\gamma=1}^{s} n_\gamma \sigma_{\gamma\gamma}^2; \quad M_{\beta\alpha} = \mu_\beta/(\mu_d + \mu_\beta);$$

$$\sigma_{\alpha\alpha}(T_2) = \sigma_{\alpha\alpha}(T_1)(T_1/T_2)^{\frac{m_d - 1,5}{2}}; \quad \sigma_{\alpha\alpha}(T_2) = \sigma_{\alpha\alpha}(T_1)(T_1/T_2)^{\frac{m_V - 0,5}{2}};$$

$a = 2.663 \cdot 10^{-23}\ \mathrm{J}^{3/2} \cdot \mathrm{K}^{-3/2} \cdot \mathrm{kmol}^{-1/2}$.

If the relationship between the observed fluxes in a two-component mixture is such that

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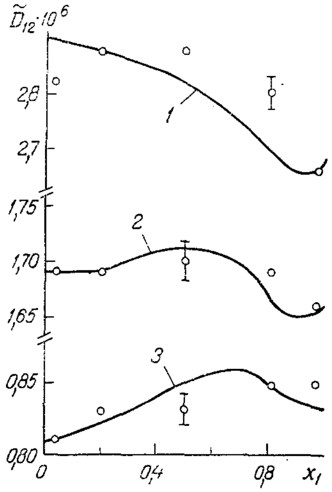

Fig. 1

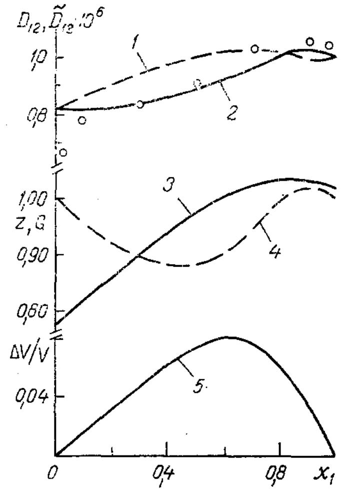

Fig. 2

Fig. 1. Concentration dependence of mutual diffusion coefficient in helium—argon system at various pressures: 1) p = 2.46 MPa; 2) 3.99; 3) 7.96; T = 290 K. Points, experiment [4]; lines, calculation with Eqs. (2), (5), (1 — δ = 4.5; 2 — 3.8, 3 — 2.3; $\sigma_{11} = 1.795\cdot10^{-10}$ m; $\sigma_{22} = 3.304\cdot10^{-10}$ m). $\tilde{D}_{12}$, m^2/sec.

Fig. 2. Properties of helium—carbon dioxide mixture at T = 295 K, p = 5.09 MPa (He—CO_2): 1) D_{12}; 2) $\tilde{D}_{12}$; 3) z; 4) G; 5) $\Delta V/V$. Points, experimental values of mutual diffusion coefficient [4]. Lines, calculations with Eqs. (2), (5), (6) for $\sigma_{11} = 1.792\cdot10^{-10}$ m; $\delta_{22} = 4.126\cdot10^{-10}$ m; δ = 3.5, D_{12}, $\tilde{D}_{12}$, m^2/sec.

$$\Gamma_{12} + \Gamma_{21} = 0, \tag{3}$$

then the diffusion is described by the mutual diffusion coefficient $\tilde{D}_{12}$:

$$\Gamma_{12} = -n\tilde{D}_{12}\nabla x_1 - x_1x_2nD_{12}(\tilde{\alpha}_p\nabla\ln p - \tilde{\alpha}_T\nabla\ln T), \tag{4}$$

where

$$\tilde{D}_{12} = GD_{12};\quad G = 1 - \frac{x_1x_2}{z}\alpha_p\frac{\partial z}{\partial x_1};\quad D_{12} = x_1D_2 + x_2D_1; \tag{5}$$

$$\alpha_p = \frac{D_1 - D_2}{D_{12}};\quad \alpha_T = \frac{D_1^T - D_2^T}{D_{12}};\quad \tilde{\alpha}_p = \alpha_p w_p;\quad \tilde{\alpha}_T = \alpha_T w_T;$$

$$w_p = 1 - \frac{p}{z}\frac{\partial z}{\partial p};\quad w_T = 1 + \frac{\alpha_p}{\alpha_T}\frac{T}{z}\frac{\partial z}{\partial T}.$$

