THE COVOLUME AND EQUATION OF STATE OF HIGH-TEMPERATURE REAL GASES

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It is shown that the equation of state of a real gas can be described under certain conditions in terms of the covolume.

The concept of covolume for describing the properties of a real gas was first proposed by Noble and Abel, prior to the appearance of Van der Waal's equation [1]. The equation of state of a real gas proposed by Noble and Abel has the form

$$P = \frac{RT}{V - b}, \tag{1}$$

where b is the covolume which has the dimension of volume.

Experimental data [1] show that the covolume remains approximately constant in a wide range of T and P for a given gas, which has led to its current widespread use [2]. This property of the covolume is difficult to explain starting from the well-known equations of state, which, as a rule, give a quite complicated dependence of the compressibility on the state parameters. In this paper the hypothesis that b remains constant is checked starting from the model of the equation of state proposed in [3, 4]. This model based on the so-called concept of ideal curves, enables describing analytically the thermodynamic properties of the gas using only one temperature-dependent function, namely, the second virial coefficient (SVC) $B(T_0)$, where $T_0 = T/(1 - \rho/\rho_0)$.

The equation of state

$$Z = 1 + \frac{B(T_0)\rho}{1 - \rho/\rho_0} \tag{2}$$

describes the behavior of a high-temperature gas over a wide range of variation of the parameters, beginning with $T \simeq 2\varepsilon/k$ under pressures of up to 5-10 kbar.

From a comparison of (1) and (2) we obtain

$$b^* = b\rho_0 = \frac{B(T_0)\rho_0}{1 + \{B(T_0)\rho_0 - 1\}}.$$

For further analysis we assume that the gas is a Lennard-Jones fluid. As shown in [4], $(2.3)\pi N\sigma^3\rho_0 \approx 2.4$. From here

$$b^* = \frac{2{,}4B^*(T^*)}{1 + \{2{,}4B^*(T_0^*) - 1\}\rho/\rho_0}, \tag{3}$$

where

$$B^*(T^*) = \frac{B(T_0)}{\frac{2}{3}\pi N\sigma^3}.$$

We note that the reduced SVC B^* at $T^* = kT/\varepsilon > 10$ varies over a small interval. Thus, in the interval $T^* = 10$-50 B^* varies from 0.46 to 0.50 [5]. Since $T_0^* = T/(1 - \rho/\rho_0) > T^*$, this property B^* is observed first at even lower temperatures. On the other hand, the term $a = (2.4B^* - 1)\rho/\rho_0$ in (3), as a rule, is much less than 1. Thus, for example, for $T^* > 10$ and $\rho/\rho_0 = 0.3$ it equal only 0.06 with $P \approx 2.8$ kbar and $T = 2000$°K if $\sigma = 3.7$ Å, which corresponds to nitrogen. At higher temperatures this condition holds up to pressures of the

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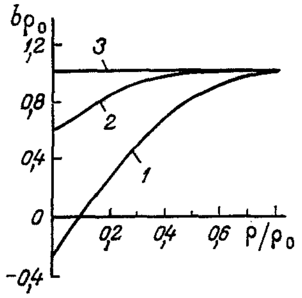

Fig. 1. Dependence of the covolume on the state parameters (the values of the dimensionless parameter $b^* = b\rho_0$ are presented): 1) $T^* = 3$; 2) 5; 3) 10.

order of 10^4 bar. The equation of state (2) is inapplicable for $\rho/\rho_0 \gtrsim 0.6$, when the term a reaches the maximum value 0.15.

The results of the above analysis lead to the conclusion that the relative constancy of the covolume is determined by two factors: the weak dependence of the SVC on T at high temperatures and the low value of the term a. It is evident from Fig. 1 that the determining factor in this case is the high value of T^*. For most components of the products of combustion (CO_2, CO, N_2, O_2, etc.) $\varepsilon/k \sim 100\text{-}300°K$, so that beginning with temperatures of the order of 1500-2000°K the covolume is approximately constant up to pressures of the order of 10^4 bar. If, however, the concentration of H_2O molecules ($\varepsilon/k = 520°K$) or metals (for Be $\varepsilon/k = 3600°K$ [6]) in the mixture is significant, then the value of the covolume depends strongly on the state parameters, and in this case it is desirable to use for calcualtions Eq. (2) and not the simplified equation of state with the covolume (1).

NOTATION

b, covolume of the gas; V, volume (molar or specific); ρ, density; ρ_0, characteristic density of the material of interest, of the order of the density of the crystal – a parameter in the equation of state (2); Z, compressibility; P, pressure; T, temperature; B, second virial coefficient; T_0, an argument of the temperature-dependent second virial coefficient; T^*, T_0^*, and B^*, reduced values of T, T_0 and B, respectively; ε/k and σ, parameters in the Lennard-Jones 12:6 intermolecular interaction potential.

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