

# Speed of Sound Measurements in Helium at Pressures from 15 to 100 MPa and Temperatures from 273 to 373 K

Carsten Wedler and J. P. Martin Trusler\*

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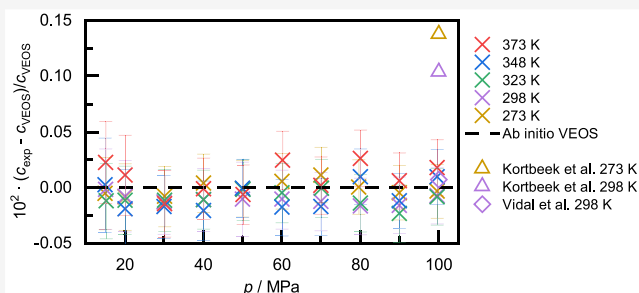
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**ABSTRACT:** The speed of sound in helium was measured along five isotherms in a temperature range from 273 to 373 K at pressures from 15 to 100 MPa with a relative expanded uncertainty ( $k = 2$ ) from 0.02 to 0.04%. A dual-path pulse-echo system was utilized to conduct these measurements. The data were compared with the reference equation of state developed by Ortiz Vega et al. At pressures up to 50 MPa, relative deviations were within the uncertainty of our measurements, while, at higher pressures, increasing negative deviations were observed up to -0.26%. We also compared the results with predictions based on the virial equation of state correct to the seventh virial coefficient, using the *ab initio* virial coefficients reported recently by Gokul et al., finding agreement to within the experimental uncertainty at all investigated states.



## 1. INTRODUCTION

Helium is a noble gas with numerous important applications in science and industry. Liquid helium is a crucial cryogen for low-temperature applications, especially cooling of superconducting magnets.<sup>1,2</sup> Due to its non-toxic nature and properties that differ markedly from air, it is a perfect gas for leak detection in high-pressure systems.<sup>3</sup> In adsorption science, helium is extensively used as an inert gas to determine the skeletal volume of adsorbent materials.<sup>4–6</sup> It is also used as a carrier gas in gas chromatography.<sup>7</sup> As it is the only gas with small dimensions, low density, high speed of sound, and low boiling point similar to hydrogen, it is also a perfect gas for calibrating instruments used in connection with hydrogen storage, transport, and utilization. Regarding hydrogen liquefaction, helium is an important refrigerant, both in pure form and as part of a mixture (e.g., helium/neon mixtures).<sup>8,9</sup> For all these applications, a reliable description of the thermophysical properties of helium is necessary. Therefore, an equation of state (EOS) to calculate thermodynamic properties of <sup>4</sup>He was developed in 1990 by McCarty and Arp.<sup>10</sup> In 2013, Ortiz Vega<sup>11</sup> published in his PhD thesis a fundamental Helmholtz energy EOS which describes the thermodynamic properties of helium more accurately than the EOS of McCarty and Arp.<sup>10</sup> However, in common thermophysical property software such as REFPROP 10.0<sup>12</sup> or TEND 5.0,<sup>13</sup> the EOS from the PhD thesis by Ortiz Vega<sup>11</sup> is superseded by an improved but unpublished EOS, also due to Ortiz Vega et al.<sup>14</sup> This EOS is dated 2015 and is called the “final” EOS in both software and is also the EOS recommended for helium by NIST.<sup>12</sup> In the PhD thesis of Ortiz Vega,<sup>11</sup> the only speed of sound data considered for

gaseous helium were those of Gammon<sup>15</sup> and Hurly et al.,<sup>16</sup> which cover pressures below about 15 MPa. Thus, the EOS was not validated for pressures above 15 MPa. The author gives an uncertainty for the calculation of the speed of sound of about 0.02%, as the EOS describes the data of Gammon<sup>15</sup> with deviations within  $\pm 0.02\%$ . For the unpublished “final” EOS by Ortiz Vega et al.,<sup>14</sup> REFPROP 10 and TEND 5.0 specify that the relative uncertainty of the speed of sound in the vapor phase is 0.01%. It is not obvious if the “final” EOS was optimized against the same data set or if additional speed of sound data was considered. However, to the best of our knowledge, no new speed of sound data in gaseous helium were published after the initial publication of Ortiz Vega.<sup>11</sup>

A review of speed of sound data in gaseous helium available in the literature is presented in Table 1. Absolute average relative deviations (AARD) of the experimental data from values calculated using REFPROP 10 with the unpublished EOS of Ortiz Vega et al.<sup>14</sup> are given. The data sets of Gammon<sup>15</sup> and Hurly et al.,<sup>16</sup> which were used for the fitting procedure described in the PhD thesis of Ortiz Vega,<sup>11</sup> show by far the lowest AARD. Therefore, it seems likely that both data sets were used to adjust the unpublished EOS of Ortiz Vega et al.<sup>14</sup> The low- and ultra-low-pressure data reported by

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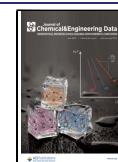


