

Thermodynamic Properties of Gases from Speed-of-Sound Measurements

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A procedure for deriving thermodynamic properties of gases from speed of sound is presented. It is based on numerical integration of ordinary differential equations (ODEs) (rather than partial differential equations—PDEs) connecting speed of sound with other thermodynamic properties in the T - p domain. The procedure enables more powerful methods of higher-order approximation to ODEs to be used (e.g., Runge-Kutta) and requires only Dirichlet initial conditions. It was tested on gaseous argon in the temperature range from 250 to 450 K and in the pressure range from 0.2 to 12 MPa, and also on gaseous methane in the temperature range from 275 to 375 K and in the pressure range from 0.4 to 10 MPa. The density and isobaric heat capacity of argon were derived with absolute average deviations of 0.007% and 0.03%, respectively. The density and isobaric heat capacity of methane were derived with absolute average deviations of 0.006% and 0.09%, respectively.

KEY WORDS: density; heat capacity; ODE; PDE; Runge-Kutta; speed of sound.

1. INTRODUCTION

Several articles dealing with numerical integration of differential equations connecting the speed of sound with other thermodynamic quantities have been published in the last 15 years. The majority of those articles have been published by two independent groups of researchers. Both groups

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were dealing with the gaseous phase only, but their approaches were quite different.

It is difficult to make a serious comparison of the results obtained by these independent groups because of differences in temperature and especially pressure ranges being considered. However, the general impression is that the approach of the first group [1–5] is rather approximate, because deviations of their results for density and heat capacity are one to two orders of magnitude higher than those of the second group [6–10].

The main disadvantage of the first approach [1–5] lies in the fact that they were using the T - ρ rather than T - p domains, although the speed of sound was measured experimentally along isobars and not along isochors. It is known that density derivatives are estimated more accurately than pressure derivatives. However, if the density is not measured, it is not possible to calculate the speed of sound along isochors without additional data from another source or by recourse to an iterative procedure. Also, this approach is based on the Euler method of numerical integration, which is not appropriate if a wider range of temperature is considered.

The second group was using the T - ρ as well as T - p domain of integration [6–10]. Their approach is based on a more accurate method of numerical integration. They were using an improved Euler method (e.g., predictor–corrector) to reduce the error caused by the truncation of the Taylor expansion after the second-order derivative. However, the main disadvantage of this approach is the need for demanding initial conditions. Namely, besides the compressibility factor, this approach requires the temperature derivative as well, along with the initial temperature (e.g., both Dirichlet and Neumann conditions). For imposing Neumann conditions correctly, one needs to know the compressibility factor at least at another temperature close to the initial one, but in practice two additional temperature points are necessary. This approach was successfully applied to the determination of the density and isochoric heat capacity of HFC-134a from speed-of-sound values, in the T - ρ domain [11].

The method of boundary conditions [12] is based on solving a single second-order partial differential equation that links the speed of sound and compressibility factor subject to only Dirichlet boundary conditions. It requires several accurate p - ρ - T data points along two isotherms and two isochors. The region in which the speed of sound is given is replaced by a discrete mesh of reduced temperature and reduced density, and all derivatives are estimated by central-difference formulae. However, the method is rather robust even with a finite-difference scheme using differential operator approximations correct only to second-order in the increments.

The idea of converting a set of second-order partial differential equations (PDEs) into a set of first-order ordinary differential equations (ODEs) is, in our opinion, the most promising. This approach was recently introduced for the liquid phase [13]. However, for the case of the gaseous phase, integration is performed with respect to temperature rather than pressure [14]. This approach enables introduction of more powerful standard methods of solving differential equations (e.g., Runge-Kutta).

