10^{th} International research/expert conference
Trends in the Development of Machinery and Associated Technology
TMT 2006, Barcelona- Lloret de Mar, Spain, 11-15 Septembar, 2006.

COMPRESSIBILITY FACTOR OF METHANE FROM THE SPEED OF SOUND MEASUREMENTS

Prof. dr. Muhamed BIJEDIĆ, dipl.ing.
Tehnološki fakultet u Tuzli, B&H

Prof. dr. Nagib NEIMARLIJA, dipl.ing.
Mašinski fakultet u Zenici, B&H

Asistent Edin BERBEROVIĆ, dipl.ing.
Mašinski fakultet u Zenici, B&H

ABSTRACT

This paper presents a new approach to the methane compressibility factor calculation by means of sound speed experimental data. The approach is based on numerical integration of differential equations connecting speed of sound with other thermodynamic properties. The method requires initial conditions in the form of compressibility factor and heat capacity to be imposed at single temperature and pressure range of interest. The method is tested with derived compressibility factor of gaseous methane in pressure range from 0.4 MPa to 6.0 MPa and temperatures between 325 K and 375 K. The calculated absolute error is 0.03%, whereas maximum error is about 0.21%.

Key words: methane, speed of sound, compressibility factor, heat capacity

1. THEORY

There are several ways to derive thermodynamic properties from speed of sound data. In the first approach restrictive assumptions are not imposed in the form of an equation of state. Speeds of sound are simply combined with other observable properties in order to obtain one or more other properties through exact thermodynamic identities. This approach can be applied on either single state or on area of thermodynamic surface [1].

In the second approach explicit or implicit parameterization of equation of state is assumed, whose parameters are fitted only to the experimentally determined speed of sound values. Resulting model can be used for determination of all other thermodynamic properties of phase inside area where assumed form of equation of state is valid [2].

Finally, some form of parameterization of equation of state can be assumed, but now with parameters fitted to sound speeds and to other thermodynamic data simultaneously. During elaboration of the method, functional form is optimized considering huge bank of terms out of which empirical form of equation of state can be constructed, and subset of selected property is found, which represents the best criteria imposed [3].

According to the Ref. [1] one of the expressions connecting the speed of sound with other thermodynamic properties has the form

$$u^{-2} = \left(\frac{M}{R\,T\,Z^2}\right)\left\{\left[Z - p\left(\frac{\partial Z}{\partial p}\right)_T\right] - \left(\frac{R}{c_{p,m}}\right)\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_p\right]^2\right\}, \qquad (1)$$

where: u [m/s] - speed of sound, M [kg/mol] - molecular weight, R [J/mol K] - universal gas constant, T [K] - thermodynamic temperature, Z [-]- compressibility factor, p [Pa] - pressure, $c_{p,m}$ [J/molK] - constant-pressure molar heat capacity.

Pressure and temperature are properties which are commonly measured experimentally. However, if one wants to calculate, for example, compressibility factors from speed of sound data, in a certain pressure and temperature range, equation (1) is not sufficient and another equation is necessary. For this purpose, the following equation from Ref.[1] is commonly used:

$$\left(\frac{\partial c_{p,m}}{\partial p}\right)_T = -\left(\frac{R}{p}\right)\left[2T\left(\frac{\partial Z}{\partial T}\right)_p + T^2\left(\frac{\partial^2 Z}{\partial T^2}\right)_p\right]. \tag{2}$$

Now, here are two nonlinear partial differential equations and one of them is of second order. In order to solve this system of differential equations one also has to impose two sets of initial conditions. They can be selected among Z, $c_{p,m}$, and $\left(\partial Z/\partial T\right)_p$. In our previous work (presented in the Ref.[4]) we introduced method based on initial conditions Z and $\left(\partial Z/\partial T\right)_p$. The approach proved good results, but on account of demanding initial conditions. Namely, if one wants to obtain reliable temperature derivative of compressibility factor, single temperature is not enough and two or more are necessary. Besides, these isotherms must be very closely spaced, which is quite demanding. For that reason, we decided to try to elaborate approach with Z and $c_{p,m}$ as initial conditions, although it was tried with liquid phase only but with limited success.

General problem concerning this approach is unavailability of quality experimental heat capacities, measured with low uncertainty. As we could not succeed to trace such data we decided to derive them from the state of the density measurements. Having available accurate relation of compressibility factor of methane from the equation , Ref.[5]:

$$Z = 1 + \delta\left(N_1\tau^{0.75} + N_2\tau\right) + \delta^2\left(N_3 + N_4\tau^{2.75}\right) + \delta^4\left(N_5 + N_6\tau\right), \tag{3}$$

where: N_1 to N_6 constants, $\tau = T_0/T$, (T_0 = 273.15 K), $\delta = \rho/\rho_0$, (ρ_0 =1 kg/m^3), we derived heat capacities from it as follows further in the text.

