VIRIAL COEFFICIENTS OF NITROGEN, OXYGEN, AND AIR AT TEMPERATURES FROM 75 to 2500°K

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The second and third virial coefficients are calculated for the (12-7, δ) model pair potential. With their help the fourth virial coefficient is determined from the experimental data on p, ρ, and T. The limit of applicability of the equation of state obtained is presented.

The equation of state for nonpolar gases and their mixtures at moderate densities was obtained previously in [1, 2]. In this equation the second and third virial coefficients are calculated for the (12-7, δ) model pair potential [3, 4] taking into account the quantum corrections and nonadditive components [5]. An empirical expression, the coefficients in which were found from an analysis of tabulated data on p, ρ, and T at pressures up to 100 MPa [6-10] is used for the fourth virial coefficient. It turned out that the region of applicability of the expression obtained in many cases (helium, neon, nitrogen) appreciably exceeds to 100 MPa.

In his work, the fourth virial coefficient was determined using data on p, ρ, and T obtained at the laboratory in Amsterdam [11-14] for pressures up to 300 MPa and the generalized experimental data obtained by Jacobsen and Stewart [15] for nitrogen at pressures up to 1000 MPa. These data not only encompass a wider range in density (pressure), but they are also the most reliable data (the error in the compressibility factor $Z = p/\rho RT$ does not exceed 0.2%). In the calculations the equation of state was given in the form of a seventh-degree polynomial in the density. The computed values of the second and third virial coefficients for the (12-7, δ) potential were used for the first terms of the polynomial. The higher order virial coefficients were found by the method of successive separation of the coefficients in the virial expansion [16]. The constants for the (12-7, δ) potential for nitrogen, oxygen, and air are presented in Table 1. They were determined from a combined analysis of the experimental data on the viscosity [17] and the second virial coefficient [18]. The computed values of the transport coefficients for nitrogen, oxygen, and air at low densities and temperatures from 50 to 3000°K are tabulated in [19]. They agree with the standard handbook data [20] within the limits of the errors indicated in the handbook.

The computed values of the second virial coefficient of nitrogen, oxygen, and air are compared in Table 2 with the generalized experimental data of [18]. As a rule, the results agree to within the limits of error indicated in [18]. The computed values of the third virial coefficient are tabulated in Table 3, and are compared with the experimental data in [5].

For the "true" virial coefficient the mean value of the corresponding coefficient in the polynomial in the section of stability is used. The values of the true fourth virial coefficients, obtained on the isotherms, were then used to determine by the method of least squares the coefficients α and β in the expression

$$D^* = \frac{D}{\left(\frac{2}{3}\pi N\sigma^3\right)^3} = \frac{\alpha(\delta)}{(T^*)^{3/4}} - \frac{\beta(\delta)}{(T^*)^{3/2}}. \tag{1}$$

This expression was used to approximate the temperature dependence of the fourth virial coefficient for $T \geqslant 0.7\ T_B$ [1, 2]. The values of the coefficients α and β determined in this manner for nitrogen, oxygen, and air are presented in Table 1.

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TABLE 1. Values of the Constants for Nitrogen, Oxygen, and Air

Gas	ε/k, K	$\sigma \cdot 10^8$, cm	δ	ν^*	Λ^*	T_B, K	α	β
Nitrogen	140	3,471	0,1000	0,085	0,201	330	2,016	2,550
Oxygen	184	3,195	0,1427	0,095	0,178	408	2,235	2,759
Air	149	3,403	0,1087	0,085	0,196	347	2,065	2,600

Note: $\delta = (r_c/\sigma)^2$, parameter expressing the nonsphericity of the molecules; $\Lambda^* = h/\sigma\sqrt{m\varepsilon}$, a quantum-mechanical parameter, $\nu^* = \frac{3}{4}\frac{\alpha C_6}{\varepsilon\sigma^9}$, three-dipole interaction constant.

TABLE 2. Comparison of Computed Values of the Second Virial Coefficient with the Generalized Experimental Data of [18]; $-B$, cm^3/mole

T, K	Nitrogen		Oxygen		Air
	exp.	calc.	exp.	calc.	calc.
75	275±8	275,6			
80	243±7	242,4			255,3
90	197±5	192,6	241±10	242,7	202,1
100	160±3	157,1	194±7	195,5	164,6
110	132±2	130,6	161±7	161,5	136,8
125	104±2	101,6	126±5	125,4	106,6
150	71,5±2	69,7	89±3	87,4	73,6
200	35,2±1	34,8	49±2	47,5	37,8
250	16,2±1	16,3	28±2	27,1	18,9
300	+4,2±0,5	+4,8	16±1	14,8	+7,3
350	—	—2,9	7,5±1	6,5	—0,5
400	—9,0±0,5	—8,5	1,0±1	+0,7	—6,2
500	—16,9±0,5	—15,6		—7,1	—13,4
600	—21,3±0,5	—20,1		—11,7	—17,9
700	—24,0±0,5	—23,1		—15,0	—21,0
800		—25,2		—17,2	—23,1
1000		—27,9		—20,2	—25,9
1200		—29,5		—22,0	—27,6
1500		—30,8		—23,7	—29,0
2000		—31,8		—25,0	—30,0
2500		—32,1		—25,5	—30,4

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*There are no generalized experimental data for air.