2. THEORY

The speed of sound, u , is a fluid property, which is readily measured with higher accuracy than the majority of other thermodynamic quantities. This property is connected to the basic thermodynamic quantities through the equation,

$$u^2 = \left(\frac{\partial p}{\partial \rho} \right)_s, \quad (1)$$

where p is the pressure, ρ is the density, and s is the entropy. Since the entropy is not measured directly, the isentropic derivative in Eq. (1) is usually replaced by corresponding derivatives at constant temperature and pressure (or density). Unlike density, pressure is a state variable which is always measured directly. Therefore, if one takes T and p as independent variables, the following equations may be derived from Eq. (1) with the aid of standard thermodynamic identities:

$$\alpha_p^2 = \frac{c_p}{T} \left[\left(\frac{\partial \rho}{\partial p} \right)_T - \frac{1}{u^2} \right], \quad (2)$$

$$c_p = T \alpha_p^2 \left[\left(\frac{\partial \rho}{\partial p} \right)_T - \frac{1}{u^2} \right]^{-1}, \quad (3)$$

$$\left(\frac{\partial \rho}{\partial T} \right)_p = -\alpha_p \rho, \quad (4)$$

$$\left(\frac{\partial \alpha_p}{\partial T} \right)_p = -\alpha_p^2 - \frac{\rho}{T} \left(\frac{\partial c_p}{\partial p} \right)_T, \quad (5)$$

where c_p is the specific heat capacity at constant pressure, T is the thermodynamic temperature, and α_p is the thermal expansion coefficient.

The set of Eqs. (2)–(5) may be solved for ρ and c_p in the range of T and p in which experimental data for u are available. Since this set of equations has no analytical solution, one has to impose initial conditions in order to get the solution numerically. In order to satisfy Eq. (1), initial conditions must be imposed along a line that crosses all of the isentropes, which pass through the region of interest. For the case of the gaseous phase, the only isotherm satisfying this criterion is the one at the lowest temperature T_0 [14]. Therefore, numerical integration is performed with respect to temperature, starting from the lowest T . If initial conditions are imposed in the form of ρ and c_p , and all derivatives with respect to pressure are estimated independently, then the set of first-order PDEs, Eqs. (2)–(5), may be solved as an initial-value problem for the set of first-order ODEs by the procedure outlined below.

The procedure is initiated by solving Eq. (2) for α_p^2 , with given values of ρ and c_p at an initial temperature T_0 , over the whole range of pressure. Then, Eqs. (4) and (5) are solved for ρ and α_p at temperature $T_1 = T_0 + \delta T$, where δT is the step of integration. Now, there are enough data for c_p to be solved at T_1 from Eq. (3). The procedure is repeated until the upper limit of temperature is reached. The speed of sound and partial derivatives $(\partial\rho/\partial p)_T$ and $(\partial c_p/\partial p)_T$ may be estimated numerically from Newtonian or Lagrangian interpolation polynomials. For that purpose, the pressure range may be divided into a number of isobars. However, it is known that an interpolation polynomial estimates derivatives at the boundary points with lower accuracy than at intermediate points [13]. For that reason, in order to keep the number of these boundary points as low as possible (e.g., two), over the whole pressure range, the number of isobars should not be greater than the order of the interpolation polynomial plus one.

3. RESULTS

3.1. Argon

The procedure recommended for deriving ρ and c_p from speed-of-sound data is tested using experimental sound-speed values in gaseous argon in the temperature range from 250 to 450 K and in the pressure range from 0.2 to 12 MPa [8]. Initial conditions, as well as reference values of ρ and c_p , are obtained from the fundamental equation of state for argon [15]. According to the authors, this equation of state estimates density with an uncertainty less than 0.02%, and heat capacity with an uncertainty within 0.3%, for temperatures up to 340 K and pressures up

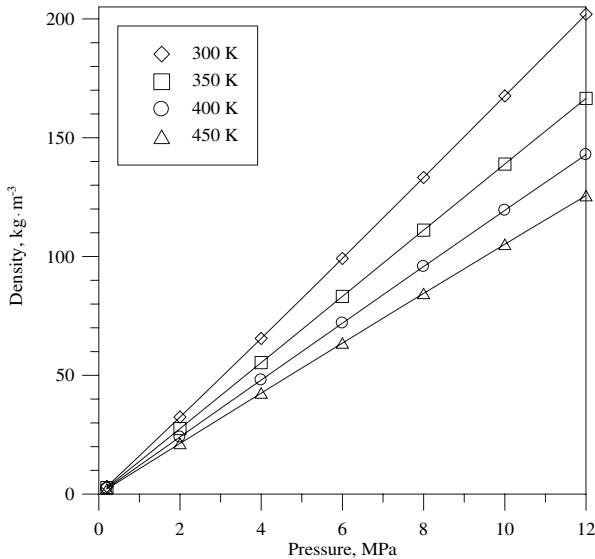


Fig. 1. Density of argon versus pressure at various temperatures; (—) this paper, (\diamond \square \circ \triangle) reference values [15].

