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CALCULATION OF GAS PROPERTIES ON THE BASIS OF THE CLUSTER MODEL

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Calculations of concentrations of clusters and some equilibrium and nonequilibrium states of gases by the formulas obtained in [Inzh.-Fiz. Zh., **54**, No. 3, 438–442 (1988)] *and on the basis of the hypothesis on the exponential size-distribution of clusters are presented.*

In modern science, it is common practice to measure the amount of a substance in moles — the measurement unit determined in terms of the structural elements in the considered system. Most of the difficulties in the description of complex systems are reduced to the determination of which objects in the system under consideration are the structural elements. In particular, in rarefied gases the molecules, which are, by definition, the carriers of the chemical properties, are taken as the structural elements. Physical properties of real gases, viz., pressure, temperature, and transport properties, are determined by thermal motion and interactions of not only molecules but also their associations, clusters, or polymolecules. The existence of clusters is caused by a complex character of interactions of electrically neutral formations from moving charges which are the molecules. A gas model, which considers them as individual subjects of the observed processes, will be called a cluster model. The main difficulty of the model is the determination of the concentrations of clusters and their dynamics with changes in the macroparameters: pressure, temperature, chemical composition of the mixture, and external effects.

In the present paper, we consider two methods of calculation of the concentration of clusters in gases. The results for the compression factor and the coefficient of viscosity obtained by these methods showed that use of the cluster model allows one to describe some observed special features of both equilibrium and nonequilibrium states and also to predict yet unknown properties of real gases.

The Dynamic Method of Determination of the Cluster Composition in Gas Mixtures. In [1, 2], the author gives a scheme of calculation of clusters in gas mixtures which is based on the kinetic theory. The calculations showed that at pressures from atmospheric to several tens of atmospheres and temperatures close to normal, dynamic clusters, mainly in the form of dimers, play an appreciable role in gases. In this method, such a pair of colliding molecules, the collision time (a quasi-bound state) of which is not less than the time of free flight of molecules determined by the formulas of the kinetic theory of gases, is believed to be a dimer. The processes of formation and decomposition of these clusters, which are described by the reversible laws of dynamics, do not lead to generation of entropy; therefore, these clusters fit into the group of dynamic clusters.

Under the conditions where trimers and quadromers begin to play an appreciable role, their concentration can be found by the iteration method, where the dimers found in the first iteration are considered to be the components with a double mass of particles and the corresponding collision cross section. Then, in subsequent iterations the concentrations of larger-size clusters are found by determining such clusters as a dimer consisting of a monomer and a dimer (trimer) or of two dimers (quadromer). By way of example, Fig. 1 gives the results of calculation of their concentrations in argon obtained after three iterations. Effective collision diameters computed by the reference data on the coefficient of self-diffusion [3] and its temperature dependence [1] were used in the calculations. The character of the distribution obtained suggests that the quantity of clusters decreases exponentially with increase in the cluster size and gives grounds for the development of another scheme of calculation of cluster concentrations in dense gases (the results of the calculations by this scheme, which will be described in what follows, are presented in Fig. 1, curves 1 and 2).

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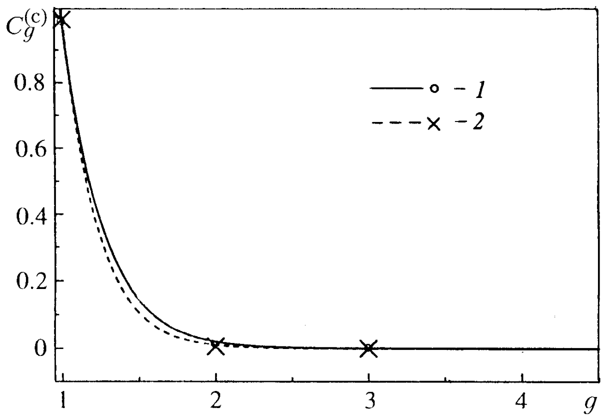