**Table 1.** Review of Speed of Sound Data in Gaseous Helium Reported in the Literature Where  $N$  is the Number of Data Points,  $T$  is the Temperature,  $p$  is the Pressure, and  $\Delta_{\text{AARD}}$  is the Absolute Average Relative Deviations of the Experimental Data Set from the Unpublished EOS (2015) of Ortiz Vega et al.<sup>14</sup> as Calculated Using REFPROP 10<sup>12</sup>

| Author(s)                                   | Year | $N$ | $T/\text{K}$ | $p/\text{MPa}$        | $\Delta_{\text{AARD}}(\%)$ |
|---------------------------------------------|------|-----|--------------|-----------------------|----------------------------|
| Gammon <sup>15</sup>                        | 1976 | 204 | 98–423       | 1–15                  | 0.005                      |
| Hurly et al. <sup>16</sup>                  | 1997 | 162 | 225–400      | 0.2–1.5               | 0.013                      |
| Van Itterbeek and Van Doninck <sup>17</sup> | 1949 | 4   | 75–90        | 0.1                   | 0.088                      |
| Van Itterbeek and Mariens <sup>18</sup>     | 1940 | 12  | 294–347      | $10^{-5}$ – $10^{-4}$ | 0.089                      |
| van Itterbeek and Thys <sup>19</sup>        | 1938 | 4   | 220–291      | 0.09–0.1              | 0.53                       |
| Kimura et al. <sup>20</sup>                 | 1987 | 20  | 298          | 10–200                | 1.49                       |
| Pitaevskaya and Bilevich <sup>21</sup>      | 1970 | 168 | 298–473      | 40–400                | 2.48                       |
| Vidal et al. <sup>22</sup>                  | 1980 | 10  | 298          | 100–1000              | 9.76                       |
| Hanayama and Kimura <sup>23</sup>           | 1995 | 20  | 295          | 52–3000               | 12.0                       |
| Kortbeek et al. <sup>24</sup>               | 1988 | 164 | 98–298       | 100–1000              | 12.3                       |
| Nishitake and Hanayama <sup>25</sup>        | 1975 | 15  | 298          | 137–1470              | 14.0                       |
| Curtis <sup>26</sup>                        | 1934 | 2   | 273          | 0.1                   | 14.6                       |

Van Itterbeek and co-workers<sup>17,18</sup> show AARDs below 0.1%. However, all other reported data show significant deviations. In addition, it becomes apparent that there is a gap in the literature for pressures of 15 to 100 MPa, as there are only very limited data available, and these show high deviations from the EOS.

The objective of the present work was to address the identified gap in the literature by providing new speed of sound data in gaseous helium at pressures from 15 to 100 MPa and at temperatures between 273 K and 373 K.

## 2. EXPERIMENTAL SECTION

The speed of sound measurements were carried out with the dual-path pulse-echo system described by Scholz et al.<sup>27</sup> and Al Ghafri et al.<sup>28</sup> In this method, an ultrasonic transducer is immersed in the fluid under study between two plane parallel end plates located at different distances. The transducer is excited to generate ultrasonic pulses that propagate through the fluid to each side. The pulses are reflected from the ends and return to the transducer, where the echoes are detected. The speed of sound is then determined by the time difference between the returning echoes and the difference between the lengths of the two paths.

The dual-path pulse-echo technique is a well-established technique for the determination of the speed of sound in liquids.<sup>29–33</sup> However, it is generally considered that pulse techniques are not well suited to measurements on gases. This is because the acoustic impedance of the fluid (the product of the sound speed and the density) is generally low, leading to weak and possibly poorly defined ultrasonic pulses.<sup>34</sup> However, Meier and Kabelac<sup>35,36</sup> have shown that the dual-path pulse-echo technique can be applied successfully to compressed gases, leading to relative uncertainties in the measured speed of sound as small as 0.01% when the acoustic impedance is sufficient. Depending on the temperature, they reported clearly

distinguishable ultrasonic signals at pressures  $\geq 7$  MPa for argon and  $\geq 20$  MPa for nitrogen. Dubberke et al.<sup>37</sup> reported measurements at pressures as low as 5 MPa for argon and nitrogen.

As shown in Figure 1, the device used in this work consisted of a ceramic piezoelectric disc transducer (Piezo Technologies,