to 12 MPa. Experimental values of the speed of sound were available at temperatures of 250, 300, 350, 400, and 450 K. The pressure range is divided into seven isobars (0.2, 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0 MPa). Sound-speed values are calculated from a Lagrangian interpolation polynomial (fourth-order with respect to temperature and pressure). Pressure derivatives of ρ and c_p are estimated by a Lagrangian interpolation polynomial of sixth-order. Numerical integration of Eqs. (4) and (5) was performed by Verner's, adaptive step-size Runge-Kutta method of sixth-order approximation. The method is very efficient, and it took just 102 steps to reach the upper limit of the temperature range.

General impressions of the results may be obtained from Figs. 1 and 2, where ρ and c_p are given as a function of pressure at four temperatures (the lowest one, along which initial conditions were imposed, is omitted). However, more detailed insight may be obtained from Figs. 3 and 4, where relative deviations are given as percentages of the corresponding reference values. From these figures, one can see that the maximum relative deviation of density is +0.035%/-0.015% and that of heat capacity is +0.07%/-0.08%. The average absolute deviation of density is 0.007%, and that of heat capacity is 0.03%.

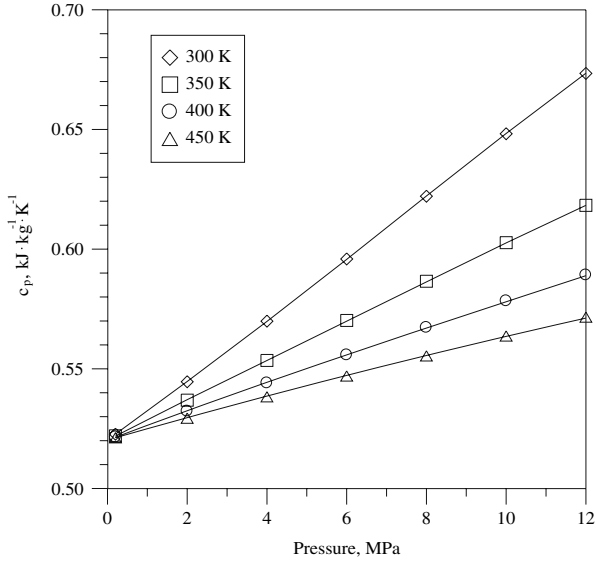


Fig. 2. Heat capacity of argon versus pressure at various temperatures; (—) this paper, (\diamond \square \circ \triangle) reference values [15].

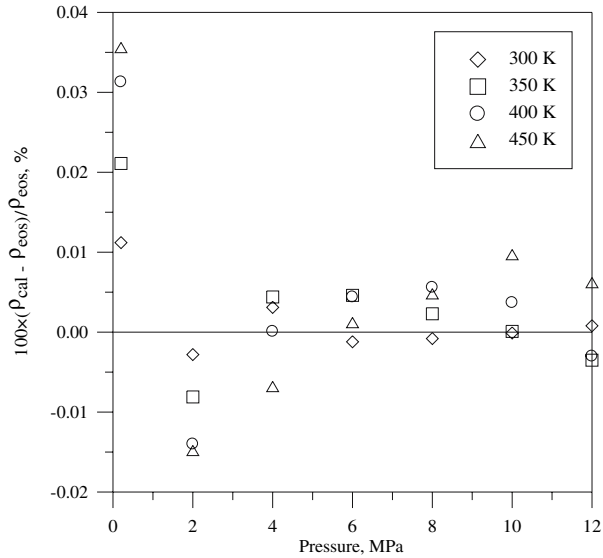


Fig. 3. Relative deviation of argon density versus pressure at various temperatures; (—) this paper, (\diamond \square \circ \triangle) reference values [15].

