VISCOSITY OF MODERATELY COMPRESSED GASES AND THEIR BINARY MIXTURES

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The temperature dependence of the first correction in the density to the coefficient of viscosity of pure gases is obtained on the basis of an effective potential function of intramolecular interaction. The universality of this dependence and the possibility of its use to calculate the coefficient of viscosity of moderately compressed gases and their binary mixtures are shown.

The coefficient of viscosity of a compressed gas can be expressed as an expansion in powers of the density:

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

whose coefficients are functions of the temperature and take account of the contributions of multiparticle collisions.

In the domain of moderate densities we can limit ourselves to the linear part of (1), where $\alpha = \eta_0^{-1} \cdot (\partial\eta/\partial\rho)_{\rho=0}$ is a coefficient taking account of the contribution of triple collisions (the first correction to the density).

In dimensionless form $\alpha^* = \alpha/b_0$ this quantity should be a universal function of the reduced temperature $T^* = kT/\varepsilon$ ($b_0 = {}^2/_3\pi N\sigma^3$, σ and ε are parameters of the Lennard-Jones potential (12-16)) for substances with a spherically symmetric intramolecular interaction. This is verified by experimental results on monatomic gases and nitrogen [1].

It is shown in [2, 3] that the intramolecular interaction in any gas can be considered as spherically symmetric if an effective potential function is used which is the potential (12-6) with temperature dependent parameters $\sigma(T)$ and $\varepsilon(T)$.

The temperature dependence of this potential appears because of taking the average of the interaction energy over all possible mutual orientations of the interacting molecules [4].

Since the function mentioned can describe both equilibrium and nonequilibrium properties, the method used here is to determine the potential parameters $\sigma(T)$ and $\varepsilon(T)$ from data on the second virial coefficient and the coefficient of viscosity of a rarefied gas.

TABLE 1.

Gas	σ, Å	ε/k, °K
Ar	3.428	120.02
Kr	3.965	165.5
Xe	4.073	224.1
Ne	2.776	37.18
He	2.620	7.740
N_2	3.664	95.92
H_2	2.947	32.02
D_2	2.949	34.17

From the expressions

$$B = b_0 B^* \tag{2}$$

$$\eta_0 = 266.93 \frac{\sqrt{MT}}{\sigma^2 \Omega^{(2\,2)^*}} \tag{3}$$

where B^* and $\Omega^{(2,2)^*}$ are the reduced second virial coefficient and the collision integral, respectively, the following dependence can be obtained:

$$\eta_0 B^{2/3} / 311.64 \sqrt{MT} = B^{*2/3} / \Omega^{(2.2)^*} = \psi^*(T^*). \tag{4}$$

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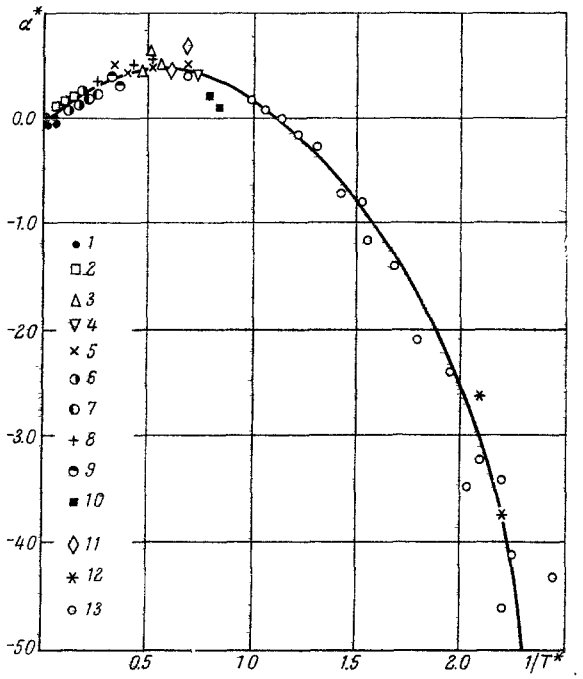

Fig. 1

TABLE 2

Gas	t, °C	σ, Å	ε/k, °K
CO	—50	3.626	102.5
	0	3.638	101.3
	75	3.650	99.7
CH_4	—50	3.744	154.5
	0	3.767	152.2
	150	3.770	149.2
CO_2	20	3.757	248.5
	31	3.771	245.3
NH_3	20	2.818	651.4
	30	2.827	636.9
H_2O	150	2.604	996.1
	300	2.660	830.4
	400	2.722	710.5

TABLE 3

Gas	T^*	Source of results
Ar	1.44—2.90	[5—11]
Kr	1.77—2.10	[7, 12]
Xe	1.33	[7]
Ne	6.0—10.0	[7—9, 13]
He	28.8—48.2	[5—7, 9]
N_2	1.91—3.89	[5—9]
H_2	5.40—13.21	[5, 14, 15]
D_2	6.53—12.38	[14]
CO	2.18—3.49	[14]
CH_4	1.44—2.84	[14]
CO_2	1.18—1.24	[16]
NH_3	0.45—0.48	[17]
H_2O	0.40—1.0	[18—21]

The specific form of the dependence (4) is determined by using values of B* and $\Omega^{(2,2)*}$ tabulated in [4] for the potential (12-6). Expanding the data in η_0 and B, we can calculate ψ^* by means of (4) by using a specially constructed graph of the dependence of T* on ψ^* to find the value of the reduced temperature. The parameter $\varepsilon/k = T/T^*$ is determined afterwards. The appropriate value of the parameter σ is found from (2) or from (3). The potential parameters determined by the method described for substances of complex molecular configuration (especially polar) depend explicitly on the temperature.