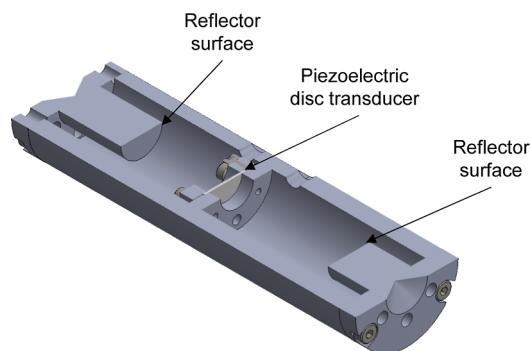


**Figure 1.** Cross-sectional view of the cylindrical ultrasonic cell.

type K360 with a diameter of 10 mm and a thickness of 0.4 mm) clamped perpendicular to the axis of a cylindrical ultrasonic cell. The cell was fabricated from Invar 36 nickel-iron alloy. Plane reflectors closed each end of the cell. According to the dual-path pulse-echo principle, the distances from the transducer disc to the two reflectors are different and, in the present work, the nominal lengths were  $L_1 = 20$  mm and  $L_2 = 30$  mm. To conduct a measurement, the transducer disc was excited by a three-cycle sinusoidal tone burst with a frequency of 5 MHz and an amplitude of  $20 V_{\text{p-p}}$ . This tone burst was generated by a function generator (Agilent, model 33220A), and the returning echoes were captured by a digital oscilloscope (Agilent, model DSO6012A). The ultrasonic cell was mounted in a pressure vessel rated for pressures up to 400 MPa. The pressure vessel was immersed in a temperature-controlled bath (Fluke, model 6020), which was filled with a water-ethylene glycol mixture. To achieve temperatures below 313 K, a copper heat exchanger, connected to a closed-circuit chiller (Huber, model CC-K6s), was immersed in the bath fluid. The pressure was regulated by using a manual syringe pump and measured by a pressure transducer (Keller, model 33X, 100 MPa full scale), both located in the piping outside of the bath. The temperature of the pressure vessel was measured with a platinum resistance thermometer (Fluke, model 5615) immersed in an axial thermometer well and connected to a resistance read-out unit (Fluke, model 1502A).

The speed of sound  $c$  was determined from the measured time delay  $\Delta t$  between the echoes returning on the short and the long paths, for which the path difference is  $2(L_2 - L_1)$ , according to the equation

$$c = \frac{2(L_2 - L_1)}{\Delta t + \tau} \quad (1)$$

Here,  $\tau$  is a small correction for diffraction given by<sup>38</sup>

$$\tau = \frac{\phi(S_2, \chi_2) - \phi(S_1, \chi_1)}{\omega} \quad (2)$$

where  $\phi(S_i, \chi_i)$  is the diffraction phase advance,  $S_i = 2L_i\lambda/b^2$ ,  $\lambda$  is the wavelength,  $b$  is the effective transducer radius,  $\chi_i = 2L_i/b$ , and  $\omega$  is the angular frequency. In the present case, the

clamping arrangement reduces the effective transducer radius to  $b = 4$  mm.

The path length difference  $\Delta L = (L_2 - L_1)$  is represented as a function of temperature and pressure as follows

$$\Delta L(T, p) = \Delta L_0 \left[ 1 + \alpha(T - T_0) - \frac{\beta}{3}(p - p_0) \right] \quad (3)$$

Here,  $\Delta L_0$  is the length difference at a reference temperature  $T_0$  and reference pressure  $p_0$ , which was determined by a calibration measurement in gaseous nitrogen at  $T_0 = 298.15$  K and  $p_0 = 70$  MPa. Additionally,  $\alpha$  is the mean thermal expansivity over the interval  $[T_0, T]$ , and  $\beta$  is the compressibility of the cell material. The thermal expansion coefficient of the Invar alloy was determined experimentally via dilatometry at the UK National Physical Laboratory at temperatures between 223 K and 473 K. From these results, the following correlation for the temperature-dependent mean thermal expansion coefficient was determined by Scholz et al.<sup>27</sup>

$$\frac{10^6 \cdot \alpha}{\text{K}^{-1}} = \sum_0^3 a_i (T/\text{K} - 298.15)^i \quad (4)$$

For the mean isothermal compressibility of Invar, Scholz et al.<sup>27</sup> established a correlation based on isothermal bulk modulus values reported by Hausch and Warlimont<sup>39</sup>

$$\frac{\beta}{\text{GPa}^{-1}} = \left( \sum_0^2 b_i (T/\text{K} - 298.15)^i \right)^{-1} \quad (5)$$

The parameters for both correlations are given in Table 2.

**Table 2. Parameters of eq 4 for Mean Thermal Expansion Coefficients and of eq 5 for Mean Isothermal Compressibility<sup>27</sup>**

|       | $i = 0$             | $i = 1$                | $i = 2$                | $i = 3$                |
|-------|---------------------|------------------------|------------------------|------------------------|
| $a_i$ | 1.650               | $8.552 \times 10^{-4}$ | $2.941 \times 10^{-5}$ | $4.397 \times 10^{-8}$ |
| $b_i$ | $1.061 \times 10^2$ | $3.155 \times 10^{-2}$ | $3.722 \times 10^{-4}$ |                        |

Before filling with gas, the vessel and connecting tubing were evacuated. Since the speed of sound in helium differs greatly from that in plausible impurities such as nitrogen and water vapor, impurities have a strong influence on measurements of the speed of sound in helium. Therefore, five filling-evacuation cycles of the vessel and the tubing were performed for both gases before the final gas samples were transferred into the system. For each cycle, the system was filled to a pressure of about 10 MPa with the gas under investigation and then exhausted to vacuum. The helium and nitrogen used are described in Table 3.