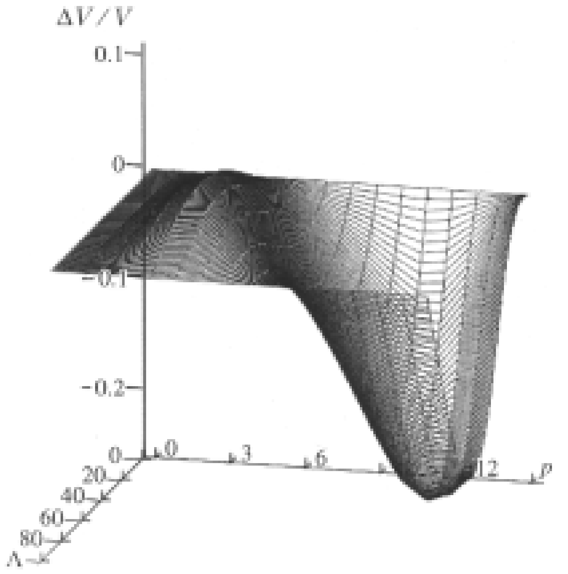

Fig. 1. Distribution of the concentration of clusters $C_g^{(c)}$ by their sizes in argon (1) and hydrogen (2) at a temperature of 200 K and a pressure of 1.5 MPa; dots, calculation by the formulas of the kinetic theory ($\delta = 6.5$) [1, 2]; curves, calculation by the formula of exponential distribution $C_g^{(c)} = C_1^{(c)} \exp[-\beta(g-1)]$.

Fig. 2. Relative excess volume of mixing $\Delta V/V$ of the hydrogen–argon mixture at a temperature of 200 K as a function of hydrogen concentration Λ (%) and pressure p (MPa).

In addition to the known characteristics of particle collisions in the cluster model [1, 2], we introduced the so-called stickiness parameter δ, whereby one can allow for special features of interactions of molecules, in particular the effects related to the changes in orientation due to collisions and to the effect of radiation. At small concentrations of dimers this parameter is determined by the distance passed by a molecule which is in a quasi-bound state during collisions. In dense gases, when the iteration method is used, the considered particle can be in a bound state; therefore, it makes an appreciable contribution to the mean stickiness parameter, since this parameter can be as large as is wished for bound particles. Any known characteristic of a real gas, e.g., the compressibility factor, can be used for calculation of δ.

This method is applicable to the description of mixtures containing several chemical components. Thus, in [1], calculations of an excess mixing volume $\Delta V/V$, which are in satisfactory agreement with the experiment, are presented. Usually, the excess volume is positive. The calculations by the described scheme showed that under certain conditions a negative excess volume can be observed, which can be applied in practice to gas packing with use of the corresponding admixtures. As an example, Fig. 2 gives a three-dimensional graph which is convenient for a search analysis; the graph shows a transition of the relative excess volume $\Delta V/V$ through zero (for the considered hydrogen–argon system this occurs at pressures higher than 6 MPa). In the calculations we used the effective collision diameters $\sigma_{11} = 0.265$ nm and $\sigma_{22} = 0.371$ nm calculated from the reference values of the coefficients of self-diffusion [3] by a formula which is a limiting relation for the true coefficient of diffusion when the concentration of the given component tends to unity. It should be noted that in [1] the latter is given with an error in the numerical coefficient a, i.e., in the calculations it should be used in the form

$$D_\alpha = 1.01397 a T^{3/2} z \left(p \sum_{\gamma=1}^{s} x_\gamma Y_{\alpha\gamma} M_{\gamma\alpha}^{-1/16} \alpha_{\alpha\gamma} \right)^{-1}, \qquad (1)$$

