VIRIAL EQUATION OF STATE OF NONPOLAR GASES

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An equation of state is studied in which the second and third virial coefficients are calculated theoretically and an empirical expression is used for the fourth virial coefficient. It is shown that this equation of state describes the experimental data on the compressibility of nonpolar gases for $T \geqslant 0.7T_B$ and $\rho \leqslant 0.8\rho_{cr}$.

As is well known [1], a theoretical equation of state for real gases at moderate densities is given by the virial expansion

$$Z = \frac{P}{\rho RT} = 1 + \rho B + \rho^2 C + \rho^3 D + \dots, \tag{1}$$

where B, C, D are the second, third, fourth, etc. virial coefficients. They depend on temperature and the interaction potential of the molecules.

It has been shown [2-6] that the (12-7, δ) pair potential

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

(where ε is the depth of the potential well, σ is the "diameter" of a molecule, r_e is the hard core, and $\delta = (r_e/\sigma)^2$ measures the deviation of molecular shape from a sphere) describes the experimental data on equilibrium (second and third virial coefficients) and transport (viscosity, thermal conductivity, and mutual diffusion) properties of nonpolar monatomic gases and their mixtures in a consistent way. In the second virial coefficient, the first- and second-order quantum corrections were taken into account and nonadditive terms were taken into account in the third virial coefficient. Then the second and third virial coefficients for a pure gas can be expressed in the form

$$B(T, \delta) = \frac{2}{3} \pi N \sigma^3 [B_{\mathrm{cl}}^* (T^*, \delta) + (\Lambda^*)^2 \Delta B_{\mathrm{qm}}^{*(1)} (T^*, \delta) + (\Lambda^*)^4 \Delta B_{\mathrm{qm}}^{*(2)} (T^*, \delta)], \tag{3}$$

$$C(T, \delta) = \left(\frac{2}{3} \pi N \sigma^3 \right)^2 [C_{\mathrm{add}}^* (T^*, \delta) + \nu^* \Delta C_{\mathrm{nonadd}}^* (T^*, \delta)], \tag{4}$$

where $T^* = kT/\varepsilon$ is the reduced temperature, $\Lambda^* = h/\sigma\sqrt{m\varepsilon}$ measures the strength of the quantum correction, and $\nu^* = \frac{3}{4} \frac{\alpha C_6}{\varepsilon \sigma^9}$ is the reduced triple-dipole interaction coefficient. Values of ν^* are given in Table 1 for several nonpolar gases.

The terms on the right-hand sides of (3) and (4) were approximated by expressions of the form

$$A^{*(n)} = \sum_{k=0}^{6} \sum_{j=0}^{3} \beta_j^{(n)} \delta^j \Delta^k, \tag{5}$$

where $\Delta = \exp\left(\frac{1}{T^*}\right) - 1$ and the $\beta_j^{(n)}$ are constants.

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TABLE 1. Characteristic Constants for Several Gases

Gas	$\frac{\varepsilon}{k}$, K	$\sigma\cdot 10^8$,cm	δ	v^*	T_B, °K	ρ_{cr}, g/cm^3
He	10,2	2,537	0	0,035	—	0,693
Ne	45,5	2,717	0	0,040	122	0,483
Ar	152	3,304	0	0,095	412	0,536
Kr	214	3,511	0	0,125	580	0,911
Xe	295	3,845	0	0,100	800	1,100
H_2	53,4	2,827	0,0688	0,085	110	0,316
N_2	140	3,471	0,1000	0,085	330	0,313
O_2	184	3,195	0,1427	0,115	407	0,436
CO_2	515	3,530	0,4335	0,035	718	0,468
CH_4	220	3,531	0,0983	0,115	519	0,164

The approximation (5) leads to good accuracy for the virial coefficients and also for their derivatives with respect to temperature. The values of $\beta_j^{(n)}$ for the additive and nonadditive components of the third virial coefficient are given in [6], where a comparison between the calculated and experimental values are also given.