As the equation (3) is explicit in T and ρ, we used the expression from the Ref.[1] to calculate constant-volume molar heat capacity

$$c_{v,m} = c_{v,m}^{ig} + \int_0^{\rho}\left(\frac{\partial c_{v,m}}{\partial \rho}\right)_T \mathrm{d}\rho\,, \tag{4}$$

where: $c_{v,m}^{ig}$ [J/mol K] - constant-volume molar heat capacity at the ideal gas state, ρ [mol/m^3] - molar density.

Partial derivative in the equation (4) was calculated by use of the equation (3) and the following expression given in the Ref.[1]

$$\left(\frac{\partial c_{v,m}}{\partial \rho}\right)_T = -\left(\frac{R}{\rho}\right)\left[2T\left(\frac{\partial Z}{\partial T}\right)_\rho + T^2\left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho\right] \tag{5}$$

and finally we obtained the following expression:

$$\left(\frac{\partial c_{v,m}}{\partial \rho}\right)_T = R\left(0.1875 N_1\tau^{0.75}\delta - 2.40625 N_4\tau^{2.75}\delta^2\right). \tag{6}$$

Constant-volume molar heat capacity at the ideal gas state, from the Ref.[6], is

$$c_{v,m}^{ig} = R\left(5.46619 - 0.015657\,T + 5.06324\cdot 10^{-5}\,T^2 - 3.78647\cdot 10^{-8}\,T^3 - 1\right). \qquad (7)$$

Relation between constant-pressure and constant-volume molar heat capacities is, according to the Ref.[7]

$$\frac{c_{p,m}}{R} = \frac{c_{v,m}}{R} + \left[Z + T\left(\frac{\partial Z}{\partial T}\right)_p\right]^2 \Bigg/ \left[Z - p\left(\frac{\partial Z}{\partial p}\right)_T\right]. \qquad (8)$$

In order to obtain constant-pressure molar heat capacity it is necessary to have temperature and pressure derivatives of compressibility factor. Thus, we obtained the following expressions:

$$\begin{aligned}(\partial Z/\partial T)_p = {}& -1.75 N_1 p T_0^{2.75}\big/\left(Z R_i T^{2.75}\right) - 2\,N_2 p T_0\big/\left(Z R_i T^3\right) - 2\,N_3 p^2\big/\left(Z^2 R_i^2 T^3\right) \\ & - 4.75\,N_4 p^2 T_0^{2.75}\big/\left(Z^2 R_i^2 T^{5.75}\right) - 4\,N_5 p^4\big/\left(Z^4 R_i^4 T^5\right) - 5\,N_6 p^4 T_0\big/\left(Z^4 R_i^4 T^6\right),\end{aligned} \qquad (9)$$

$$\begin{aligned}(\partial Z/\partial p)_T = {}& N_1 T_0^{0.75}\big/\left(Z R_i T^{1.75}\right) + N_2 T_0^{0.75}\big/\left(Z R_i T^2\right) + 2 N_3 p\big/\left(Z R_i T\right)^2 \\ & + 2 N_4 p T_0^{2.75}\big/\left(Z^2 R_i^2 T^{4.75}\right) + 3 N_5 p^3\big/\left(Z R_i T\right)^4 + 3 N_6 p^3 T_0\big/\left(Z^4 R_i^4 T^5\right),\end{aligned} \qquad (10)$$

where $R_i = R/M$, individual gas constant.

Having the initial conditions obtained from the equations (3) to (10), and the experimental sound speeds, we can solve system of equations (1) and (2) numerically.

Given Z and $c_{p,m}$, the equation (1) is solved for $\left(\partial Z/\partial T_0\right)_p$, and the equation (2) for $\left(\partial^2 Z/\partial T_0^2\right)_p$, at initial temperature T_0 and pressure range of interest. Now, we have enough information to calculate Z at temperature $T_1 = T_0 + \delta T$, from Taylor series (sufficiently to the second derivative)

$$Z_1 = Z_0 + \delta T\left(\frac{\partial Z}{\partial T_0}\right)_T + \frac{1}{2}(\delta T)^2\left(\frac{\partial^2 Z}{\partial T_0^2}\right)_p, \qquad (11)$$

as well as $\left(\partial Z/\partial T_1\right)_p$ from the expression

$$\left(\frac{\partial Z}{\partial T_1}\right)_p = \left(\frac{\partial Z}{\partial T_0}\right)_p + \delta T\left(\frac{\partial^2 Z}{\partial T_0^2}\right)_p. \qquad (12)$$

Having calculated $\left(\partial Z/\partial p\right)_{T_1}$ from the equation (10), and $\left(\partial c_{p,m}/\partial p\right)_{T_1}$ from Lagrange interpolating polynomial, Ref. [7], the procedure had been repeated until the end of temperature range was approached.