where $\alpha_{\alpha\gamma} \equiv \sqrt{\frac{2\mathbf{M}_\alpha \mathbf{M}_\gamma}{\mathbf{M}_\alpha + \mathbf{M}}}\, \sigma^2_{\alpha\gamma}\, \Omega^{(1.1)*}_{\alpha\gamma}$; $M_{\alpha\gamma} \equiv \frac{m_\gamma}{m_\alpha + m_\gamma} = \frac{\mathbf{M}_\gamma}{\mathbf{M}_\alpha + \mathbf{M}_\gamma}$ is the relative mass, $a = 2663.5 \cdot 10^{-25}\ \mathrm{J}^{3/2}\mathrm{K}^{-3/2} \times \mathrm{kmole}^{-1/2}$; summation in (1) is taken over all indices from γ to 1 up to the number of components in the mixture s; the superscripts at $\Omega^{(1.1)*}$ reflect the degree of the cosine of the deflection angle and the dimensionless relative velocity in the integrals with respect to these variables [4].

Method of Exponential Size-Distribution of Clusters. The method is based on the assumption that the quantity of clusters decreases with increase in the cluster size, i.e., the quantity of molecules included; the portion of clusters decreases exponentially. Besides the above-described calculations of concentrations of clusters by the iteration method (Fig. 1), the results of computer experiments produce the basis for this assumption. For example, in [5] this distribution was obtained for argon by the method of molecular dynamics and the Monte Carlo method. The distribution can be considered as a partial case of the Gibbs distribution if we assume that the energy of the cluster is in proportion to the quantity of molecules included in it, g:

$$n_g = n_1 \exp\left[-\beta\,(g-1)\right], \tag{2}$$

where n_1 is the number of molecules (monomers) included in the clusters per volume unit and β is the normalizing factor.

For description of the transport processes in real gases when each cluster subcomponent is treated as an individual subject, it is convenient to use the concentration found relative to the total number density of clusters of all types:

$$C_g^{(c)} \equiv \frac{n_g}{\sum\limits_{g=1}^{r} n_g}, \tag{3}$$

where r is the largest size of clusters allowed for in the present problem with the molecules being included into consideration as monomers with number density n_1.

The formula of exponential distribution (2) gives the following group of equations for $C_g^{(c)}$ and β:

$$C_1^{(c)} \left(1 + \sum_{g=2}^{r} \exp\left[-\beta\,(g-1)\right]\right) = 1\,. \tag{4}$$

One more equation for these quantities can be obtained from the determination of the mean molar mass of the cluster mixture:

$$\langle \mathbf{M} \rangle = \sum_{g=1}^{r} C_g^{(c)} \mathbf{M}_g = \sum_{g=1}^{r} C_g^{(c)} g\, \mathbf{M}_1\,. \tag{5}$$

The cluster model of gas allows for the variability of the number of structural elements and, thus, the quantity of moles with change in the state parameters; it is convenient to present the equation of state for each cluster subcomponent in the form of the virial equation [4] taking into account only the second virial coefficient written for a certain quantity of moles. Then, the mean molar mass of the whole cluster mixture is determined by the formula

$$\langle \mathbf{M} \rangle = \frac{\rho R T}{p\,(1-b)}, \tag{6}$$

where b is the correction to the eigenvolume of particles related to the volume occupied by the gas.

Expressing the concentration of a g-dimensional cluster $C_g^{(c)}$ in terms of the concentration of monomers $C_1^{(c)}$ by (2), with account for (6) we obtain

$$\frac{\rho RT}{(1-b)\,p\,\mathbf{M}_1} = C_1^{(c)} \sum_{g=1}^{r} \left\{ g \exp\left[-\beta\,(g-1)\right] \right\} . \tag{7}$$

Thus, the system of $r+1$ equations for determining $C_g^{(c)}$ and β is written as follows:

$$C_1^{(c)} \sum_{g=1}^{r} \left\{ g \exp\left[-\beta\,(g-1)\right] \right\} - \frac{\rho RT}{p\,\mathbf{M}_1\,(1-b)} = 0\,, \quad C_1^{(c)} \left(1 + \sum_{g=2}^{r} \exp\left[-\beta\,(g-1)\right] \right) - 1 = 0\,,$$

$$C_1^{(c)} \exp\left[-\beta\,(g-1)\right] - C_g^{(c)} = 0\,, \tag{8}$$

where g changes from 1 to r.

