THE EQUATION OF STATE FOR A MIXTURE OF NONPOLAR GASES AT MODERATE DENSITIES

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UDC 536.75

The virial equation of state for the (12-7, δ) pair model potential is extended to mixtures of nonpolar gases. The applicability of the equation is examined, and it is shown that calculations agree with experiment within the error of the measurements.

In [1], a study was made of the equation of state for nonpolar gases

$$Z = \frac{p}{\rho RT} = 1 + \rho B(T) + \rho^2 C(T) + \rho^3 D(T) + \ldots, \tag{1}$$

in which the second virial coefficient B(T) and the third one C(T) were calculated for the (12-7, δ) pair model potential [2], while an empirical expression was used for D(T). Equation (1) describes the experimental data on the compressibility for ten nonpolar gases (helium, neon, argon, krypton, xenon, hydrogen, nitrogen, oxygen, carbon dioxide, and methane) at $T \geqslant 0.7\ T_B$ and $\rho \leqslant 0.8\rho_{cr}$, where T_B is the Boyle temperature and ρ_{cr} is the density at the critical point on the saturation line.

The virial equation of state in principle is applicable not only to pure gases but also to mixtures [3, 4]; however, allowance must be made for the interactions between the differing molecules in a mixture, and the virial coefficients are dependent on the mixture composition. In particular, the virial coefficients are put in the following form for a binary mixture:

$$B_{\text{M}} = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22}, \tag{2}$$

$$C_{\text{M}} = x_1^3 C_{111} + 3x_1^2 x_2 C_{112} + 3x_1 x_2^2 C_{122} + x_2^3 C_{222}, \tag{3}$$

$$D_{\text{M}} = x_1^4 D_{1111} + 4x_1^3 x_2 D_{1112} + 6x_1^2 x_2^2 D_{1122} + 4x_1 x_2^3 D_{1222} + x_2^4 D_{2222}, \tag{4}$$

where x_1 and x_2 are the volume concentrations, while B_{12}, C_{112}, C_{122}, D_{1112}, D_{1122}, D_{1222} are the mixed virial coefficients. These coefficients are dependent on the potential energy of the interaction between the differing molecules. One uses the same model potential as for the pure components to describe them, while the force constants are determined by means of combination relations.

Kong [5] has derived the combining rules in general form. It has been shown [6] that these rules can be used for a (12-7, δ) pair model potential in a consistent description of the experimental data on the mixed second virial coefficient and the neutral-diffusion coefficients for nonpolar gases.

The Rowlinson–Sumner–Sutton [7] approximation can be used to calculate the mixed higher virial coefficients. Values have been calculated for the third virial coefficient [8] that agree with the experimental data [9] within the limits of the discrepancies of the measurements in the different sources for the (12-7, δ) pair potential and the Mijuno–Kihara nonadditive three-particle potential.

The following is the form for the fourth virial coefficient for the (12-7, δ) potential in the Rowlinson–Sumner–Sutton approximation [7]:

$$D_{ijkl} = \left(\frac{2}{3}\pi N \sigma_{ijkl}^3\right)^3 \cdot D^*(T^*_{ijkl}, \delta_{ijkl}). \tag{5}$$

By definition

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 48, No. 1, pp. 114-118, January, 1985. Original article submitted September 29, 1983.

TABLE 1. Comparison of Calculated Values for the Compressibility Factor $Z = p/\rho RT$ for Binary Gas Systems with the Experimental Data of [10-16], $\delta Z = \left| \frac{Z_{\text{exp}} - Z_{\text{calc}}}{Z_{\text{exp}}} \right|$

System	T, K	p_{max}, MPa	δZ_{av}, %	δZ_{max}, %
N_2—He [10]	273—373	29,9—23,3	0,4	1,2
N_2—Ar [11]	273	26,1	0,1	0,6
N_2—H_2 [12]	278—511	27,6—55,2	0,3	0,6
N_2—O_2 [13]	250—1500	25—100	0,2	0,4
CO_2—He [14]	373	11,1	0,1	0,3
CO_2—Ar [15]	373	12,0	0,1	0,5
CO_2—C_2H_6 [16]	511	27,6	0,3	0,6

$$a_{ijkl} = \sqrt{\sigma^2_{ijkl} - r^2_{iejkl}}, \quad T^*_{ijkl} = \frac{kT}{\varepsilon_{ijkl}}, \quad \delta_{ijkl} = \frac{r^2_{eijkl}}{\sigma^2_{ijkl}}, \tag{6}$$

where

$$a_{ijkl} = \sqrt[6]{a_{ij}a_{ik}a_{il}a_{jk}a_{jl}a_{kl}}, \tag{7}$$

$$\varepsilon_{ijkl} = \sqrt[6]{\varepsilon_{ij}\varepsilon_{ik}\varepsilon_{il}\varepsilon_{jk}\varepsilon_{jl}\varepsilon_{kl}}, \tag{8}$$

$$r^2_{eijkl} = \frac{1}{6}\left(r^2_{eij} + r^2_{eik} + r^2_{eil} + r^2_{ejk} + r^2_{ejl} + r^2_{ekl}\right) = \frac{1}{2}\left(r^2_{eij} + r^2_{ekl}\right). \tag{9}$$

The empirical expression employed for pure gases [1] may be employed for D^* (T^*_{ijkl}, δ_{ijkl}) but with different arguments. This enables one to calculate the additive fourth virial coefficients for gas mixtures on the basis of six pair interactions as appearing in the four-particle interaction. As the nonadditivity in the potential energy is not incorporated here, the calculations give acceptable accuracy for not very low temperatures (for pure gases at $T \geqslant 0.7\ T_B$).