The virial equation of state for the pair potential (2) with approximation (5) for the second and third virial coefficients was used to calculate the compressibility and the thermodynamic functions for several nonpolar gases (see Table 1) at moderate densities. Comparison with the accepted handbook values [7-13] shows that when $\rho \leqslant 0.35\rho_{cr}$ (where ρ_{cr} is the density at the critical point along the saturation line) deviations did not exceed the experimental errors and the numerical analysis of the experimental P, ρ, T data (0.2-0.4%) which was used to compute the handbook values.

An analysis of the deviations of the compressibility from the experimental data for $\rho \geqslant 0.35\rho_{cr}$ showed that the range of applicability of the equation of state (1) can be extended by including an empirical fourth virial coefficient:

$$D = \left(\frac{2}{3}\pi N\sigma^3\right)^3 \left[0.287\,(\delta)^{9/2} + \frac{\alpha(\delta)}{(T^*)^{3/4}} - \frac{\beta(\delta)}{(T^*)^{3/2}}\right]. \tag{6}$$

Equation (6) describes the first two terms of an asymptotic expansion of the fourth virial coefficient for potential (2) at high temperatures. The third term and the coefficients α(δ) and β(δ) are determined empirically:

$$\alpha(\delta) = 1.278 + 15.93\delta - 34.36\delta^2, \tag{7}$$

$$\beta(\delta) = 1.633 + 25.51\delta - 58.60\delta^2. \tag{8}$$

With the fourth virial coefficient given above included, the range of applicability of the equation of state (1) can be widened to $T \geqslant 0.7T_B$ (T_B is the Boyle temperature) and $\rho \leqslant 0.8\rho_{cr}$. Then for the gases listed in Table 1, the deviations between the calculated compressiblity and the handbook values [7-13] did not (as a rule) exceed ±0.4%. An exception occurred for light gases (hydrogen, helium, neon) at temperatures below 200°K and also for hydrogen and oxygen at temperatures above 700°K. In the low temperature case, the deviations are apparently due to the effect of higher-order quantum corrections on the equilibrium properties of light gases. At high temperatures the deviations may come from the absence of reliable experimental data. According to an estimate in [11], the errors in the density of oxygen given there for temperatures of 700-1500°K and pressures of 100 MPa were on the order of 1.0-1.4%. Deviations between the handbook values [11] and our calculated values for the density of oxygen were within this experimental error.

Also the calculated values for the speed of sound in nitrogen and carbon dioxide agreed with the measurements of [14, 15] to within ±0.3%.

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IR SPECTROSCOPIC ESTIMATION OF THE BINDING ENERGIES OF WATER MOLECULES ADSORBED ON DISPERSED SYSTEMS.

PART 3. γ-Al_2O_3

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There are three modes of interaction between water molecules and centers in γ-Al_2O_3, which arise from marked differences in hydrogen-bond energy.

γ-aluminum oxide is a classical adsorbent with an extensively hydroxylated surface. It has a defective cubic spinel lattice with space group Fd3m, while the vacant cation sites in a tetrahedral environment are stabilized by hydroxyl ions.

We have examined the structure of adsorbed water by IR and nuclear magnetic resonance methods, as well as by direct measurement of the bound water density. These methods require data on the structure and disposition of the active surfaces, and these were obtained (Fig. 1) as follows.

The coordinates of the oxygen and aluminum atoms within the unit cell (7.895·7.895 Å) in projection on any plane were taken from [1], in particular on the (001) plane for space group Fd3m. However, an aluminum atom is always in an octahedral environment of oxygen atoms, and only a small proportion of these atoms have incomplete coordination, so the surface can be represented as consisting of oxygen atoms at two levels, as shown in Fig. 1. A feature of γ-Al_2O_3 is that some of the surface oxygen atoms are replaced by OH groups.

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