**Table 3. Description of the Gas Samples Used for the Speed of Sound Experiments, Where  $x$  Denotes Mole Fraction**

| Gas      | CAS number | Supplier | Purity $x$            | Purification method |
|----------|------------|----------|-----------------------|---------------------|
| helium   | 7440-59-7  | BOC      | 0.99999 <sup>a</sup>  | none                |
| nitrogen | 7727-37-9  | BOC      | 0.999995 <sup>b</sup> | none                |

<sup>a</sup>Impurities (stated by supplier):  $x(\text{N}_2) \leq 5.0 \times 10^{-6}$ ,  $x(\text{H}_2\text{O}) \leq 2.0 \times 10^{-6}$ ,  $x(\text{O}_2) \leq 2.0 \times 10^{-6}$ ,  $x(\text{H}_2) \leq 1.0 \times 10^{-6}$ ,  $x(\text{CO}_2) \leq 0.5 \times 10^{-6}$ , and  $x(\text{C}_x\text{H}_y) \leq 0.5 \times 10^{-6}$ . <sup>b</sup>Impurities (stated by supplier):  $x(\text{H}_2\text{O}) \leq 1.0 \times 10^{-6}$ ,  $x(\text{O}_2) \leq 1.0 \times 10^{-6}$ ,  $x(\text{H}_2) \leq 1.0 \times 10^{-6}$ ,  $[x(\text{CO}) + x(\text{CO}_2)] \leq 1.0 \times 10^{-6}$ , and  $x(\text{C}_x\text{H}_y) \leq 0.5 \times 10^{-6}$ .

The reference EOS of Span et al.<sup>40</sup> was used to calculate the speed of sound in nitrogen. Span et al.<sup>40</sup> state that the uncertainty in the speed of sound at our calibration conditions is 0.6%, which was a conservative estimation made in the absence of validation data. With this high estimated uncertainty, nitrogen would have not been a suitable calibration gas. However, Meier and Kabelac<sup>36</sup> showed by measuring several isotherms from 275 to 400 K and pressures up to 100 MPa that the uncertainty of the EOS is actually much lower. For the isotherm measured at 300 K, close to our calibration temperature of 298.15 K, they report relative deviations from the EOS within  $\pm 0.01\%$ . Due to this reason, the deviations reported by Meier and Kabelac<sup>36</sup> from the nitrogen EOS of about  $\pm 0.01\%$  were assumed as the relative standard uncertainty for the speed of sound  $c_0$  in nitrogen at calibration conditions.

The uncertainties of the measurements were estimated considering the working equation given by Scholz et al.,<sup>27</sup> in which the path difference  $\Delta L$  was eliminated in favor of the time difference  $\Delta t_0$  and speed of sound  $c_0$  in nitrogen at calibration temperature  $T_0$  and pressure  $p_0$ . The uncertainty contribution of the diffraction term was neglected, as the influence of  $\tau$ , in general, is small. The standard uncertainty is given by

$$\begin{aligned} u(c) &= \left[ \left( \left( \frac{\partial c}{\partial c_0} \right) u(c_0) \right)^2 + \left( \left( \frac{\partial c}{\partial T_0} \right) u(T_0) \right)^2 \right. \\ &\quad + \left( \left( \frac{\partial c}{\partial p_0} \right) u(p_0) \right)^2 + \left( \left( \frac{\partial c}{\partial \Delta t_0} \right) u(\Delta t_0) \right)^2 \\ &\quad + \left( \left( \frac{\partial c}{\partial \Delta t} \right) u(\Delta t) \right)^2 + \left( \left( \frac{\partial c}{\partial \alpha} \right) u(\alpha) \right)^2 \\ &\quad \left. + \left( \left( \frac{\partial c}{\partial \beta} \right) u(\beta) \right)^2 + \left( \left( \frac{\partial c}{\partial T} \right) u(T) \right)^2 + \left( \left( \frac{\partial c}{\partial p} \right) u(p) \right)^2 \right]^{0.5} \end{aligned} \quad (6)$$

For the time differences, an amplitude-dependent standard uncertainty was considered, as it was observed that at low pressures (*i.e.*, small acoustic impedances), the weak echo signals influenced the repeatability of the measured time differences. To address this, the standard uncertainty of  $\Delta t$  was related to the amplitude  $A_1$  of the first echo as follows

$$u(\Delta t) = 0.0005 \mu\text{s} + 0.0005 \mu\text{s} \cdot \frac{100 \cdot \text{mV}}{A_1} \quad (7)$$

Due to different acoustic impedances, the amplitude measured depended on the gas under study and the pressure. In nitrogen, an amplitude of 127 mV was measured at a temperature of 298.15 K and a pressure of 30 MPa, while at the same temperature, an amplitude of 665 mV was measured at a pressure of 100 MPa. In helium, the smallest amplitude of 19 mV was measured at a temperature of 348.15 K and a pressure of 15 MPa, while the highest amplitude of 169 mV was measured at a temperature of 273.15 K and a pressure of 100 MPa. Therefore, the influence of the amplitude on the standard uncertainty of  $\Delta t$  was significantly greater for helium than for nitrogen. For the thermal expansion coefficient and

the isothermal compressibility, relative standard uncertainties of about 10 and 1%, respectively, were assumed as reported by Scholz et al.<sup>27</sup> The standard uncertainty in the temperature measurement is 0.015 K.<sup>27</sup> The standard uncertainty of pressure was estimated from the total uncertainty given by the manufacturer (0.05% of full scale) considered as a rectangular distribution. With a divisor of  $\sqrt{3}$ , this leads to a standard uncertainty in pressure of 0.03 MPa.

