

COMPRESSIBILITY FACTOR OF NITROGEN FROM THE SPEED OF SOUND MEASUREMENTS

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ABSTRACT

This paper presents a new approach to the nitrogen 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. It is tested with derived compressibility factor of nitrogen in pressure range from 0.3 MPa to 10.2 MPa and temperatures between 300 K and 350 K. Calculated absolute average error is 0.018%, and maximum error better than 0.12%.

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

1. INTRODUCTION

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 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 experimental speeds of sound. 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 the criteria imposed [3].

2. THEORY

One of expressions connecting the speed of sound, u [m/s], with other thermodynamic properties has the form, Ref. [1]:

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

where: 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/mol K] - constant-pressure molar heat capacity.

Pressure and temperature are thermal properties which are commonly measured experimentally. However, if one wants to calculate, for example, compressibility factors from speed of sound data, in some 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:

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

Now, we have 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 $(\partial Z/\partial T)_p$. In our previous work (presented in Ref. [4]) we introduced method based on initial conditions Z and $(\partial Z/\partial T)_p$. 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 and 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 state of the art density measurements. Having available accurate relation of compressibility factor of nitrogen from the equation, Ref. [5]:

$$Z = 1 + \delta(N_1 + N_2 \tau^{1.25}) + \delta^2(N_3 \tau^{0.5} + N_4 \tau^{2.5}) + \delta^4 N_5, \quad (3)$$

where: N_1 to N_5 constants, $\tau = T_0/T$, ($T_0 = 273.15$ K), $\delta = \rho/\rho_0$, ($\rho_0 = 1$ kg/m³), we derived heat capacities from it as the follows further in the text.

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

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

where: $c_{v,m}^{ig}$ [J/mol K] - constant-volume molar heat capacity in ideal gas state, ρ [mol/m³] - molar density.

Partial derivative in the equation (4) we calculated using the equation (3) and following expression given in the Ref. [1]

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

Closed form relation obtained from equations (3) and (5) is

$$\left(\frac{\partial c_{v,m}}{\partial \rho}\right)_T = -R(0,3125N_2 \tau^{1.25}\delta - 0,125N_3 \tau^{0.5}\delta^2 + 1,875N_4 \tau^{2.5}\delta^2), \quad (6)$$

while, following expression for ideal gas molar heat capacity, from the Ref. [6], is used

$$c_{v,m}^{ig} = R(3,500571 + 1,115488 \cdot 10^{-20} T^7 - 1). \quad (7)$$

According to the Ref. [7] relation between constant-pressure and constant-volume molar heat capacities is

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

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:

$$\begin{aligned} (\partial Z/\partial T)_p = & -N_1 p / (ZR_i T^2) - 2,25 N_2 p T_0^{1,25} / (ZR_i T^{3,25}) - 2,5 N_3 p^2 T_0^{0,5} / (Z^2 R_i^2 T^{3,5}) \\ & - 4,5 N_4 p^2 T_0^{2,5} / (Z^2 R_i^2 T^{5,5}) - 4 N_5 p^4 / (Z^4 R_i^4 T^5), \end{aligned} \quad (9)$$

$$\begin{aligned} (\partial Z/\partial p)_T = & N_1 / (ZR_i T) + N_2 T_0^{1,25} / (ZR_i T^{2,25}) + 2 N_3 p T_0^{0,5} / (Z^2 R_i^2 T^{2,5}) \\ & + 2 N_4 p T_0^{2,5} / (Z^2 R_i^2 T^{4,5}) + 4 N_5 p^3 / (ZR_i T)^4, \end{aligned} \quad (10)$$

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 $(\partial Z/\partial T_0)_p$, and the equation (2) for $(\partial^2 Z/\partial T_0^2)_p$, 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 (suffiviently to the second derivative

$$Z_1 = Z_0 + \delta T (\partial Z/\partial T_0)_p + \frac{1}{2} (\delta T)^2 (\partial^2 Z/\partial T_0^2)_p, \quad (11)$$

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

$$(\partial Z/\partial T_1)_p = (\partial Z/\partial T_0)_p + \delta T (\partial^2 Z/\partial T_0^2)_p. \quad (12)$$

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

3. RESULTS AND CONCLUSIONS

The recommended method for deriving thermodynamic properties from speed of sound [8] is tested with derived compressibility factor of gaseous nitrogen in pressure range from 0.3 MPa to 10.2 MPa, and temperatures between 300 K and 350 K. Fig. 1 gives an impression of error propagation in Z . Calculated absolute average error is 0.018%, and maximum error better than 0.12%.

It must be noted that error increases as temperature decreases, which is expected, because compressibility factors at next temperature are calculated from values of Z and $c_{p,m}$ calculated at preceding temperature. Error increases with pressure too and, on account of that, upper limit of pressure is determined by maximum acceptable error. Generally, the method is very sensitive to initial conditions, and even very small error in initial conditions drastically cuts down pressure and temperature range in which Z may be calculated with acceptable error. This presumes application of approved methods of numerical interpolation (e.g. Lagrange interpolating polynomial in 3 to 5 points) for speeds of sound calculations at isobars and isotherms along which numerical integration is conducted. Computing with double precision is necessary in order to keep truncation error in acceptable limits.

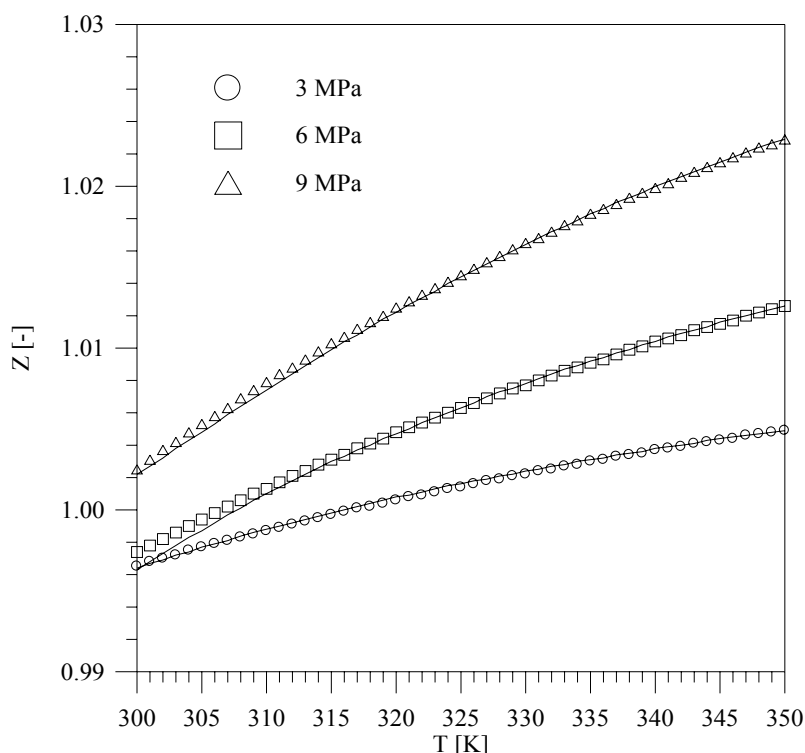


Figure 1. Z vs. T , full line this work, \circ \square \triangle equation (3).

4. REFERENCES

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