The equation of state of (1)-(4) and the combining rules for the pair potential, the three-particle potential [8], and the four-particle one of (7) and (8) have been used to calculate the compressibilities of seven binary gas systems (nitrogen—helium, nitrogen—argon, nitrogen—hydrogen, nitrogen—oxygen (air), carbon dioxide—helium, carbon dioxide—argon, and carbon dioxide—ethane) at moderate densities. Air was considered as a binary mixture of nitrogen (volume concentration $x_1 = 0.7808$) and oxygen ($x_2 = 0.2192$); the molecular mass of air was taken as 28.964. Table 1 compares the calculated values of the compressibility factor with the corresponding measurements [10-16]. Table 2 gives a comparison of calculations and experiments [11] for nitrogen—argon mixtures. The mean deviation for the seven binary systems is 0.2%, while the maximum is 1.2%. In other words, the equation of state describes the experimental p, ρ, T, and x data within the error of the measurements.

The region of application for (1) can be determined approximately for gas mixtures in the general case as follows:

$$\rho \leqslant \frac{0.5}{\sum\limits_i \sum\limits_j x_i x_j b_{0ij}} \tag{10}$$

for $T \geqslant 0.7 \sum\limits_i \sum\limits_j x_i x_j T_{Bij}$, where b_{0ij} and T_{Bij} are constants in the (12-7, δ) pair interaction potential [2, 6].

For binary mixtures,

$$\rho \leqslant \frac{0.5}{x_1^2 b_{011} + 2x_1x_2b_{012} + x_2^2 b_{022}} \tag{11}$$

for $T \geqslant 0.7(x_1^2 T_{B11} + 2x_1x_2T_{B12} + x_2^2 T_{B22})$.

TABLE 2. Comparison of the Calculated Values of the Compressibility Factor $Z = p/\rho RT$ for Nitrogen–Argon Mixtures with the Experimental Data of [11], T = 273.15°K, x_1 Being the Volume Nitrogen Concentration, with Values of δZ (average and maximum) in Percent

$x_1 = 0$			$x_1 = 0{,}2015$			$x_1 = 0{,}4845$			$x_1 = 0{,}7990$			$x_1 = 1{,}000$		
p, MPa	exp	calc	p, MPa	exp	calc	p, MPa	exp	calc	p, MPa	exp	calc	p, MPa	exp	calc
1,068	0,9903	0,9901	1,021	0,9914	0,9915	0,977	0,9931	0,9933	0,928	0,9950	0,9951	0,887	0,9962	0,9962
2,284	0,9795	0,9790	2,114	0,9827	0,9827	2,068	0,9859	0,9861	1,953	0,9903	0,9901	1,946	0,9923	0,9922
4,192	0,9637	0,9628	4,025	0,9686	0,9687	3,871	0,9752	0,9757	3,699	0,9829	0,9828	3,548	0,9875	0,9872
6,554	0,9463	0,9450	6,311	0,9540	0,9542	6,096	0,9644	0,9652	5,850	0,9766	0,9764	5,626	0,9836	0,9831
8,773	0,9325	0,9311	8,196	0,9440	0,9443	8,101	0,9574	0,9583	7,746	0,9736	0,9732	7,779	0,9827	0,9819
10,20	0,9250	0,9237	9,868	0,9369	0,9375	9,595	0,9535	0,9548	9,274	0,9726	0,9723	8,956	0,9834	0,9825
13,67	0,9124	0,9116	12,84	0,9287	0,9302	12,81	0,9508	0,9524	12,36	0,9758	0,9754	12,49	0,9913	0,9901
15,96	0,9090	0,9084	15,54	0,9265	0,9287	15,27	0,9530	0,9554	14,92	0,9831	0,9827	14,49	0,9993	0,9979
21,84	0,9159	0,9167	20,60	0,9359	0,9393	20,88	0,9739	0,9760	20,40	1,012	1,011	20,89	1,041	1,038
26,12	0,9345	0,9353	25,65	0,9609	0,9636	25,60	1,004	1,005	25,41	1,052	1,048	24,83	1,076	1,070
δZ_{av}	0,08		δZ_{av}	0,08		δZ_{av}	0,09		δZ_{av}	0,05		δZ_{av}	0,10	
δZ_{max}	0,15		δZ_{max}	0,36		δZ_{max}	0,25		δZ_{max}	0,38		δZ_{max}	0,56	

For nonpolar gases, there is the following relation between the constant b_0 for the (12-7, δ) potential and the density at the critical point on the saturation line:

$$b_0 = 0.61/\rho_{cr}. \tag{12}$$

Then from (12), the applicability range for (1) for pure gases is written as

$$\rho \leqslant 0.8_{cr} \text{ for } T \geqslant 0.7T_B. \tag{13}$$

If one restricts oneself to the second and third virial coefficients in (1), it can be used for densities $\rho \leqslant 0.15\rho_{cr}$ at the critical temperature for a pure gas and for $\rho \leqslant 0.40 \cdot \rho_{cr}$ at temperatures exceeding the Boyle temperature.

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