CALCULATION OF THE COEFFICIENT OF VISCOSITY OF MODERATELY COMPRESSED GASES

V. R. Kamenetskii

UDC 532.133

A method is set forth for calculating the coefficients of viscosity of gases of moderate density on the basis of allowance for dimerization and the use of an effective potential function of the intermolecular interaction. The example of water vapor and ammonia show that the method is fairly reliable.

The formalism of rigorous kinetic theory, taking into account binary collisions of molecules, enables one to calculate the transport coefficients of only rarefied gases.

For dense systems, one must take into account the contribution from collisions of higher order, and at the present time this presents greater difficulties. However, for a gas of moderate density this problem can be solved by using the notations of a molecular association.

The coefficient of viscosity of a gas is expressed as an expansion in powers of the pressure:

$$\eta = \eta_0 (1 + \alpha p + \ldots), \tag{1}$$

the coefficients being functions of the temperature and they take into account the contributions of triple and higher order collisions.

In the region of moderate densities, it is sufficient to consider only the linear part of Eq. (1), in which $\alpha = \eta^{-1}(\partial\eta/\partial p)_{p=0}$ is the coefficient that takes into account the contribution of triple collisions.

If one regards a gas of moderate density as an equilibrium mixture of monomers and dimers, then, as Stogryn and Hirschfelder have shown [1], a triple collision can be represented as a binary collision between a monomer and a dimer.

In accordance with the conclusions of [1], the coefficient of viscosity of such a gas can be represented by the sum

$$\eta = \eta_m + \eta_c, \tag{2}$$

where η_m is the coefficient of viscosity of the binary mixture of momomers and dimers, and η_c is the contribution due to transport by collisions.

TABLE 1. Coefficients of Eq. (7)

i	a_i	
	T^*=0,3—3,416	T^*=3,416—10,0
0	3,421524	3,414047
1	—0,979053	2,481028
2	—5,430678	—59,471495
3	8,471780	880,26772
4	—6,686845	—5560,7765
5	3,305877	18654,443
6	—1,011695	—34021,774
7	0,172360	31815,555
8	—0,012369	—11904,267

If we substitute into (2) the corresponding expressions for η_m and η_c, we can obtain an expression for the coefficient α in dimensionless form, this being valid for the Lennard-Jones potential [1]:

$$RT\alpha/b_0 = -B_d^*\{0.5113 + 0.2481\,[6\,(D_{12}/D_{11}) - 4.5455\,(D_{11}/D_{12})]\} + 0.1750\,[B^* + T^*\,(dB^*/dT^*)]. \tag{3}$$

Here

$$D_{12}/D_{11} = \frac{1}{2}\sqrt{3}\,(\sigma_{11}/\sigma_{12})^2\,(\Omega_{11}^{(1,1)*}/\Omega_{12}^{(1,1)*}),$$

$$b_0 = 2/3\pi N\sigma^3,\ B_d^* = (B_b + B_m)/b_0.$$

Technological Institute of the Refrigeration Industry, Odessa. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 26, No. 5, pp. 844-848, May, 1974. Original article submitted December 18, 1973.

TABLE 2. Potential Parameters of CO_2, NH_3, and H_2O

Gas	t, °C	ψ^*	T^*	ε/k, °K	σ, Å
CO_2	20	1,054	1,166	251,4	3,756
	30	1,017	1,224	247,7	3,773
NH_3	20	2,057	0,450	651,4	2,818
	30	1,958	0,476	636,9	2,827
H_2O	150	2,247	0,425	996,1	2,604
	300	1,486	0,690	830,4	2,660
	400	1,226	0,947	710,5	2,722

The indices 11 and 12 refer to the interaction between two monomers, and a monomer and a dimer, respectively.

The method can be applied to simple gases with spherically symmetric intermolecular interaction.

Singh and his collaborators [4-6] applied Eq. (3) to complicated gases for which the interaction energy between the molecules is determined by not only the distance but also the mutual orientation.

For polar substances they used the Stockmayer potential (12-6-3), and for substances whose molecules have a quadrupole moment they used the potential (12-6-5) introduced by Smith, Munn, and Mason [11]. In addition, the authors of [4-6] assumed that the molecules that make up a dimer are in a position that corresponds to maximal energy of attraction, and also that there is an equal probability of all relative orientations of interacting molecules.

Although the results of these papers agree qualitatively with the experimental data (for example, they reproduce the anomalous pressure dependence of the coefficient of viscosity of water vapor and ammonia), the quantitative agreement between the calculated values of α and the experimental values is inadequate. This is apparently due to the insufficiently plausible assumption and the potential functions used.

Danon and Amdur [7], solving this problem only for polar gases, used a previously averaged Stockmayer potential (12-6-3), reduced to the form (12-6) with temperature dependent parameters and reduced dipole moment. The values they calculated of α for NH_3 and H_2O agree better with the experimental data, although the discrepancies still remain significant.

In the present paper we attempt to apply the approach developed in [1] to gases of any molecular structure, using an effective potential function of intermolecular interaction.