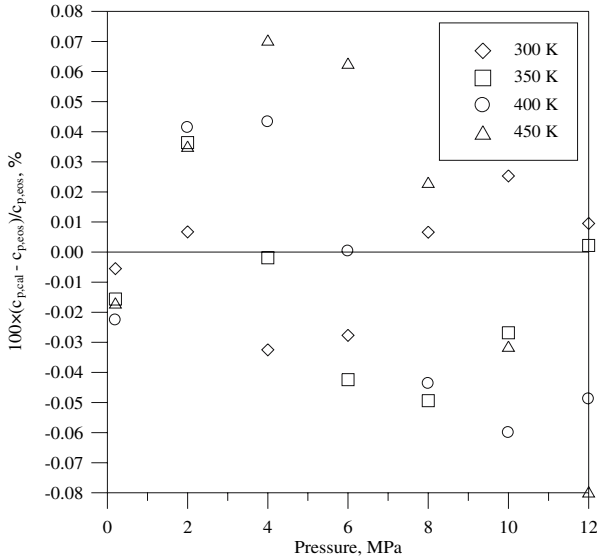


Fig. 4. Relative deviation of argon heat capacity versus pressure at various temperatures; (—) this paper, (◇ □ ○ △) reference values [15].

3.2. Methane

Our recommended procedure for deriving ρ and c_p from speed-of-sound data is also tested on methane. Experimental sound-speed values in gaseous methane were available in the temperature range from 275 to 375 K and in the pressure range from 0.4 to 10 MPa [6]. Initial conditions, as well as reference values of ρ and c_p , are obtained from the fundamental equation of state for methane [16]. According to the authors, this equation of state estimates density with an uncertainty of 0.03%, and heat capacity with an uncertainty within 1%, for temperatures up to 350 K and pressures up to 12 MPa. Experimental values of the speed of sound were available at temperatures of 275, 300, 325, 350, and 375 K. The pressure range is divided into six isobars (0.4, 2.0, 4.0, 6.0, 8.0, and 10.0 MPa). Calculation of the speed of sound was the same as for argon except that a fifth-order interpolation polynomial was used to estimate pressure derivatives. The method of numerical integration was also the same, but this time the integration was accomplished in just 53 steps.

General impressions of the results may be obtained from Figs. 5 and 6, where ρ and c_p are given as a function of pressure at four temperatures (the lowest one, along which initial conditions were imposed, is omitted).

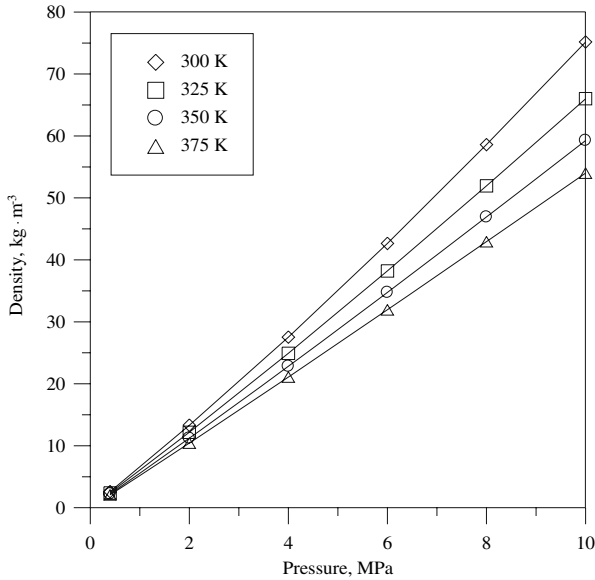


Fig. 5. Density of methane versus pressure at various temperatures; (—) this paper, (\diamond \square \circ \triangle) reference values [16].

However, more detailed insight may be obtained from Figs. 7 and 8, where relative deviations are given as percentages of corresponding reference values. From these figures, one can see that the maximum deviation of density is $+0.04\%/-0.009\%$ and that of heat capacity is $+0.08\%/-0.46\%$. The average absolute deviation of density is 0.006% , and that of heat capacity is 0.09% .

4. CONCLUSIONS

The speed of sound is a thermodynamic property, which is readily measured with higher accuracy than the majority of other thermodynamic properties. However, in order to maintain this accuracy when deriving related thermodynamic properties from the speed of sound, sophisticated numerical methods must be employed. In the first place, PDEs linking speed of sound with other thermodynamic quantities (e.g., density, heat capacity) have to be converted into ODEs. In this way, more powerful methods of higher-order approximation to ODEs (e.g., Runge-Kutta) may be employed. If the gaseous phase is considered, numerical integration is performed with respect to temperature, and all pressure derivatives are estimated using interpolation polynomials of the appropriate order (e.g.,