It is seen from the relations obtained that to find the unknown concentrations one should use experimental data on the gas density at certain pressures and temperatures. The correction to the eigenvolume can be expressed in terms of the effective collision diameter of molecules:

$$b = \frac{2\psi}{3} n^{(n)} \pi \sigma^3 . \tag{9}$$

The parameter ψ makes it possible to allow for the fact that in the formation of clusters the eigenvolume can also change.

An essential reason for the nonideality of gases in the cluster model is the variability of the quantity of cluster moles, which is caused by their formation or decomposition with change in the parameters of state. A convenient form of the equation of state of a real gas is the expression

$$p = z n^{(n)} kT . \tag{10}$$

The compressibility factor gives a portion of the molecules participating in creating pressure, which allows one to describe it in the form

$$z = \frac{1}{(1-b)} \sum_{g=1}^{r} C_g^{(n)} , \tag{11}$$

$$C_g^{(n)} = \frac{n_g}{n^{(n)}} = \frac{n_g}{\sum_{g=1}^{r} g n_g} . \tag{12}$$

The concentrations $C_g^{(n)}$ determined in terms of the quantities $C_g^{(c)}$ found from the system of equations (8) can be expressed as

$$C_g^{(n)} = C_g^{(c)} \frac{n^{(c)}}{\sum_{g=1}^{r} g n_g} = C_g^{(c)} \frac{1}{\sum_{g=1}^{r} g C_g^{(c)}} . \tag{13}$$

Thus, we obtained the final formula for the compressibility factor

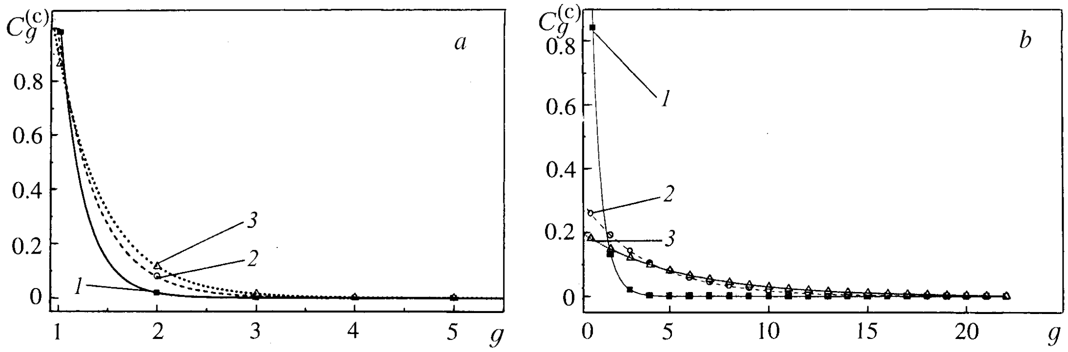

Fig. 3. Distribution of the concentration of clusters by their sizes as a function of pressure calculated by the formula of exponential distribution $C_g^{(c)} = C_1^{(c)} \times \exp[-\beta(g-1)]$ in hydrogen (a) at a temperature of 200 K [1) 5, 2) 50, and 3) 100 MPa] and argon (b) at a temperature of 273 K [1) 5, 2) 30, and 3) 35 MPa].

