VIRIAL COEFFICIENTS FOR CARBON MONOXIDE, ETHYLENE, AND PROPYLENE, AT TEMPERATURES UP TO 1500 K

R. M. Sevast'yanov and R. A. Chernyavskaya

UDC 536.75

For the paired model potential (12-7, δ) we have calculated the second and the third virial coefficients; for the fourth coefficient we have used a semiempirical expression. We present the boundary of applicability for the derived equation of state.

In [1, 2] we find a generalization of the paired model potential (12-7, δ) relative to the case of nonpolar multiatomic molecules of arbitrary shape. It is demonstrated that this potential describes in consistent fashion the various experimental data (including the coefficient of thermal conductivity) for nonpolar gases and mixtures [1-8]. In particular, in [1, 3, 4] we find a calculation of the second and third virial coefficients for methane (the parameter of molecular nonsphericity δ = 0.0631), for ethane (δ = 0.1493), and for propane (δ = 0.2070); nitrogen (δ = 0.1000); oxygen (δ = 0.1427); and air (δ = 0.1087); neon (δ = 0); argon (δ = 0); and krypton (δ = 0); all of these at temperatures ranging from 60-200 K to 1500-3000 K. By means of these coefficients, from the corresponding experimental p, V, T data, we have isolated the fourth virial coefficient for whose description in the case of $T^* = kT/\varepsilon \geq 1$ we used the following expression [1, 3, 4]:

$$D^* = \frac{D}{(b_0)^3} = \frac{\alpha(\delta)}{(T^*)^{3/4}} - \frac{\beta(\delta)}{(T^*)^{3/2}}, \quad (1)$$

where α(δ) and β(δ) are empirical coefficients. The values of these coefficients for the gases being examined here (with the exception of oxygen) (δ = 0-0.2070) can be generalized in the form of the polynomials:

$$\alpha(\delta) = 1.278 + 8.169\delta - 7.892\delta^2, \quad (2)$$

$$\beta(\delta) = 1.692 + 10.678\delta - 20.982\delta^2. \quad (3)$$

Refinement of the coefficients α(δ) and β(δ) for oxygen in accordance with correlations (2) and (3) leads to the best agreement between theory and the generalized experimental data [9]. In this case it is significant that the values of the fourth virial coefficient are expressed in terms of the constant paired model potential and contain no other empirical constants.

Let us also cite the relationship between the Boyle temperature (B = 0), the inversion temperature ($B - B_1 = 0$), and the constants of the potential (12-7, δ). In the classical approximation (i.e., without consideration of the quantum correction factors) we have:

$$T_B = (\varepsilon/k)(2.714 - 3.651\delta + 1.415\delta^2), \quad (4)$$

$$T_i = 1.880 T_B \quad \text{(independent of } \delta). \quad (5)$$

In the present paper, on the basis of a combined analysis of the generalized experimental data on viscosity [10], thermal conductivity [11], and the second virial coefficient [12-14], we have determined the values of the constant paired model potential (12-7, δ) for carbon monoxide, ethylene, and propylene (see Table 1). Here, unlike ethylene and propylene, for the carbon monoxide it was not possible in a consistent manner to describe the experimental data with respect to the second virial coefficient, with respect to viscosity, and to thermal conductivity. In Table 2 the theoretical values of the second virial coefficient are compared with the experimental data [12-14]. As a rule, the results are in agreement within the limits of measurement error.

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 57, No. 4, pp. 590-593, October, 1989. Original article submitted April 20, 1988.

TABLE 1. Values of the Constants for Carbon Monoxide, Ethylene, and Propylene

Substance	ε/k, K	$\sigma \cdot 10^8$, cm	$r_e \cdot 10^8$, cm	δ	ν^*	α	β	T_B, K
Carbon monoxide	147	3,510	1,116	0,1011	0,080	2,023	2,557	342
Ethylene	334	3,920	1,390	0,1257	0,125	2,180	2,703	761
Propylene	464	4,452	2,009	0,2036	0 095	2,614	2,996	941

Note. $\nu^* = (3/4)(\alpha C_6/\varepsilon\sigma^9)$, the reduced parameter of the nonadditive three-dipole interaction; T_B, the Boyle temperature.

TABLE 2. Comparison of Theoretical Values (I) of the Second Virial Coefficient against Experimental Data [12-14]

T, K	Carbon monoxide		Ethylene		Propylene	
	I	[12, 13]	I	[14]	I	[14]
100	—178,0	—180±5				
150	—79,9	—80,0±4				
200	—41,0	—42,2±3	—309,0	—		
250	—20,4	—	—199,1	—201±2	—492,2	—
300	—7,80	—7,8*	—138,4	—138±1	—338,1	—343±5
350	+0,72	+1,2*	—100,0	—99±1	—246,5	—
400	6,84	7,8*	—73,70	—71,5±1	—186,2	—183±5
450	11,21		—54,60	—51,7±1	—143,6	
500	14,68		—40,14		—112,0	—106±3
600	19,64		—19,75		—68,42	
700	22,97		—6,10		—39,90	
800	25,32		+3,66		—19,86	
1000	28,35		16,66		+6,35	
1200	30,14		24,32		22,69	
1500	31,62		31,72		37,60	

---

*These values have been obtained by interpolation of the data from Michels and co-authors [13].