### 3. RESULTS AND DISCUSSION

**3.1. Calibration Measurements in Nitrogen.** As described above, a one-point calibration was performed with nitrogen gas at  $T_0 = 298.15$  K and  $p_0 = 70$  MPa. By adjusting  $\Delta L_0$ , the deviation of the measurement from the EOS of Span et al.<sup>40</sup> was reduced to zero at that point, yielding  $2\Delta L_0 = 19.6972$  mm. Additional measurements were carried out along the same isotherm at pressures between 30 and 100 MPa. In all cases, a small correction was applied to account for the long vibrational relaxation time of nitrogen, as detailed by Meier and Kabelac.<sup>36</sup> In Figure 2, relative deviations of the

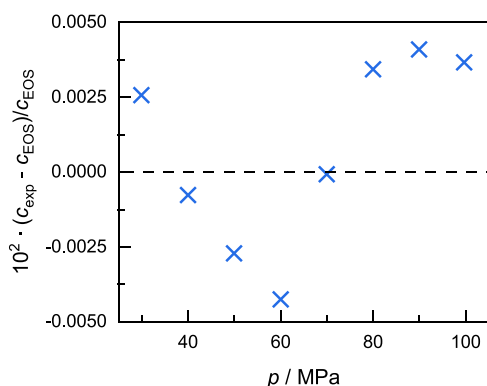


**Figure 2.** Relative deviations of the experimentally determined speed of sound values  $c_{\text{exp}}$  in nitrogen at a temperature of 298.15 K from the values calculated with the EOS (dashed line) of Span et al.<sup>40</sup>

experimentally determined speed of sound values in nitrogen from the values calculated with the EOS of Span et al.<sup>40</sup> are shown. Based on the calibration, the experimental speeds of sound are in excellent agreement with the EOS with all deviations within  $\pm 0.005\%$ .

**3.2. Measurements in Helium.** The speed of sound in helium was measured along five isotherms at temperatures of (273, 298, 323, 348, and 373) K. Each isotherm consisted of ten different pressures, ranging from (15 to 100) MPa. Measurements below 15 MPa could not be analyzed properly, as the echoes were not clearly distinguishable. The experimental speeds of sound are shown as a function of pressure in Figure 3 and listed in Table 4 with the corresponding temperature  $T$ , pressure  $p$ , and expanded uncertainties  $U_c(c)$ . The speeds of sound increase with increasing temperature and increasing pressure consistently. The expanded uncertainties were based on eq 6 with a coverage factor  $k = 2$ . As an example, the uncertainty budget for the measurement at  $T = 323$  K and  $p = 40$  MPa is detailed in Table 5. Since, on the one hand, the uncertainty of the time differences is a function of the signal amplitude according to eq 7 and, on the other hand, the absolute speed of sound values is increasing with pressure, the values of the expanded

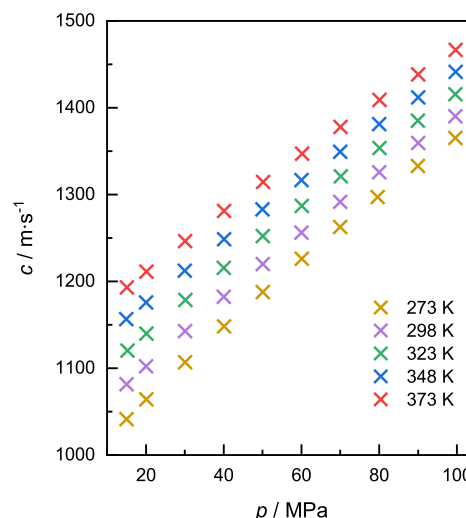


**Figure 3.** Measured speed of sound values in helium at five different temperatures.

uncertainty initially decrease and then increase with increasing pressure.

**3.3. Comparison of Measurements with the Helmholtz Equation of State.** In Figure 4, we compare the experimental speeds of sound with the unpublished EOS of Ortiz Vega et al.<sup>14</sup> as implemented in REFPROP 10 along each isotherm individually. The experimental values are shown with the corresponding relative expanded uncertainty. In addition, we also plot the comprehensive data set reported by Gammon,<sup>15</sup> two data points reported by Kortbeek et al.,<sup>24</sup> and one data point reported by Vidal et al.<sup>22</sup> For the five investigated isotherms, the deviations from the EOS show a consistent trend. Up to pressures of 50 to 60 MPa, the experimental values are in very good agreement with the EOS, with deviations within  $\pm 0.03\%$ , which is within the expanded uncertainty of the measurements. With further pressure increases, negative deviations of increasing magnitude can be observed. The worst deviations, observed at the greatest pressure, improve progressively with increasing temperature from  $-0.26\%$  at  $T = 273$  K to  $-0.15\%$  at  $T = 373$  K.

