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TRANSPORT PROPERTIES OF NITROGEN, OXYGEN, CARBON DIOXIDE, AND AIR AT LOW DENSITIES AND TEMPERATURES FROM 50 TO 3000°K

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We calculate the viscosity and thermal conductivity, the Prandtl number, and the Eucken factor for a (12-7, δ) pair model potential. The calculated values agree with correlated experimental data within the limits of error of the measurements.

The Chapman—Enskog theory establishes a functional relation between the transport coefficients of a rarefied monatomic gas and the pair potential energy (potential) of the interparticle interaction [1, 2]. The calculation of the potential energy of the interparticle interaction over a wide range of distances is extremely difficult. Therefore, model potentials are generally used [2, 3]. However, the known pair potential models of the interaction (Lennard–Jones, Buckingham, Kihara, etc.) are unsuitable for calculations, since the principle of corresponding states [4] is not actually satisfied for them.

It was shown in [5, 6] that the (12-7) two-parameter pair model potential

$$\varphi(r) = 5.1042\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{7} \right],$$ (1)

where ε is the depth of the potential well and σ is the molecular diameter, gives a consistent description of various experimental data on the properties of monatomic gases at low densities; i.e., for it the principle of corresponding states is satisfied. This permitted the calculation of transport coefficients of monatomic gases and binary mixtures of them for low densities and temperatures from 100 to 6000°K [7]. Subsequent measurements [8] confirmed the accuracy of the calculations.

A generalization of the pair potential (1) was proposed in [9, 10] for nonpolar polyatomic molecules

$$\varphi(r) = \begin{cases} \infty & r \leqslant r_e \\ 5.1042\varepsilon \left[\left(\frac{\sigma^2 - r_e^2}{r^2 - r_e^2} \right)^6 - \left(\frac{\sigma^2 - r_e^2}{r^2 - r_e^2} \right)^{7/2} \right], & r \geqslant r_e, \end{cases}$$ (2)

where r_e is the distance between the outer atoms forming the core of the molecule. It was shown that the three-parameter pair model potential (2) gives a consistent description of various experimental data on the properties of nonpolar polyatomic gases whose molecules have very different geometric structures [9]. The Kong combining rules [11] were generalized in [10] to the case of the potential (2), which permitted the calculation of thermodynamic properties of nonpolar polyatomic gases and mixtures of them for low and medium densities over a wide range of temperatures.

The present article presents calculated values of transport coefficients of air and its components (nitrogen, oxygen, carbon dioxide). The viscosity was calculated with the Chapman—Enskog theory, taking account of the Kihara correction in higher approximations [1, 2]. The thermal conductivity was calculated by using results of the nonlinearized Mason—Monchik theory [12], refined by Antye [13]:

TABLE 1. Viscosity and Thermal Conductivity

T, K	Viscosity $\mu \cdot 10^8$ (Pa·sec)				Thermal conductivity $\lambda \cdot 10^4$ (W/m·°K)			
	nitrogen	oxygen	air	carbon dioxide	nitrogen	oxygen	air	carbon dioxide
50	359	428	371		50,9	52,0	50,9	
60	419	494	432		60,1	60,7	60,0	
80	540	627	556		78,5	78,3	78,2	
100	664	762	681		96,9	96,0	96,6	
140	910	1032	931		133,6	131,3	132,9	
180	1148	1301	1174		168,4	166,1	167,8	
220	1373	1564	1406	1192	201,5	199,8	201,2	120,9
260	1583	1816	1625	1352	232,7	232,7	232,7	145,8
300	1782	2057	1831	1509	262,0	265,0	262,7	171,5
400	2228	2608	2297	1883	329,1	344,0	332,5	237,8
600	2978	3543	3080	2617	451,8	495,5	461,6	374,3
800	3614	4330	3744	3285	570,2	633,6	584,6	509,0
1000	4180	5026	4334	3897	683,6	757,2	700,1	635,7
1400	5183	6247	5377	4970	890,0	971,1	908,0	858,2
1800	6072	7322	6299	5891	1071	1155	1090	1046
2200	6886	8299	7142	6707	1234	1320	1253	1209
2600	7642	9207	7926	7448	1384	1471	1403	1355
3000	8355	10060	8663	8133	1522	1612	1542	1488

$$\lambda = \lambda_{trans} + \lambda_{rot} + \lambda_{vib},\tag{3}$$

$$\lambda_{trans} = \frac{5}{2}\mu\left(\frac{3}{2}R - \Delta\right),\tag{4}$$

$$\lambda_{rot} = \rho D (C_{rot} + \Delta),\tag{5}$$

$$\lambda_{vib} = \rho D C_{vib},\tag{6}$$

where

$$\Delta = \frac{5C_{rot}}{\pi Z_{rot}}\left(1 - \frac{2}{5}\frac{\rho D}{\mu}\right)\left[1 + \frac{2}{\pi Z_{rot}}\left(\frac{5C_{rot}}{3R} + \frac{\rho D}{\mu}\right)\right]^{-1}.\tag{7}$$

Equations (3)-(7) were derived under the assumption that the coefficients of diffusion transport of internal degrees of freedom are equal to the coefficient of self-diffusion, and that the number of collisions Z_{vib} necessary to achieve equilibrium between the vibrational and translational energies is of the order 10^3-10^5, so that the term C_{vib}/Z_{vib} can be neglected in comparison with the term C_{rot}/Z_{rot}.

The number of collisions Z_{rot} necessary to establish equilibrium between the rotational and translational energies was calculated with the O'Neal—Brokaw theory [14]:

$$Z_{rot}^{-1} = \frac{5\pi}{12}\frac{\frac{4J}{m\sigma^2}\exp\left(\frac{\varepsilon}{kT}\right)}{\left(1 + \frac{4J}{m\sigma^2}\right)^2\Omega^{(2.2)*}},\tag{8}$$

where J is the moment of inertia; m, mass of the molecule; and ε, σ, force constants of the pair potential (2).