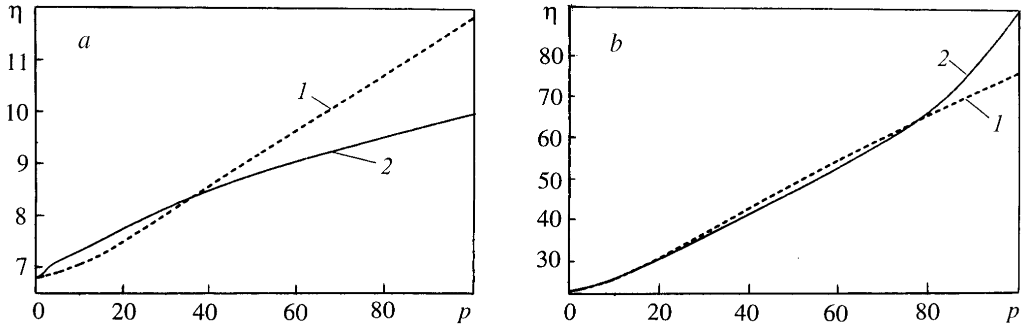

Fig. 4. Dependence of the coefficient of viscosity of hydrogen (a) and argon (b) on pressure at a temperature of 200 K (a) and 300 K (b): 1) [3]; 2) calculation on the basis of the cluster model allowing for clusters up to $g = 20$ (a) and $g = 30$ (b) using the viscous effective collision diameter calculated from the coefficient of viscosity at a normal pressure.

$$z = \frac{1}{(1-b)} \sum_{g=1}^{r} \frac{C_g^{(c)}}{\sum_{g=1}^{r} g C_g^{(c)}} \tag{14}$$

which is used for calculation.

Calculations and Comparison with Reference Data. Figure 3 and Tables 1 and 2 give the results of the calculations of cluster concentrations based on the solution of the system of equations (8) for a number of gases (argon, methane, hydrogen, water vapor) at different parameters of state. The required values of density and the molar volume were taken from [3, 6, 7]. It is seen from Table 1 that, using the suggested method, we obtained data on quantity of clusters, which contain up to 30 molecules, in argon at $T = 273$ K and a pressure of 30–40 MPa. The effect of clusters on the compressibility factor is shown by the example of methane (Table 3). Similarly to argon (Table 4), the compressibility factor calculated for methane is in good agreement with the available reference data.

The applicability of the cluster model to the description of transport properties is illustrated by the example of calculations of the coefficient of viscosity (Fig. 4) with account for the fact that, under the given conditions, the gas is considered as a multicomponent mixture of cluster subcomponents. The coefficient of viscosity of the cluster gas is calculated by the formula of the kinetic theory of a multicomponent mixture, which for dense gases is written as [2]

TABLE 1. Relative Number Concentrations (number fractions) of Clusters $C_g^{(c)}$ for Argon at a Temperature of 273 K (σ = 0.348 nm, found from the reference data for the coefficient of self-diffusion [3])

Size of the g cluster	Pressure p, MPa			
	5	25	35	40
1	0.8420	0.3606	0.1814	0.10498
2	0.1330	0.2306	0.1486	0.09436
3	0.0210	0.1474	0.1217	0.08482
4	$3.3197 \cdot 10^{-3}$	0.0943	0.0996	0.07624
5	$5.2443 \cdot 10^{-4}$	0.0603	0.0816	0.06853
6	$8.2848 \cdot 10^{-5}$	0.0385	0.0668	0.06160
7	0	0.0246	0.0547	0.05537
8	0	0.0158	0.0448	0.04977
9	0	0.0101	0.0367	0.04474
10	0	$6.4413 \cdot 10^{-3}$	0.0301	0.04022
11	0	$4.1185 \cdot 10^{-3}$	0.0246	0.03615
12	0	$2.6334 \cdot 10^{-3}$	0.0202	0.03249
13	0	$1.6838 \cdot 10^{-3}$	0.0165	0.02921
14	0	$1.0766 \cdot 10^{-3}$	0.0135	0.02625
15	0	$6.8837 \cdot 10^{-4}$	0.0111	0.02360
16	0	$4.4014 \cdot 10^{-4}$	$9.0659 \cdot 10^{-3}$	0.02121
17	0	$2.8143 \cdot 10^{-4}$	$7.4243 \cdot 10^{-3}$	0.01907
18	0	$1.7994 \cdot 10^{-4}$	$6.0800 \cdot 10^{-3}$	0.01714
19	0	$1.1506 \cdot 10^{-4}$	$4.9791 \cdot 10^{-3}$	0.01541
20	0	0	$4.0775 \cdot 10^{-3}$	0.01385
21	0	0	$3.3392 \cdot 10^{-3}$	0.01245
22	0	0	$2.7345 \cdot 10^{-3}$	0.01119
23	0	0	$2.2394 \cdot 10^{-3}$	0.01006
24	0	0	$1.8339 \cdot 10^{-3}$	$9.04073 \cdot 10^{-3}$
25	0	0	$1.5018 \cdot 10^{-3}$	$8.12650 \cdot 10^{-3}$
26	0	0	$1.2299 \cdot 10^{-3}$	$7.30471 \cdot 10^{-3}$
27	0	0	$1.0072 \cdot 10^{-3}$	$6.56603 \cdot 10^{-3}$
28	0	0	$8.2482 \cdot 10^{-4}$	$5.90205 \cdot 10^{-3}$
29	0	0	$6.7546 \cdot 10^{-4}$	$5.30521 \cdot 10^{-3}$
30	0	0	$5.5316 \cdot 10^{-4}$	$4.76873 \cdot 10^{-3}$