The data of Gammon,<sup>15</sup> who measured up to 15 MPa, agree very well with the EOS. This is no surprise as this is one of the two primary data sets used for the development of the EOS. But as the data are also in very good agreement with the present results, they can be interpreted as validating the presented work at  $p = 15$  MPa. Vidal et al.<sup>22</sup> reported one data point at  $p = 100$  MPa and  $T = 298$  K, which is also in very good agreement with the present work. Measurements at higher pressure by Vidal et al.<sup>22</sup> also follow this consistent trend (not shown here). The two data points reported by Kortbeek et al.<sup>24</sup> at  $p = 100$  MPa and  $T = (273 \text{ and } 298)$  K, respectively, show also negative deviations from the EOS, but at around  $-0.11\%$ , their values are closer to the calculated values than ours. However, Kortbeek et al.<sup>24</sup> report that the lowest pressure at which they could measure was 130 MPa, and the values reported at 100 MPa were obtained by extrapolation. Hanayama and Kimura,<sup>23</sup> Kimura et al.,<sup>20</sup> and Pitaevskaya and Bilevich<sup>21</sup> reported data in the pressure range up to 100 MPa as well, but the deviations of their data from the EOS range in that pressure regime are between  $-2.1$  and  $+5.5\%$  and show no clear pressure-depending trend, which is the reason why they are not shown in Figure 4. These large

**Table 4. Experimental Speed of Sound Data  $c$  in Helium with Expanded Uncertainties  $U(c)$  with a Coverage Factor of  $k = 2$  at Temperature  $T$  and Pressure  $p$ <sup>a</sup>**

| $T/K$   | $p/\text{MPa}$ | $c/(\text{m}\cdot\text{s}^{-1})$ | $U(c)/(\text{m}\cdot\text{s}^{-1})$ | $T/K$   | $p/\text{MPa}$ | $c/(\text{m}\cdot\text{s}^{-1})$ | $U(c)/(\text{m}\cdot\text{s}^{-1})$ |
|---------|----------------|----------------------------------|-------------------------------------|---------|----------------|----------------------------------|-------------------------------------|
| 273.157 | 14.998         | 1041.55                          | 0.34                                | 323.154 | 60.097         | 1287.27                          | 0.34                                |
| 273.160 | 20.117         | 1064.15                          | 0.32                                | 323.155 | 70.090         | 1321.24                          | 0.35                                |
| 273.160 | 30.100         | 1106.95                          | 0.30                                | 323.155 | 80.055         | 1353.90                          | 0.36                                |
| 273.160 | 40.111         | 1148.36                          | 0.30                                | 323.154 | 89.961         | 1385.49                          | 0.36                                |
| 273.160 | 50.040         | 1187.73                          | 0.30                                | 323.154 | 99.565         | 1415.62                          | 0.35                                |
| 273.162 | 60.063         | 1226.20                          | 0.31                                | 348.135 | 14.943         | 1156.64                          | 0.49                                |
| 273.160 | 69.949         | 1262.85                          | 0.31                                | 348.141 | 20.066         | 1175.85                          | 0.42                                |
| 273.161 | 79.566         | 1297.16                          | 0.32                                | 348.138 | 29.999         | 1212.61                          | 0.34                                |
| 273.161 | 89.988         | 1333.23                          | 0.33                                | 348.138 | 40.077         | 1248.63                          | 0.33                                |
| 273.160 | 99.569         | 1365.46                          | 0.33                                | 348.139 | 49.945         | 1283.11                          | 0.34                                |
| 298.153 | 15.049         | 1081.51                          | 0.39                                | 348.139 | 60.008         | 1316.73                          | 0.34                                |
| 298.153 | 20.053         | 1102.39                          | 0.35                                | 348.137 | 69.999         | 1349.35                          | 0.34                                |
| 298.154 | 30.061         | 1143.06                          | 0.33                                | 348.137 | 80.000         | 1381.46                          | 0.34                                |
| 298.152 | 40.046         | 1182.23                          | 0.33                                | 348.140 | 90.039         | 1412.15                          | 0.35                                |
| 298.151 | 50.016         | 1219.97                          | 0.41                                | 348.142 | 99.657         | 1441.39                          | 0.36                                |
| 298.153 | 59.989         | 1256.45                          | 0.33                                | 373.147 | 15.061         | 1193.40                          | 0.44                                |
| 298.154 | 69.979         | 1291.79                          | 0.34                                | 373.148 | 20.080         | 1211.48                          | 0.43                                |
| 298.152 | 79.978         | 1326.03                          | 0.34                                | 373.148 | 30.068         | 1246.54                          | 0.37                                |
| 298.154 | 90.017         | 1359.44                          | 0.34                                | 373.151 | 40.133         | 1281.26                          | 0.35                                |
| 298.153 | 99.567         | 1390.42                          | 0.35                                | 373.150 | 50.151         | 1314.55                          | 0.35                                |
| 323.153 | 15.234         | 1120.50                          | 0.38                                | 373.150 | 60.131         | 1347.24                          | 0.35                                |
| 323.157 | 20.108         | 1139.91                          | 0.35                                | 373.153 | 70.004         | 1377.99                          | 0.35                                |
| 323.155 | 30.113         | 1178.65                          | 0.33                                | 373.150 | 80.113         | 1409.27                          | 0.36                                |
| 323.154 | 40.056         | 1215.84                          | 0.32                                | 373.153 | 89.994         | 1438.45                          | 0.36                                |
| 323.153 | 50.060         | 1252.14                          | 0.35                                | 373.146 | 99.653         | 1466.72                          | 0.37                                |