TABLE 3. Theoretical Values of the Third Virial Coefficient and the Limits of Applicability for the Proposed Equation of State

T, K	C, cm^6/mole^2			$P_{\max}$, MPa		
	carbon monoxide	ethylene	propylene	carbon monoxide	ethylene	propylene
100	2292					
150	3064					
200	2097	5787		11,0		
250	1628	10670	3969	19,4		
300	1395	8867	23060	28,9		
350	1272	7043	21770	39,0	9,04	
400	1202	5732	18170	49,3	13,4	
450	1158	4827	15040	62,1	18,6	7,72
500	1130	4197	12650	73,5	24,5	10,6
600	1096	3423	9585	97,6	37,5	17,6
700	1076	2998	7865	122	51,7	25,9
800	1060	2748	6850	148	66,3	35,1
1000	1036	2490	5816	200	81,2	44,8
1200	1014	2357	5361	254	96,0	54,9
1500	993,1	2255	5050	338	133	75,1

The divergence between the theoretical and experimental values of the carbon monoxide transport properties is considerably greater than for the other gases, including those studied earlier in [1-4]. The calculated values of viscosity at a temperature of 150 K ($\mu = 926 \cdot 10^{-8}$ Pa·sec) are lower by 9.4%, while at a temperature of 1200 K ($\mu = 4518 \cdot 10^{-8}$ Pa·sec) they are higher by 3.2% than the experimental data [10]. Conversely, the theoretical values of the coefficient of thermal conductivity at a temperature of 150 K ($\lambda = 135.3 \cdot 10^{-4}$ W/(m·K) are higher by 2.5%, while at a temperature of 1200 K ($\lambda = 688.7 \cdot 10^{-4}$ W/(m·K) they are lower by 13.0% than the experimental generalized data [11].

In calculating the third virial coefficient (see Table 3) we took into consideration the nonadditivity of the potential energy of three-particle interactions [15]. The fourth virial coefficient was calculated on the basis of correlations (1)-(3).

We compared the experimental values of the compressibility coefficient Z = pV/RT for carbon monoxide [13, 16], ethylene [17-19], and propylene [20] with the values calculated by means of the virial equation of state, broken off at the fourth virial coefficient. Analysis showed that the limits of applicability for this equation of state in terms of density increases as the temperature rises and when $T^* \geq 1$ can approximately be described in the form

$$\rho \leqslant \frac{0.55}{B + T\dfrac{dB}{dT}}, \tag{6}$$

where B is the second virial coefficient.

The pressure values corresponding to this boundary in terms of density can be found in Table 3. Within the limits of these pressures the deviations between the theoretical and experimental values of the coefficient of compressibility do not exceed ±0.5%; the magnitude of the mean-square error is 0.2%.

LITERATURE CITED

1. R. M. Sevast'yanov and R. A. Chernyavskaya, Inzh.-Fiz. Zh., 53, No. 4, 589-592 (1987).
2. R. M. Sevast'yanov and K. I. Voroshilova, Inzh.-Fiz. Zh., 53, No. 6, 983-986 (1987).
3. R. M. Sevast'yanov and R. A. Chernyavskaya, Inzh.-Fiz. Zh., 51, No. 1, 121-124 (1986).
4. R. M. Sevast'yanov and R. A. Chernyavskaya, Inzh.-Fiz. Zh., 52, No. 6, 974-977 (1987).
5. R. M. Sevast'yanov and N. A. Zykov, Inzh.-Fiz. Zh., 48, No. 1, 114-118 (1985).
6. N. A. Zykov, R. M. Sevast'yanov, and K. I. Voroshilov, Inzh.-Fiz. Zh., 43, No. 1, 77-82 (1982).
7. R. M. Sevast'yanov and R. A. Chernyavskaya, Inzh.-Fiz. Zh., 48, No. 2, 263-266 (1985).
8. R. M. Sevast'yanov, N. A. Zykov, and K. I. Voroshilov, Inzh.-Fiz. Zh., 49, No. 2, 284-287 (1985).
9. V. V. Sychev, A. A. Vasserman, et al., The Thermodynamic Properties of Oxygen [in Russian], Moscow (1981).
10. I. F. Golubev and N. E. Gnezdilov, The Viscosity of Gaseous Mixtures [in Russian], Moscow (1971).
11. N. B. Vargaftik, L. P. Filippov, et al., Thermal Conductivity of Liquids and Gases [in Russian], Moscow (1978).
12. S. F. Barrieros, J. C. Calado, et al., J. Chem. Thermodynamics, 19, No. 9, 941-944 (1987).
13. A. Michels, J. Lupton, et al., Physica, 18, 121-127 (1952).
14. J. H. Dymond and E. B. Smith, The Virial Coefficients of Pure Gases and Mixtures. A Critical Compilation, Oxford (1980).
15. N. A. Zykov, R. M. Sevast'yanov, and R. A. Chernyavskaya, Inzh.-Fiz. Zh., 44, No. 3, 477-451 (1983).
16. R. D. Goodwin, J. Phys. Chem. Reference Data, 14, No. 4, 849-932 (1985).
17. N. J. Trappeniers, T. Wassenaar, and G. J. Wolkers, Physica, 82A, No. 2, 305-311 (1976).
18. D. R. Douslin and R. H. Harrison, J. Chem. Thermodyn., 8, No. 4, 301-330 (1976).
19. V. V. Sychev, A. A. Vasserman, et al., Thermodynamic Properties of Ethylene [in Russian], Moscow (1981).
20. H. Marchman, H. W. Prengle, and P. Matard, Ind. Eng. Chem., 41, No. 6, 2658-2667 (1949).