In contrast with the Parker theory [15], in [14] the effect of a hard core of polyatomic molecules ($r \leq r_e$, $\varphi = \infty$) was taken into account. It should be noted that the potential (2) is strictly justified only for linear molecules, and then only at large distances [9]. The pair interaction between other nonpolar molecules can be described in the form (2) if the cores of the molecules are sufficiently elongated in any one direction so that they can be considered quasilinear. In this approximation

$$\frac{4J}{m\sigma^2} = \left(\frac{r_e}{\sigma}\right)^2 = \delta\tag{9}$$

and

$$Z_{rot}^{-1} = \frac{5\pi}{12}\frac{\delta}{(1 + \delta)^2\Omega^{(2.2)*}}\exp\left(\frac{1}{T^*}\right).\tag{10}$$

TABLE 2. Prandtl Number and Eucken Factor

T, K	Prandtl No. $Pr = \mu\, C_p/\lambda$				Eucken factor $f = \lambda/\mu\, C_v$			
	nitrogen	oxygen	air	carbon dioxide	nitrogen	oxygen	air	carbon dioxide
50	0,732	0,749	0,732		1,913	1,870	1,912	
60	0,724	0,741	0,724		1,933	1,889	1,934	
80	0,716	0,729	0,714		1,956	1,920	1,962	
100	0,712	0,722	0,708		1,967	1,938	1,977	
140	0,708	0,716	0,703		1,978	1,957	1,991	
180	0,709	0,712	0,703		1,976	1,965	1,991	
220	0,708	0,713	0,702	0,746	1,978	1,961	1,993	1,786
260	0,707	0,713	0,702	0,744	1,979	1,961	1,994	1,759
300	0,707	0,713	0,702	0,743	1,979	1,957	1,995	1,735
400	0,707	0,713	0,702	0,741	1,976	1,938	1,988	1,691
600	0,708	0,716	0,703	0,749	1,951	1,887	1,956	1,622
800	0,710	0,718	0,705	0,751	1,915	1,851	1,919	1,590
1000	0,712	0,720	0,707	0,753	1,884	1,828	1,889	1,570
1400	0,715	0,721	0,710	0,755	1,845	1,806	1,849	1,549
1800	0,716	0,722	0,711	0,757	1,825	1,795	1,815	1,538
2200	0,717	0,722	0,711	0,758	1,814	1,790	1,781	1,532
2600	0,717	0,722	0,712	0,759	1,807	1,786	1,759	1,527
3000	0,718	0,723	0,712	0,759	1,803	1,785	1,738	1,524

Thus, to calculate Z_{rot} it is necessary to know only the constants of the potential (2) and the collision integrals $\Omega^{(2,2)*}$. The force constants of the potential (2) are given in [9, 10]. The collision integrals $\Omega^{(l,s)*}$ (T^*, δ) ($l = 1$, 2; s = 1, 2, 3) for the potential (2) were calculated numerically for the temperatures cited $T^* = (kT/\varepsilon) = 0.3$–100, and for values of the nonsphericity parameter of the molecules $\delta = 0$–0.5. The relative error of the calculated values of the collision integrals does not exceed $\pm 0.5\%$.

The calculated values of the viscosity and thermal conductivity of nitrogen, oxygen, carbon dioxide, and air are listed in Table 1. Air was treated as a binary mixture of nitrogen (volume concentration $x_1 = 0.7615$) and oxygen ($x_2 = 0.2385$). The molecular weight of air is equal to

$$m = x_1 m_1 + x_2 m_2 = 28.964, \tag{11}$$

the dissociation and formation of nitric oxide was not taken into account.

The calculated values are in agreement with correlated experimental data of [16, 17] within the limits of the differences between the measurements of the different experimenters, which is commonly regarded as an objective estimate of the error of the measurements. For nitrogen, oxygen, and air at temperatures from 120 to 2500°K these errors are $\pm 2\%$ for the viscosity and $\pm 5\%$ for the thermal conductivity [16]. The errors of the measurement of the transport properties of carbon dioxide at low (T = 200°K) and high (T = 2500°K) temperatures can reach $\pm 10\%$ [17].

Table 2 lists the calculated values of the Prandtl number and the Eucken factor. The Eucken factor takes account of the effect of inelastic collisions of molecules leading to a redistribution of energy between translational and rotational degrees of freedom. For monatomic gases the Eucken factor is 2.5; for air and its components (nitrogen, oxygen, carbon dioxide) at temperatures up to 3000°K the Eucken factor varies from 1.98 to 1.52.

Thus, the pair model potential (2) can be successfully employed to calculate transport properties of nonpolar polyatomic gases and mixtures of them at low densities. No other empirical constants are used in the calculations except the force constants of the pair potential of the interaction.

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DEPENDENCE OF THE TRANSPORT PROPERTIES OF

LIQUIDS ON THE SOUND VELOCITY AND DENSITY

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Linear relations expressing the transport properties of liquids as a function of the sound velocity and the density are derived according to the Shirokov dimensionless group, Rao's rule, and the author's formula $\eta = m + n\lambda$.

The dimensionless group of Shirokov [1] is known to qualitatively consolidate four thermophysical properties of liquids in the form

$$\frac{\eta u^2}{T\lambda} = 1. \tag{1}$$

According to Rao's rule [2, 3], the sound velocity in a liquid is proportional to the third power of the density of the medium:

$$u \approx \rho^3. \tag{2}$$

According to our data [4], the transport properties of liquids along the isotherms are linked by a linear relation:

*Deceased.