<sup>a</sup>Standard uncertainties are  $u(T) = 0.015$  K and  $u(p) = 0.03$  MPa.**Table 5. Uncertainty Budget for the Speed of Sound in Helium at a Pressure of  $p = 40.056$  MPa and a Temperature of  $T = 323.154$  K, in Which  $c_{0,\text{EOS}}$  is the Calculated Speed of Sound in Nitrogen at Calibration Conditions,  $\Delta t_0$  is the Time Difference at Calibration Conditions,  $\Delta t$  is the Time Difference at Measurement Conditions,  $\alpha$  is the Mean Thermal Expansion Coefficient over the Interval  $[T_0, T]$ , and  $\beta$  is the Isothermal Compressibility at Measurement Conditions<sup>a</sup>**

| Quantity           | Value                                  | Standard uncertainty                   | Sensitivity coefficient                                      | Uncertainty contribution           |
|--------------------|----------------------------------------|----------------------------------------|--------------------------------------------------------------|------------------------------------|
| $c_{0,\text{EOS}}$ | 707.34 $\text{m}\cdot\text{s}^{-1}$    | 0.0707 $\text{m}\cdot\text{s}^{-1}$    | 1.719                                                        | 0.122 $\text{m}\cdot\text{s}^{-1}$ |
| $\Delta t_0$       | 27.8421 $\mu\text{s}$                  | 0.0005 $\mu\text{s}$                   | 43.664 $\text{m}\cdot\text{s}^{-1}\cdot\mu\text{s}^{-1}$     | 0.022 $\text{m}\cdot\text{s}^{-1}$ |
| $T_0$              | 298.152 K                              | 0.015 K                                | 0.069 $\text{m}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$         | 0.001 $\text{m}\cdot\text{s}^{-1}$ |
| $p_0$              | 69.961 MPa                             | 0.03 MPa                               | 1.43 $\text{m}\cdot\text{s}^{-1}\cdot\text{MPa}^{-1}$        | 0.041 $\text{m}\cdot\text{s}^{-1}$ |
| $\Delta t$         | 16.2016 $\mu\text{s}$                  | 0.0012 $\mu\text{s}$                   | 75.036 $\text{m}\cdot\text{s}^{-1}\cdot\mu\text{s}^{-1}$     | 0.091 $\text{m}\cdot\text{s}^{-1}$ |
| $\alpha$           | $1.65 \times 10^{-6} \text{ K}^{-1}$   | $1.65 \times 10^{-7} \text{ K}^{-1}$   | $3.04 \times 10^4 \text{ m}\cdot\text{s}^{-1}\cdot\text{K}$  | 0.005 $\text{m}\cdot\text{s}^{-1}$ |
| $\beta$            | $9.33 \times 10^{-6} \text{ MPa}^{-1}$ | $9.33 \times 10^{-8} \text{ MPa}^{-1}$ | $1.2 \times 10^4 \text{ m}\cdot\text{s}^{-1}\cdot\text{MPa}$ | 0.001 $\text{m}\cdot\text{s}^{-1}$ |
| $T$                | 323.154 K                              | 0.015 K                                | 0.199 $\text{m}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$         | 0.003 $\text{m}\cdot\text{s}^{-1}$ |
| $p$                | 40.056 MPa                             | 0.03 MPa                               | 1.06 $\text{m}\cdot\text{s}^{-1}\cdot\text{MPa}^{-1}$        | 0.031 $\text{m}\cdot\text{s}^{-1}$ |

<sup>a</sup>Combined expanded uncertainty ( $k = 2$ ) of  $c = 0.32 \text{ m}\cdot\text{s}^{-1}$ .

deviations might also be a reason why the data sets were not considered for the development of the EOS.