It has been previously shown in [2] that as effective potential one can use a two-parameter potential of the type (12-6) with temperature-dependent parameters $\sigma(T)$ and $\varepsilon(T)$. The temperature dependence of the parameters of such a potential appears as a result of averaging of the interaction energy over all possible mutual orientations of the interacting molecules.

The intermolecular interaction of any gas can be assumed to be spherically symmetric, which greatly facilitates the calculation of the thermal properties of substances to a sufficient accuracy.

Since the effective potential function must describe equally successfully both the equilibrium and the nonequilibrium properties, we used the following method of determining the potential parameters $\sigma(T)$ and $\varepsilon(T)$ from the data on the second virial coefficient and the coefficient of viscosity of a rarefied gas. From the expressions

$$B = 2/3\pi N\sigma^3 B^*, \tag{4}$$

$$\eta_0 = 266.93 \frac{\sqrt{MT}}{\sigma^2\Omega^{(2,2)*}} \tag{5}$$

it is not difficult to obtain the dependence

$$\frac{\eta_0 B^{2/3}}{311.64\sqrt{MT}} = \frac{B^{*2/3}}{\Omega^{(2,2)*}} = \psi^*(T^*). \tag{6}$$

The actual form of (6) is determined by means of the values of B^* and $\Omega^{(2,2)*}$ tabulated in [3].

Having data on η_0 and B at our disposal, we can use Eq. (6) to calculate ψ^*, and, by a specially constructed graph of T^* as a function of ψ^*, find the value of the reduced temperature. After this we find the parameter $\varepsilon/k = T/T^*$.

The corresponding value of the parameter σ is found from (4) or (5).

TABLE 3. Comparison of Calculated and Experimental Values of $RT\alpha/b_0$ for Ammonia and Water Vapor

	t, °C	Calculated values				Experimental values		
		[5]	[6]	[7]	data of this paper	[8]	[9]	[10]
NH_3	20	—3,85	—1,88	—3,07	—4,01			—3,73
	30	—3,64	—1,76	—2,89	—3,65			—2,62
	170	—6,44		—4,41	—3,84	—1,60		
	200	—6,18		—3,81	—3,28	—2,63		
	230	—5,85		—3,27	—2,81	—0,83		
	270	—5,64		—2,96	—2,30	—0,19		
H_2O	149		—5,36		—4,33		—4,12	
	176		—4,96		—3,73		—4,07	
	195		—4,78		—3,36		—3,38	
	214		—4,60		—3,06		—2,44	
	148		—5,39		—4,36		—4,56	
	192		—4,79		—3,42		—3,24	
	234		—4,26		—2,76		—0,82	
	275		—3,75		—2,25		—0,82	

Instead of plotting T^* against ψ^*, one could use the analytic expression obtained in this paper:

$$T^* = \sum_{i=0}^{n} a_i \psi^{*i}. \tag{7}$$

Equation (7) has two sets of coefficients corresponding to the two ranges of variation of the reduced temperature: $T^* = 0.3\text{-}3.416$ and $T^* = 3.416\text{-}10.0$ (the value $T^* = 3.416$ corresponds to the reduced Boyle temperature for the Lennard-Jones potential, for which $\psi^* = 0$). The values of these coefficients are given in Table 1.

The values of the potential parameters of carbon dioxide, ammonia, and water vapor determined in this way exhibit a clearly expressed temperature dependence, as can be seen from Table 2.

Using the parameters we have obtained, we calculated the values of $RT\alpha/b_0$ for superheated water vapor and ammonia. The values of B_d^* were obtained from the table in [1] and the values of $\Omega^{(1,1)*}$, B^*, and dB^*/dT^* from [3].

The parameters of the monomer—dimer interaction were calculated by means of the relations obtained in (1) for the potential (12-6)

$$\varepsilon_{12}/\varepsilon_{11} = 1.32;\ \sigma_{12}/\sigma_{11} = 1.16. \tag{8}$$

The results of the calculations are given in Table 3 and they reveal a fairly good agreement between the calculated and experimental values of $RT\alpha/b_0$. For comparison we also give in Table 3 the results of [5-7], which were obtained in a more complicated manner. They agree less well with the experimental data.

Analysis of the results of this paper indicates a sufficient reliability of the method, which enables one to determine fairly accurately the influence of pressure on the coefficient of viscosity of gases of complicated molecular structure.

NOTATION

η	is the coefficient of viscosity of a compressed gas;
η_0	is the coefficient of viscosity of a rarefied gas;
B	is the second virial coefficient;
B_b, B_m	are the contributions of bound and metastably bound dimers to the second virial coefficient, respectively;
$B_d = B_b + B_m$	is the total contribution of dimers to the second virial coefficient;
D	is the coefficient of diffusion;
$\Omega^{(1,1)*}$, $\Omega^{(2,2)*}$	are the reduced collision integrals used to calculate the coefficients of diffusion and viscosity, respectively;
σ, ε	are the parameters of the potential of the intermolecular interaction;
R	is the gas constant;
N	is Avogadro's number.

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