12th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2008, Istanbul, Turkey, 26-30 August, 2008

# THE VOLUME EXPANSIVITY AND THE ISOTHERMAL COMPRESSIBILITY COEFFICIENTS OF METHANE DERIVED FROM THE SPEED OF SOUND

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**Key words**: methane, volume expansivity, isothermal compressibility, speed of sound

## 1. THEORY

### 1.1. The thermodynamic speed of sound

The thermodynamic speed of sound (i.e., the speed of sound at zero frequency) in a fluid, $u$, m/s, is defined by the Laplace's equation $u^2 = (\partial p/\partial \rho)_s$, where: $\rho$, kg/m$^3$, is the density of the substance, $p$, N/m$^2$, is the pressure, $s$, J/kg·K, is the specific entropy. Since $\rho = 1/v$ the Laplace's equation has the following form, Ref. [2, p.127]:

$$u^2 = -v^2 \left(\frac{\partial p}{\partial v}\right)_s \tag{1}$$

Combining the above equation with important relationship, rarely mentioned in the literature, that determines the following derivative, Ref. [2, p.124]:

$$\left(\frac{\partial p}{\partial v}\right)_s = \left(\frac{\partial p}{\partial v}\right)_T - \frac{T}{c_v}\left(\frac{\partial p}{\partial T}\right)_v^2 \tag{2}$$

we obtain

$$u^2 = v^2 \left[\frac{T}{c_v}\left(\frac{\partial p}{\partial T}\right)_v^2 - \left(\frac{\partial p}{\partial v}\right)_T\right] \tag{3}$$

An equivalent form of Eq. (3) can be found by replacing the derivative $(\partial p/\partial T)_v$ in terms of the cyclic equation, according to Ref. [1, p.636]:

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T \tag{4}$$

so that, Eq. (3) results

$$u^2 = v^2\left[\frac{T}{c_v}\left(\frac{\partial p}{\partial v}\right)_T^2\left(\frac{\partial v}{\partial T}\right)_p^2 - \left(\frac{\partial p}{\partial v}\right)_T\right] \tag{5}$$

**1.2. The volume expansivity and the isothermal compressibility coefficients**
Generally, any property of a system with simple and pure substance is often expressed as a function of the two basic thermodynamic properties, for example, temperature and pressure ($T$, $p$), or specific volume and temperature ($v$, $T$), etc. Thus, the specific volume dependence on temperature and pressure is:

$$v = v(T, p) \tag{6}$$

Since $p$, $v$, and $T$ are the thermodynamic properties the following total differential of function $v$ is defined as:

$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial p}\right)_T dp \tag{7}$$

The partial derivatives in Eq. (2) have the physical significance in the following expressions, according to Refs. [1,2]:

$$\alpha_p \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p, \mathrm{K}^{-1} \tag{8}$$

$$\alpha_T \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T, \mathrm{Pa}^{-1} \tag{9}$$

The above equations in the literature are known as the coefficient of volume expansivity, and the coefficient of isothermal compressibility, respectively.

**1.3. Average absolute and relative deviation**
Average absolute deviation (*AAD*) is calculated according to expression

$$AAD[\%] = \frac{100}{M(N-1)}\sum_{i=1}^{M}\sum_{j=2}^{N}\frac{\left|X_{i,j}^{\mathrm{cal}} - X_{i,j}^{\mathrm{eos}}\right|}{X_{i,j}^{\mathrm{eos}}} \tag{10}$$

and relative deviation (*RD*) according to expression

$$RD[\%] = 100\frac{X_{i,j}^{cal} - X_{i,j}^{eos}}{X_{i,j}^{\mathrm{eos}}},\quad i = 1, M \ \text{ and } \ j = 1, N \tag{11}$$

where: $M$ is the number of isobars, $N$ is the number of isotherms, $X$ is the value of a coefficient, superscript *cal* denotes the calculated value of a coefficient, and superscript *eos* denotes the reference value of a coefficient obtained from the fundamental equation of state.

**2. RESULTS AND CONCLUSION**
Numerical procedure is used for deriving the volume expansivity and the isothermal compressibility coefficients of gaseous methane from its speed of sound, Ref. [3], in the temperature range 275-375 K, and in the pressure range 0.4-10 MPa. The temperature range is divided into 5 isotherms (e.g. 275 K, 300 K, 325 K, 350 K, and 375 K), and the pressure range is divided into 6 isobars (e.g. 0.4 MPa, 2 MPa, 4 MPa, 6 MPa, 8 MPa, and 10 MPa). The set of equations (1) to (5) is solved numerically by combined Adams-Moulton, Ref. [4, p.404], and Runge-Kutta, Ref. [5, p.93], method. All pressure derivatives are estimated by Lagrange interpolating polynomial, Ref. [6, p.55], of fifth-degree. Figs. 1-

4 give an impression of the results obtained. Initial values of $\rho$ and $c_p$, Ref. [3], are specified along isotherm at 275 K, and therefore this isotherm is omitted. Estimated absolute average deviation of calculated values of the volume expansivity and the isothermal compressibility coefficients, with reference to corresponding reference values, Ref. [3], is 0.052% and 0.011%, respectively.