It can be assumed with sufficient accuracy that the laser interferometry method permits measurement of $\tilde{D}_{12}$ [4], calculation of which requires knowledge of the state of the mixture for all concentration values. Such information can be obtained from kinetic theory within the framework of the cluster model of dense gases [7, 9]. In the approximation which considers the existence of dimers only (r = 2), this model leads to the following expressions for equilibrium properties:

$$p = znkT,\quad z = z_0 + \Delta V/V + V_0/V, \tag{6}$$

$$z_0 = \sum_{\alpha=1}^{s}\sum_{g=1}^{r} x_\alpha[1 + y^0_{\alpha g}(1 - g_\alpha)],\quad \frac{V_0}{V} = \frac{2}{3}\pi n\sum_{\alpha=1}^{s} x_\alpha\sigma^3_{\alpha\alpha},$$

$$\frac{\Delta V}{V} = \sum_{\alpha=1}^{s}\sum_{g=1}^{r} x_\alpha[y_{\alpha g}(1 - g_\alpha) - y^0_{\alpha g}(1 - g_\alpha)],$$

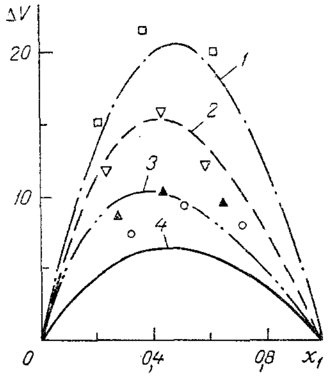

Fig. 3. Excess volume in hydrogen—argon system at T = 170.5 K as a function of molar fraction of hydrogen. Experimental data [10]: 1) p = 7.5 MPa; 2) 5.0 MPa; 3) 2.5 MPa; 4) 0.5 MPa. Lines, calculation with Eq. (6) for Lennard-Jones potential for various values of parameter δ: 1) δ = 1.2; 2) 1.2; 3) 1.3; 4) 3.0; ΔV, cm^3/mole.

where ΔV/V is the relative excess mixing volume; V_0/V is the relative intrinsic molecular volume.

Results of calculations by these expressions are presented in Figs. 1-3. Comparison of theory with experiment [4] reveals that the theory properly reflects the experimentally observed change in diffusion coefficient ratio upon increase in pressure [4]. Experiment and theory (Fig. 1) indicate decrease in $\tilde{D}_{12}$ with increase in concentration of the light component x_1 at low pressures (curves 1 and 2) with increase occurring at higher pressures (curve 3).

It is evident from Fig. 2 that at pressures above 2 MPa for a helium—carbon dioxide the thermodynamic factor G becomes significant. At low pressures theory describes experiment better with high values of the parameter δ, which indicates how many times larger is the path traversed by particles in the dimer than the collision parameter [7, 9]. With increase in pressure the value of δ in this model decreases.

The data presented in Fig. 3 indicate that Eq. (6) properly describes the concentration dependence of absolute excess mixing volume ΔV [10], which allows its use in calculating transport properties of mixtures.

For more accurate consideration of the fractions of clusters of various powers it is necessary to solve the system of Boltzmann equations written for each cluster gas [9].

NOTATION

W, convection velocity; n_α, partial numerical density of component α; p, pressure; T, temperature; z, mixture compressibility factor; D_α, diffusion coefficient; D_α^T, thermodiffusion coefficient; $Y_{\alpha\beta}$, partial Enskog correction; μ, mass of kmol; σ, effective diameter of solid spheres; m_d, exponent in temperature dependence of self-diffusion coefficient; m_V, exponent in temperature dependence of viscosity coefficient; $y_{\alpha g}$, fraction of g-dimensional clusters containing molecules of component α in mixture; $y_{\alpha g}^{o}$, fraction of clusters in pure gas; x_α, numerical fraction; δ, ratio of particle path in dimer to collision diameter; G, thermodynamic factor.