The values of σ and ε for simple gases (monatomic, nitrogen, hydrogen, deuterium) turn out to be practically constant, which agrees with the essential representations about the nature of intramolecular interaction in these gases.

The values of σ and ε for simple gases are presented in Table 1 and for gases with complex intramolecular interaction in Table 2.

The experimental data on viscosity of substances listed in Tables 1 and 2 and the potential parameters obtained were used to calculate the values of α^*.

The sources of these data, as well the ranges of the reduced temperatures included, are indicated in Table 3.

TABLE 4

Mixture	σ_{12}, Å	$(\varepsilon/k)_{12}$, °K	x_1	x_2	$\alpha_m^{(1)}$	$\alpha_m^{(2)}$	Source of exptl. results
			0.1374	0.8626	8.700	8.740	
He—CO_2	3.188	43.85	0.4905	0.5095	7.094	7.683	[22]
			0.9586	0.0414	2.576	2.732	
			0.2062	0.7938	8.68	9.02	
			0.4350	0.5650	10.23	10.61	
Ne—CO_2	3.266	43.95	0.6203	0.3797	10.59	10.71	[23]
			0.7103	0.2897	10.45	10.48	
			0.8762	0.1238	9.67	9.57	
			0.598	0.402	9.83	6.10	
Ne—Ar	3.102	66.80	0.332	0.668	13.87	11.95	[24]
			0.099	0.901	17.26	16.05	
			0.2661	0.7339	15.73	15.44	
Ne—N_2	3.220	59.72	0.5112	0.4888	12.53	11.03	[22]
			0.7521	0.2479	9.78	7.55	
			0.1990	0.8010	23.48	23.44	
N_2—Ar	3.546	107.2	0.3862	0.6138	22.82	22.62	[22]
			0.5946	0.4054	22.27	22.09	
			0.7737	0.2263	21.95	21.64	
			0.741	0.259	1.814	2.170	
Ne—He	2.698	16.96	0.567	0.433	0.977	1.383	[24]
			0.350	0.650	0.170	0.305	
			0.154	0.846	—0.331	—0.279	
			0.051	0.949	—0.509	—0.651	

The dependence of α^* on T^* gases as obtained from the experimental results is represented in the figure: 1) He, 2) Ne, 3) Kr, 4) Xe, 5) Ar, 6) H_2, 7) D_2, 8) N_2, 9) CO, 10) CO_2, 11) CH_4, 12) NH_3, 13) H_2O.

This dependence is described analytically by an approximate expression obtained by least squares

$$\alpha^* = -0.151955 + 2.541259T^{*-1} - 3.108299T^{*-2} + 0.527637T^{*-3} + 0.507413T^{*-4} - 0.230422T^{*-5} . \quad (5)$$

The spread of the points around a curve constructed by using (5) will, as a rule, correspond to tolerances in the values of α obtained by the authors of the experimental results.

The investigation conducted permits arrival at the deduction that the temperature dependence of the first correction in the density to the coefficient of viscosity is universal, since it turns out to be valid for substances of different nature.

The concept of an anomalous dependence of the coefficient of viscosity of water vapor and ammonia on the pressure is false. Other polar substances, for example, alcohols, are probably also characterized by a negative influence of the pressure on the coefficient of viscosity in the range of reduced temperatures $T^* < 1.0$. This assumption requires experimental verification by using precise measurements of the viscosity of gaseous alcohols at moderate pressures.

The universal dependence obtained can be used also to evaluate the coefficient of viscosity of moderately compressed gas mixtures.

The analysis conducted showed that the first correction in the density for a binary mixture can be expressed by analogy with the second virial coefficient as

$$\alpha_m = \alpha_i x_i^2 + 2\alpha_{ij} x_i x_j + \alpha_j x_j^2 . \quad (6)$$

The term α_{ij} taking account of the diverse interactions is determined by using the rule of combination:

$$\sigma_{ij} = {}^1/_2 (\sigma_i + \sigma_j) \quad (7)$$

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} \quad (8)$$

$$\alpha_{ij} = {}^2/_3 \pi N \sigma_{ij}^3 \alpha_{ij}^* . \quad (9)$$

The quantity α_{ij}^* is also a universal function of the reduced temperature and is calculated by using (5).

Such an approach permits obtaining values of α_m to sufficient accuracy by means of data for pure components without relying on experimental results on the viscosity of the mixture at elevated pressures.

The above is illustrated in Table 4, in which the computed $\alpha_m^{(1)}$ and experimental $\alpha_m^{(2)}$ values of the first correction in the density for the mixtures (cm³/mole) of $He-CO_2$, $Ne-CO_2$, Ne–Ar, $Ne-N_2$, N_2–Ar, and Ne–He are compared at t = 20°C.

The discrepancies between the calculated and experimental results are not large and are commensurate with the error in the values α of the pure components as determined from test data on the viscosity.

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