2. RESULTS AND CONCLUSIONS

The recommended method for deriving thermodynamic properties from speed of sound is tested with determined compressibility factor of gaseous methane in the pressure range from 0.4 MPa to 6.0 MPa, and temperatures between 325 K and 375 K. Figure 1. gives an impression of error propagation in Z. Calculated average error is 0.03%, and maximum error is about 0.21%.

It must be noted that we tried to conduct these calculations with different sources of initial conditions for $c_{p,m}$, including several sound equations of state, but never obtained results better than those given at Figure 1. This means that recommended method requires high quality initial values of $c_{p,m}$, in order to describe thermodynamic pvT surface correctly. To date, no such experimental data are available and there is no guarantee it will be available in near future. However, in this paper we tried to prove that new state of the experimental densities may be used to generate heat capacities accurately enough to be used as initial conditions in deriving thermodynamic properties from speed of sound data.

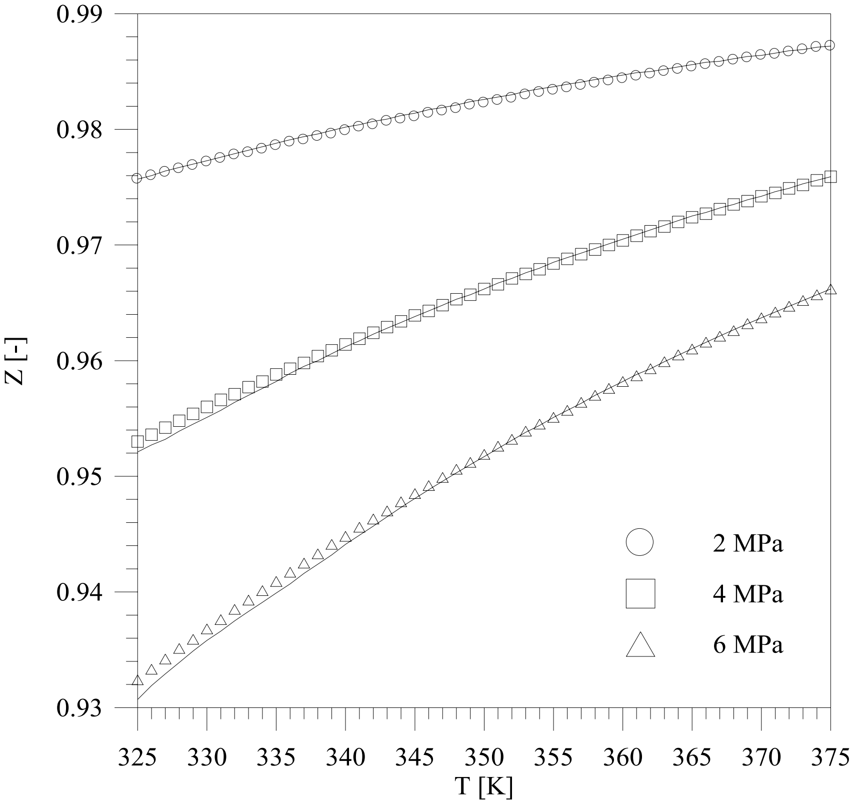

Figure 1. *Z vs. T, full line this work,* ○ □ Δ *equation* (3)

3. REFERENCES

[1] Estrada-Alexanders, A. F., Trusler, J. P. M., Zarari, M. P., Determination of thermodynamic properties from the speed of sound, *International Journal of Thermophysics*, **16** (3) (1995) 663-673.

[2] Gillis, K. A., Moldover, M. R., Practical determination of gas densities from the speed of sound using square-well-potentials, *International Journal of Thermophysics*, **17** (6) (1996) 1305-1324.

[3] Schmidt, R., Wagner, W., A new form of the equation of state for pure substances and its application to oxygen, *Fluid Phase Equilibria*, **19** (1985) 175-200.

[4] Bijedić, M., Neimarlija, N., Đidić, E., Compressibility factor of gases from the speed of sound, *Technical Gazette* **11** (1-2) (2004) 3-9.

[5] Pieperbeck, N., Kleinrahm, R., Wagner, W., Jaeschke, M., Results of (pressure, density, temperature) measurements on methane and on nitrogen in the temperature range from 273.15 K to 323.15 K at pressures up to 12 MPa using a new apparatus for accurate gas-density measurements, *Journal of Chemical Thermodynamics*, **23** (1991) 175-194.

[6] Setzmann, U., Wagner, W., A New Equation of State and Tables of Thermodynamic Properties for Methane Covering the Range from the Melting line to 625 K and Pressures up to 1000 MPa, *Journal of Physical and Chemical Reference Data*, **20** (6) (1991) 1061-1155.

[7] Trusler, J. P. M., Zarari, M., The Speed of Sound and Derived Thermodynamic Properties of Methane at Temperatures Between 275 K and 375 K and Pressures up to 10 MPa, *Journal of Chemical Thermodynamics*, **24**, (1992) 973-991.