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VOLUME-VISCOUS PROPERTIES OF MERCURY CONTAINING A GASEOUS PHASE

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The rheological model of a liquid with heredity is used to analyze experimental results on normal stress relaxation in mercury. A low end estimate of viscosity at low frequencies is obtained.

A model of a viscous compressible liquid with heredity, generalizing the linear-viscous Navier–Stokes model, was proposed in [1]. This model has been employed to describe a liquid with large volume relaxation time. In the present study the theory of [1] will be used to describe behavior of liquid mercury containing fine air bubbles. For rapid volume deformations of the mixture, system equilibrium is disrupted as regards the processes of solution and heat exchange between the components, which manifests itself macroscopically by the appearance of relaxation processes in the liquid, i.e., heredity.

The fundamental relationships of [1] will be presented below in slightly changed notation.

We assume that the stress tensor in a liquid particle in a fixed Cartesian coordinate system at the time t_0 can be represented in the form

$$p^{ij}(t_0) = -p(\rho_0, T_0)\delta^{ij} + \tau^{ij}(t_0), \tag{1}$$

where $\rho_0 = \rho(t_0)$, $T_0 = T(t_0)$ are the density and temperature in the particle at the time t_0; $p = p(\rho, T)$ is the pressure; the viscous stress tensor τ^{ij} depends on ρ_0 and the values of the temperature T and the deformation rate tensor $e_{ij} = 1/2(v_{i,j} + v_{j,i})$ in the particle at all times preceding t_0:

$$\tau^{ij}(t_0) = \tau^{ij}[\rho_0, T(t \leqslant t_0), e_{kl}(t \leqslant t_0)]. \tag{2}$$

It will be assumed that if at $t \leq t_0$ $T = T(t) = T_0$ and $e_{kl} = 0$, then $\tau^{ij}(t_0) = 0$. We introduce the notation $\tilde{e} = e^i_i$, $S_{ij} = e_{ij} - (1/3)\tilde{e}\delta_{ij}$. Let the liquid be isotropic, while functional (2) is a linear integral operator of $\theta = dT/dt$ and e_{ij}. Then because of isotropicity, to specify Eq. (2) three kernels $K_i = K_i(\rho_0, T_0, t)$, $i = 1, 2, 3$ are sufficient:

$$\tau^{ij}(t_0) = \delta^{ij}\int\limits_{-\infty}^{t_0} K_1(\rho_0, T_0, t_0 - t)\tilde{e}(t)\,dt + 2\int\limits_{-\infty}^{t_0} K_2(\rho_0, T_0, t_0 - t)s^{ij}(t)\,dt + \delta^{ij}\int\limits_{-\infty}^{t_0} K_3(\rho_0, T_0, t_0 - t)\theta(t)\,dt. \tag{3}$$

It should be noted that Eq. (3) is of limited applicability. In the general case of nonlinear viscoelasticity in place of the tensor e_{ij} in Eqs. (2), (3), we must use the tensor ε_{ij} (where ε_{ij} is the finite deformation tensor [3, 4]). Moreover in the expression for τ^{ij} terms nonlinear in ε_{ij} may appear. It can be shown that the general case leads to Eq. (3) for small deformations or for media with sufficiently short relaxation times.

Integration over time in Eq. (3) is performed for a fixed liquid particle. The kernels $K_i = K_i(\rho, T, t)$, $i = 1, 2, 3$ are in fact defined for $t \geq 0$, however it is convenient to predefine them, taking $K_i(\rho, T, t) = 0$ at $t < 0$. We may then take the upper integration limit in Eq. (3) equal to infinity. For brevity, we will omit the dependence of K_i on ρ and T below.

Following [2], we require that for cyclical processes, where $\rho \to \rho_1$, $T \to T_1$, $e_{ij} \to 0$ as at $t \to \pm\infty$.

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