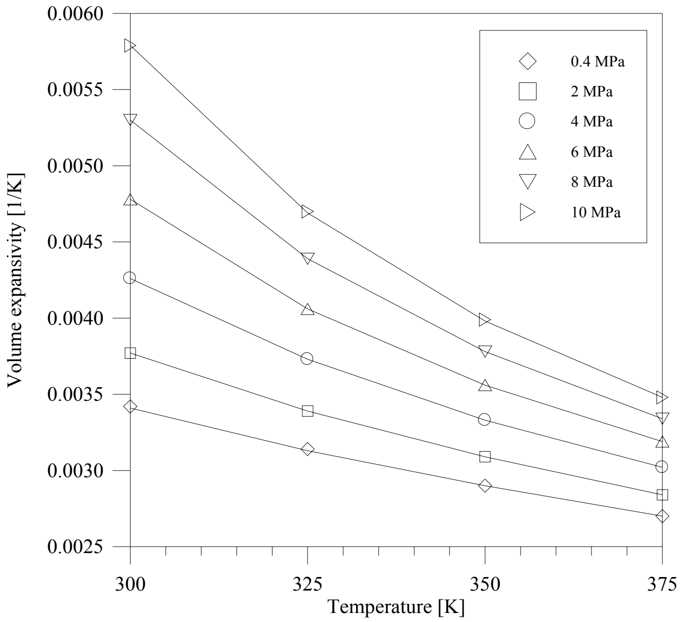


*Figure 1. Volume expansivity of methane vs. temperature;full line this work; symbols Ref. [3].*

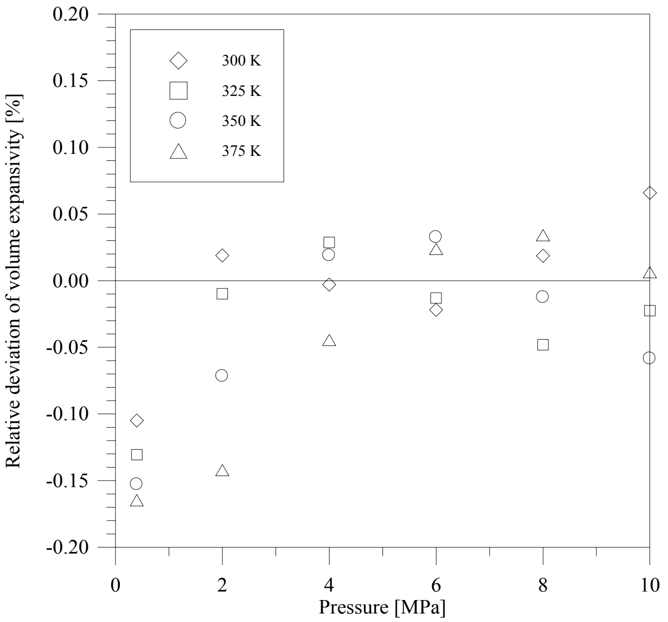


*Figure 2. Relative deviation of methane volume expansivity vs. pressure; symbols this work; full line Ref. [3].*

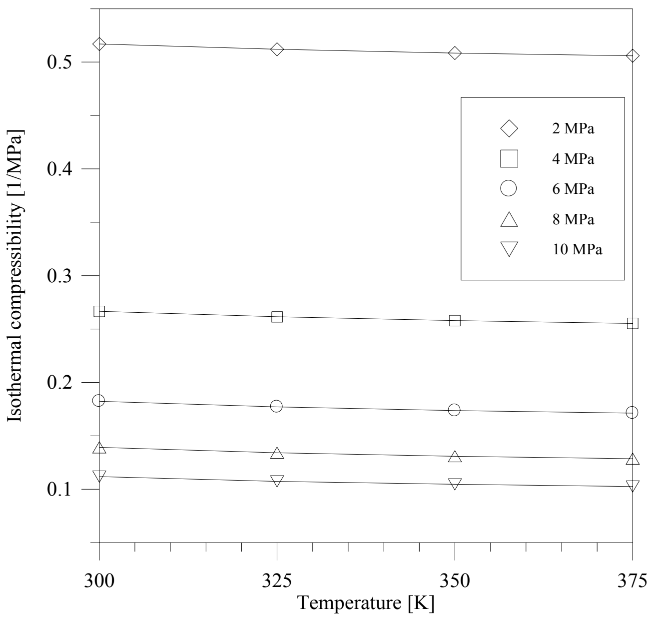


*Figure 3. Isothermal compressibility of methane vs. temperature;full line this work; symbols Ref. [3].*

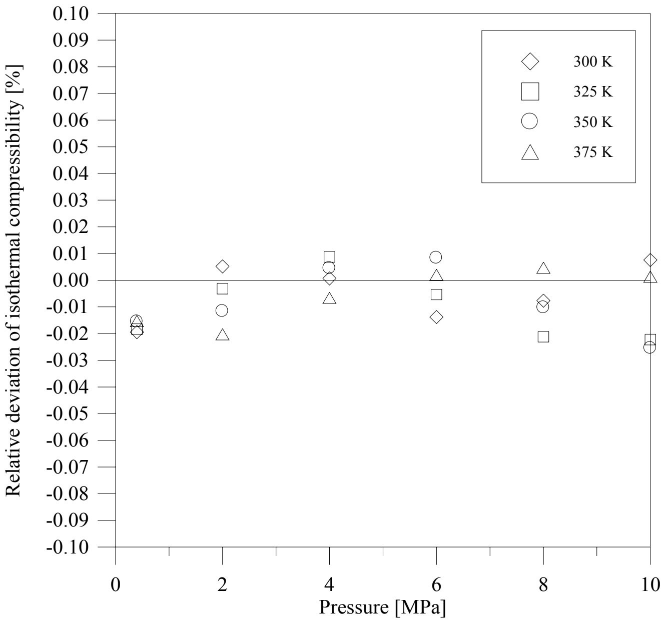


*Figure 4. Relative deviation of methane isothermal compressibility vs. pressure; symbols this work; full line Ref. [3].*

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