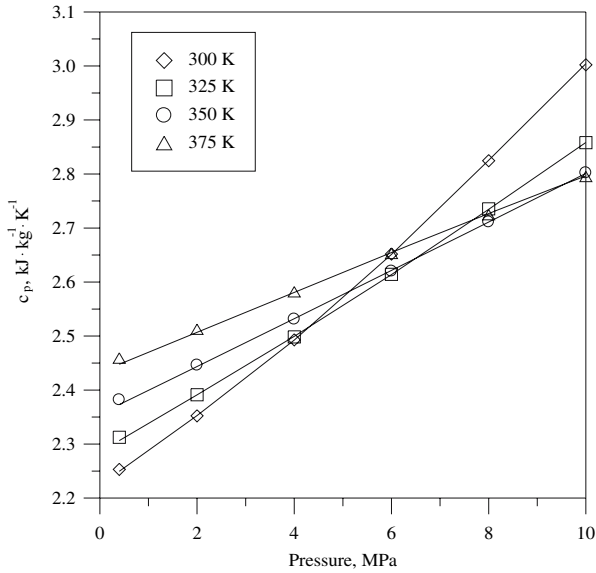


Fig. 6. Heat capacity of methane versus pressure at various temperatures; (—) this paper, (\diamond \square \circ \triangle) reference values [16].

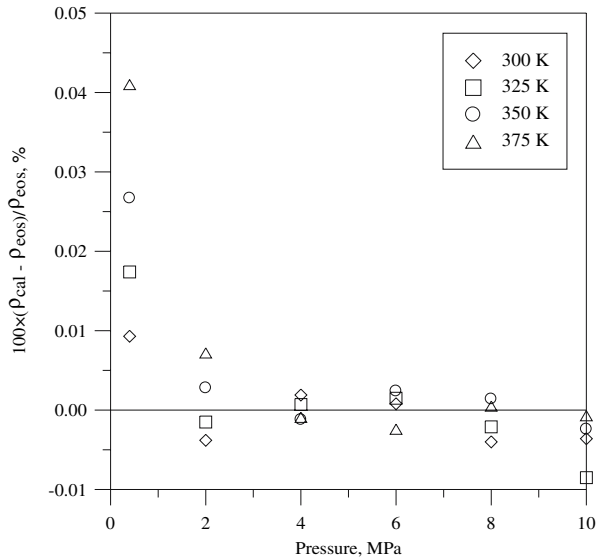


Fig. 7. Relative deviation of methane density versus pressure at various temperatures; (—) this paper, (\diamond \square \circ \triangle) reference values [16].

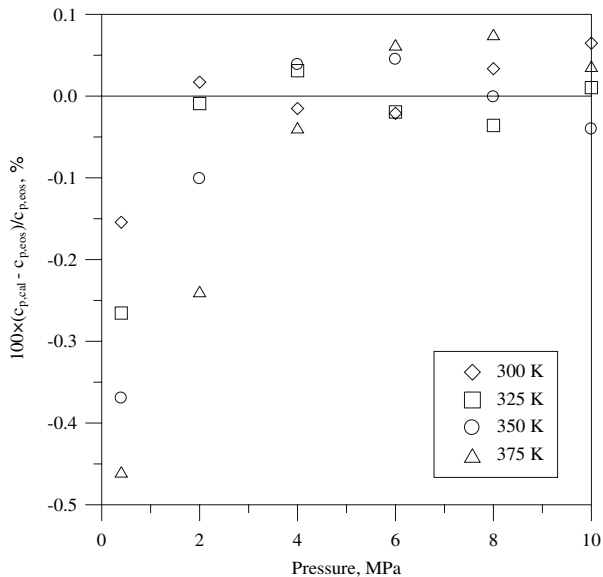


Fig. 8. Relative deviation of methane heat capacity versus pressure at various temperatures; (—) this paper, (◇ □ ○ △) reference values [16].

Lagrangian, Newtonian, etc.). However, because interpolation polynomials estimate the derivative at boundary points with lower accuracy than at intermediate points, it is recommended to divide the pressure range into a number of isobars that can be covered by one polynomial of reasonable order. Finally, as this method can be used to solve initial-value problems, the solution is highly dependent on the accuracy of the density and heat-capacity values that are imposed along the initial isotherm.

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