EXPERIMENTAL CHECK OF CERTAIN METHODS OF DETERMINING P–V–T RELATIONS OF N₂–O₂ MIXTURES IN THE GAS AND VAPOR REGIONS

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The lack of trustworthy data on the P–V–T relation in gaseous N₂–O₂ mixtures has been pointed out in [1]. A measuring system which could be used for determining coefficients of compressibility of such mixtures at 100–350 K and pressures up to 10 MPa with a relative error of no more than 0.5% was described in the earlier paper. The present paper will consider the possibility of determining P–V–T relations in gaseous N₂–O₂ mixtures, first through the generalized form of the law of corresponding states and the modified Prausnitz–Gunn rule [2] (method I) and then by a method based on the Krichevskii–Kazarnovskii equation (method II) [3]. Absolute and relative values of the deviation between results obtained with the aid of these two methods were calculated from experimentally measured coefficients of compressibility for the mixtures in question. We first describe in detail the procedures followed in calculating the coefficients of compressibility.

Method I. The generalized law of corresponding states for gaseous mixtures can be expressed in terms of reduced parameters obtained from the so-called pseudocritical constants, quantities which can be estimated by several different procedures. For mixtures of nonpolar components with similar critical parameters, evaluation can proceed through the modified Prausnitz–Gunn rule [2] and the equations

\[ T_{ps, cr} = \sum_i y_i T_{cr, i} \]  
\[ V_{ps, cr} = \sum_i y_i V_{cr, i} \]  
\[ z_{ps, cr} = \sum_i y_i z_{cr, i} \]  
\[ P_{ps, cr} = \rho_{ps, cr} T_{ps, cr} V_{ps, cr} \] 

in which \( V \) is the molar volume, in \( m^3/kmole \); \( y_i \) is the mole fraction of the i-th component of the mixture; \( P \) is the pressure, in Pa; \( T \) is the temperature, in °K; \( z \) is the coefficient of compressibility; \( R \) is the universal gas constant, in \( J/(kmole·°K) \). Here, and in what follows, the subscript "cr" indicates a parameter of a pure component estimated at the critical point while the subscript "ps. cr" indicates a parameter of the mixture estimated at the pseudo-critical point; \( i \) indicates that it is the parameter of the i-th component which is in question.

After having obtained the pseudocritical constants, the reduced temperature and pressure can be calculated from the defining equations \( \tau = T/T_{ps, cr} \) and \( \tau = P/P_{ps, cr} \).

Coefficients of compressibility are usually calculated from the generalized diagram of [2]. Here it is more useful to work through the equation

\[ z_{mix}(\tau, \tau) = y_N z_{N}(\tau, \tau) + y_O z_{O}(\tau, \tau) \] 

where \( z_N \) and \( z_O \) are the coefficients of compressibility of pure nitrogen and oxygen at the indicated values of the reduced parameters.

For N₂–O₂ mixtures, values obtained through this equation are more precise than those calculated by the method of [2].

A second equation which can be used for calculating coefficients of compressibility of various gases, including nitrogen [4], oxygen [5], and air [6], has the form...
Fig. 1. Constant relative error curves for the determination of P-V-T relations in air; \( \delta \), %: 1) 0.3; 2) 0.5; 3) 0.8; 4) 1; 5) 1.5; 6) 2.

\[
z_l(\tau_l, \omega_l) = 1 + \sum_{k=1}^{10} \sum_{j=0}^{7} B_{kj}(\omega_l^k/\gamma_l^j)
\]

Here \( \omega = V_{cr}/V \) designates the reduced density, and the subscript \( l \) indicates that it is the parameter of the \( l \)-th component which is in question. By following the procedure of [4], the \( z_l (\pi_l, \tau_l) \) relation can be developed through computer calculations.

The possibilities of method I can be illustrated for the case of air, a binary mixture with \( Y_{N_2 A} = 0.7821, Y_{O_2 A} = 0.2179 \) [3, 7]. We have developed a Fortran-IV program which permits the coefficient of compressibility of air to be determined simultaneously through Eq. (5) and Eq. (6), thus permitting estimation of the error inherent in method I. Figure 1, showing the relative error in coefficients of compressibility calculated for air under various conditions, makes it clear that this error was greatest at points in the critical region.

Method II. This method, based on the Krichevskii-Kazarnovskii equation of state for gaseous \( N_2-O_2 \) mixtures

\[
z_{mix}(T, V, y) = \left(1 + \sum_{k=1}^{10} \sum_{j=0}^{7} B_{N_kj} \frac{\omega_{N_k}}{\tau_{N_k}}\right) y_{N_k} + \left(1 + \sum_{k=1}^{10} \sum_{j=0}^{7} B_{O_kj} \frac{\omega_{O_k}}{\tau_{O_k}}\right) y_{O_k} + \left(\sum_{k=1}^{10} \sum_{j=0}^{7} B_{12kj} \frac{\omega_{N_k} \omega_{O_k}}{\tau_{N_k} \tau_{O_k}}\right) y_{N_k} y_{O_k}
\]

was developed in [3]. Here the coefficients \( B_{2kj} \) and \( B_{12kj} \) are determined from the expressions

\[
B_{2kj} = \left(\frac{T_{cr. O_k}}{T_{cr. N_k}}\right)^j \left(\frac{V_{cr. O_k}}{V_{cr. N_k}}\right)^k \cdot B_{O_kj}
\]

\[
B_{12kj} = \frac{1}{y_{N_k} y_{O_k}} \left(\frac{T_{cr. A}}{T_{cr. N_k}}\right)^j \left(\frac{V_{cr. A}}{V_{cr. N_k}}\right)^k \cdot B_{N_kj} - \frac{1}{y_{O_k}} B_{N_kj} - \frac{1}{y_{N_k}} B_{O_kj}
\]

The \( B_{kj} \) are the coefficients of Eq. (5), with subscripts \( N_2, O_2, \) and \( A \) referring to \( N_2, O_2, \) and air, respectively, and \( \omega_{N_2} = V_{cr. N_2}/V; \tau_{N_2} = T/T_{cr. N_2}. \)

The analysis of the errors inherent in method II given in [3] is based on the data of [8] which cover certain high-density \( N_2-O_2 \) mixtures at points far removed from the critical region. The situation here is unsatisfactory since analysis should certainly cover both