$$\eta = \sum_{\alpha=1}^{s} \frac{x_\alpha h \sqrt{T}}{\sum\limits_{\gamma=1}^{s} \chi_{\alpha\gamma} x_\gamma \sigma_{\alpha\gamma}^2 \sqrt{\frac{2M_{\gamma\alpha}}{\mathbf{M}_\alpha}} \left(5M_{\alpha\gamma}\,\Omega_{\alpha\gamma}^{(1.1)*} + 3M_{\gamma\alpha}\,\Omega_{\alpha\gamma}^{(2.2)*}\right)}, \tag{15}$$

where $h = 8009 \cdot 10^{-29}\ \mathrm{J}^{1/2}\mathrm{K}^{-1/2}\mathrm{kmole}^{1/2}$.

The radial function with account for momentum transfer in collisions at a distance of the effective diameter has the form [8]

TABLE 2. Relative Number Concentrations (number fractions) of Clusters $C_g^{(c)}$ and the Parameter β (water vapor at the saturation line; calculation in the approximation taking account of decamers with an effective collision diameter found by the coefficient of viscosity at atmospheric pressure and the corresponding temperature [3])

Size of the g cluster, parameter β	$p = 0.101325$, $T = 373.15$	$p = 0.47597$, $T = 423.15$	$p = 1.5551$, $T = 473.15$	$p = 18.674$, $T = 633.15$
1	0.9828	0.9495	0.886	0.3160
2	0.0169	0.0480	0.101	0.2162
3	$2.915 \cdot 10^{-4}$	$2.425 \cdot 10^{-3}$	0.011	0.1478
4	0	$1.225 \cdot 10^{-4}$	$1.305 \cdot 10^{-3}$	0.1011
5	0	0	$1.484 \cdot 10^{-4}$	0.0692
6	0	0	0	0.0473
7	0	0	0	0.0324
8	0	0	0	0.0221
9	0	0	0	0.0151
10	0	0	0	0.0104
β	4.0615	2.985	2.174	0.3798

TABLE 3. Compressibility Factor of Methane at $T = 300$ K (calculation by formula (14) in the approximation taking account of clusters to 30mers)

p, MPa	Compressibility factor z		p, MPa	Compressibility factor z	
	[6]	calculation		[6]	calculation
0.1	0.9983	0.9989	25	0.8630	0.8630
0.5	0.9916	0.9925	30	0.9152	0.9152
1.0	0.9933	0.9934	35	0.9770	0.9771
5.0	0.9196	0.9186	40	1.0438	1.0430
10	0.8553	0.8553	45	1.1133	1.1127
15	0.8228	0.8228	50	1.1839	1.1803
20	0.8283	0.8284	60	1.3266	1.2536