TABLE 3. Computed Values of the Third-Virial Coefficient and the Limit of Applicability of the Proposed Equation of State

T, K	C, cm^6/mole^2			p_{max}, MPa		
	nitrogen	oxygen	air	nitrogen	oxygen	air
75	—12750					
80	—5405		—10030			
90	+1011	—12460	—939,0			
100	3023	—2801	+2096			
110	3526	+774,6	3041			
125	3393	2397	3174			
150	2757	2499	2657			
200	1882	1716	1801			
250	1478	1247	1389	21,4		21,2
300	1281	1003	1185	31,5	30,9	31,6
350	1176	868,3	1077	42,0	43,5	42,6
400	1118	789,8	1015	52,6	56,7	53,9
500	1055	711,0	951,3	78,2	83,9	80,3
600	1025	674,2	921,5	104	116	107
700	1006	655,0	903,4	129	148	134
800	991,4	642,9	890,2	156	180	161
1000	967,2	627,0	869,5	210	245	218
1200	945,2	615,3	851,1	267	313	278
1500	914,4	599,8	825,1	356	418	370
2000	870,7	576,2	787,8	509	602	530
2500	831,8	556,4	754,3	671	790	698

Taking into account the fourth virial coefficient made it possible to more than double the size of the region of applicability of the equation of state for both pure gases and mixtures. The boundary of the region of applicability increases with the temperature and can be approximately described by

$$\rho \leqslant \frac{0{,}55}{B + T\dfrac{dB}{dT}}, \qquad (2)$$

where B is the second virial coefficient. The pressures corresponding to this boundary with respect to the density are presented in Table 3 for nitrogen, oxygen, and air. It is evident that at temperatures above 600°K they exceed 100 MPa. For all gases studied the differences between the computed values of the thermodynamic functions and the corresponding handbook data [6-10, 15] do not exceed ±0.1% for the entropy, ±0.5% for the density and enthalpy, and ±1.0% for the speed of sound. As in the past [1, 2], the light gases (helium, neon, and hydrogen) at temperatures below 200°K, as well as oxygen, are exception. Calculations for oxygen on some isotherms are in good agreement with handbook data [8], while on other isotherms they are in good agreement with the data given in the monograph [21].

The force constants and virial coefficients of air were presented in this paper. Air was regarded not as a mixture of nitrogen, oxygen and argon, but rather as a hypothetical pure gas. This approximation holds well, since for the system nitrogen—oxygen—argon the thermodynamic effects of mixing are small [22].

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SUBLIMATION IN A FLAT CHANNEL WITH A MOVABLE WALL AND A PERMEABLE WALL

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The effect on the process of heat exchange in a narrow slotted channel of an asymmetrical suction of subliming vapor through a permeable wall in the presence of a parallel movable wall has been examined.

In [1], the one-dimensional problem for Couette flow has been solved and tested experimentally. In [2], the mechanism of heat- and mass-transfer in the sublimation process in flat channels is studied. In the present work, the process of heat exchange in a slotted channel when the subliming vapor is sucked through the heat-generating wall is examined under assumption [3].

Consider a steady process of heat- and mass-exchange in a flat slotted channel of height H (Fig. 1). We assume that the upper subliming wall moves in its plane with the constant velocity U*. The vapor, subliming in the channel with the velocity v_W of the upper movable wall, is sucked out with velocity v_0 through the lower wall, affected by the outer heat flow of intensity q. In this case, the flow of vapor can be described in the dimensionless form by the Navier—Stokes equations in combination with the continuity equation and boundary conditions

$$(\mathbf{v}\cdot\nabla)\,\mathbf{v} = -\nabla p + \frac{1}{\mathrm{Re}}\,\Delta\mathbf{v}, \tag{1}$$

$$\nabla\cdot\mathbf{v} = 0, \tag{2}$$

$$u(0) = 0,\ v(0) = \beta,\ u(1) = \frac{U^*}{v_c},\ v(1) = 1, \tag{3}$$

where $\beta = v_0/v_W$ is the dimensionless coefficient of suction of the subliming vapor ($0 \leqslant \beta \leqslant 1$).

We seek a solution of system (1), (2) with the boundary conditions (3) as in [2].

$$u = -xf'(y),\ v = f(y). \tag{4}$$

In this case, Eq. (2) is an identity, while Eq. (1) and conditions (3) take the form

$$f'^2 - ff'' + \frac{1}{\mathrm{Re}}\,f''' = -\frac{1}{x}\,\frac{\partial p}{\partial x}, \tag{5}$$

$$\begin{gathered} ff' - \frac{1}{\mathrm{Re}}\,f'' = -\frac{\partial p}{\partial y}, \\ f'(0) = 0,\ f(0) = \beta,\ f'(1) = U,\ f(1) = 1, \end{gathered} \tag{6}$$

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