TABLE 4. Values of the Normalizing Factor β in (2) and the Compressibility Factor z for Argon at $T = 273$ K

p, MPa	β	z	
		calculation by (14)	data of [7]
5	1.8453	0.9591	0.9568
30	0.2987	0.9608	0.9620
35	0.1998	1.0026	1.0033
40	0.1066	1.0485	1.0507

$$\chi_{\alpha\gamma} = \frac{1}{S^3 (1 + s_{\alpha\gamma})} \left\{ S^2 + 3 \frac{\sigma_{\alpha\alpha}\sigma_{\gamma\gamma}}{\sigma_{\alpha\alpha} + \sigma_{\gamma\gamma}} S S_3 + 2 \left(\frac{\sigma_{\alpha\alpha}\sigma_{\gamma\gamma}}{\sigma_{\alpha\alpha} + \sigma_{\gamma\gamma}} \right)^2 S_2^2 \right\}, \tag{16}$$

$$S_2 = \frac{\pi n}{6} \sum_{\gamma=1}^{s} x_\gamma \sigma_{\gamma\gamma}^2 , \quad S = 1 - \frac{\pi n}{6} \sum_{\gamma=1}^{s} x_\gamma \sigma_{\gamma\gamma}^3 , \quad s_{\alpha\gamma} = \frac{\sigma_{\alpha\gamma}}{\tau_\alpha} \sqrt{\frac{m_\alpha}{3kT}} .$$

As applied to the cluster mixture of one chemical component, in these formulas the size of the g cluster plays the role of the component number α and summation is taken over the sizes of all clusters under consideration, including monomers. Thus, for example, in Fig. 4, the coefficient of gas viscosity is found as the sum of all partial contributions of cluster subcomponents, i.e., summation is taken with respect to all clusters under consideration. As is seen from the graphs presented, the cluster model describes, with an error within 20%, the experimental dependence of the viscosities of argon and hydrogen on pressure. In this case, one of the reasons which leads to this dependence is revealed: the increase of pressure results in an increase in the portion of heavy clusters whose partial coefficient of viscosity is larger and, therefore, they contribute more to the momentum flux. One reason for the discrepancies is that in the calculations one has to use parameters which characterize collisions of particles and which in due course were found by the formulas based on the model of invariability of the number of moles. Some quantities, i.e., the parameters of packing or stickiness, have not been used earlier; therefore, there are no reliable methods of their determination. The calculations conducted indicate that the variability of the number of moles greatly affects the properties of gases. Therefore, use of even not well-developed methods of determination used in the above-stated computation schemes of the parameters makes it possible to obtain interesting results within the framework of the suggested cluster model of a real gas.

NOTATION

D_α, true coefficient of diffusion, m^2/sec; x_γ, number fraction of the molecules of the component γ; s, number of components in the mixture; n_g, number of clusters per volume unit, which contain g molecules, m^{-3}; g, number of molecules in the cluster; $\Delta V/V$, relative excess volume of mixing; Λ, concentration of hydrogen, %; a, dimensional numerical factor; $\Omega^{(1.1)*}$ and $\Omega^{(2.2)*}$, dimensionless collision integrals; z, compressibility factor; T, temperature, K; p, pressure, MPa; $Y_{\alpha\gamma}$, radial function; m_α, molecule mass, kg; $\sigma_{\alpha\gamma}$, effective collision diameter of the molecules, m; σ_{11} and σ_{22}, effective collision diameters of the molecules of the first and second gas, respectively; δ, stickiness parameter; $M_{\alpha\gamma}$, reduced mass; $\langle \mathbf{M} \rangle$, molar mass of the cluster mixture, kg/kmole; $\mathbf{M}_g$, molar mass of the g-dimensional cluster; ρ, density, kg/m^3; k, Boltzmann constant, J/K; R, universal gas constant, J/(mole·K); $C_g^{(n)}$, concentration (fraction) of clusters relative to the number of molecules, $C_g^{(c)}$, concentration of clusters relative to the total density of clusters; ψ, parameter of packing; $n^{(n)}$ and $n^{(c)}$, number density of all molecules and all clusters, respectively, m^{-3}; r, size of the largest cluster; η, coefficient of viscosity, μPa·sec; h, dimensional coefficient; τ, time of free flight, sec. Indices: α and γ, numbers of chemical components in the mixture; (c), cluster.

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