**3.4. Comparison with Data from *Ab Initio* Acoustic Virial Coefficients.** The EOS of helium is amenable to theoretical evaluation based on *ab initio* interatomic potential-energy functions. Starting from such interatomic potentials, one can evaluate the temperature-dependent virial coefficients  $B_n$  in the virial EOS (VEOS)

$$Z = (p/\rho RT) = 1 + B_2\rho + B_3\rho^2 + B_4\rho^3 + \dots \quad (8)$$

Here,  $Z$  is the compressibility factor,  $\rho$  is the molar density, and  $B_n$  is the  $n^{\text{th}}$  temperature-dependent virial coefficient. The second virial coefficient  $B_2$  rigorously depends only upon the interatomic pair-potential-energy function, while the higher-order virial coefficients involve many-body interactions and

require non-additive corrections to the interatomic potential energy. The virial EOS leads in turn to a similar power-series expansion for the “acoustic compressibility factor”  $Z_a$  as follows

$$Z_a = \left( \frac{Mc^2}{\gamma_0 RT} \right) = 1 + \Omega_2\rho + \Omega_3\rho^2 + \Omega_4\rho^3 + \dots \quad (9)$$

Here,  $\gamma_0 = 5/3$ , and  $\Omega_n$  is the  $n^{\text{th}}$  acoustic virial coefficient, which is related to the corresponding, and all lower order, ordinary virial coefficients  $B_n$  and their first two temperature derivatives. The EOS in this form has been studied in detail by Gokul et al.<sup>41</sup> on the basis of the *ab initio* pair potential of Przybytek et al.<sup>42,43</sup> and the non-additive three-body correction of Cencek et al.<sup>44</sup> Gokul et al.<sup>41</sup> present precise calculations of the acoustic virial coefficient up to order  $n = 7$ , estimates of the

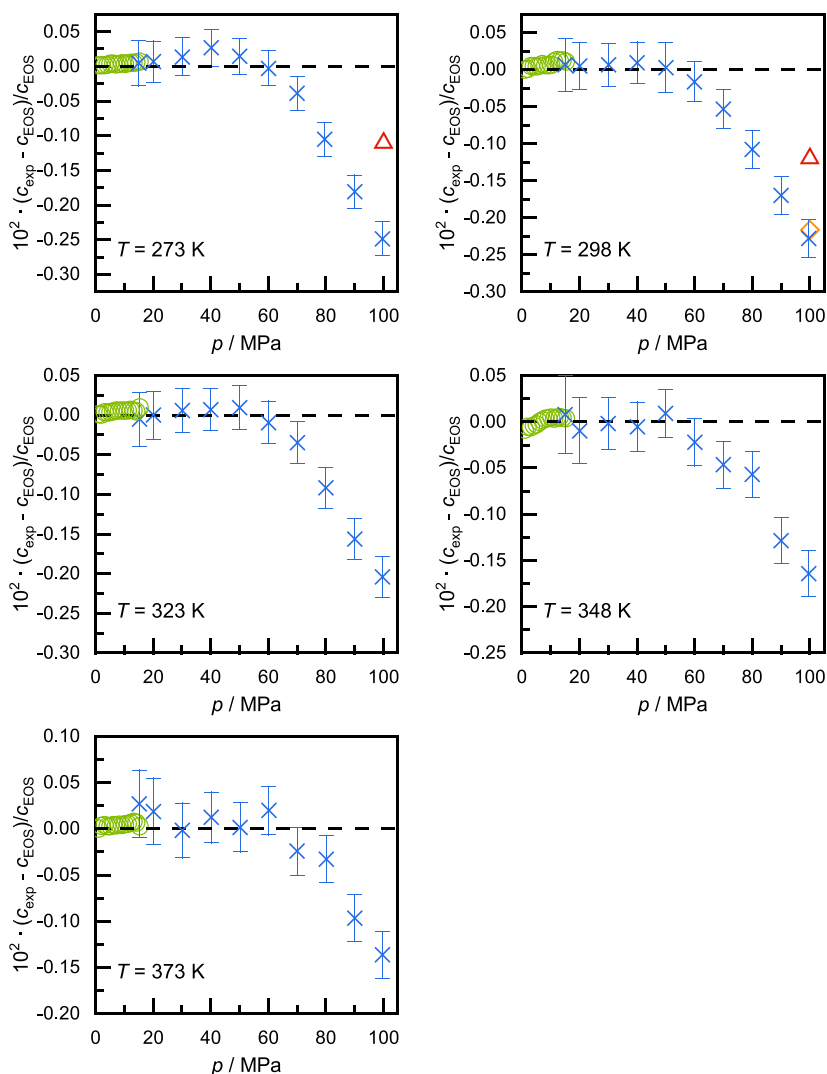


**Figure 4.** Relative deviations of the experimentally determined speeds of sound  $c_{\text{exp}}$  in helium at five different temperatures from the values calculated with the unpublished EOS of Ortiz Vega et al. (dashed line):<sup>14</sup> ×, this work; ○, Gammon;<sup>15</sup> ◇, Vidal et al.,<sup>22</sup> △, Kortbeek et al.<sup>24</sup>

statistical uncertainty of each coefficient, and correlations of both  $B_n$  and  $\Omega_n$  as functions of temperature.

To apply this EOS, we first solved eq 8 for the molar density corresponding to the experimental temperatures and pressure and then used eq 9 to evaluate the speed of sound using, in both equations, coefficients up to  $n = 7$  as correlated by Gokul et al.<sup>41</sup> We did not make use of the pressure-series expansion of  $Z_a$  reported by Gokul et al.<sup>41</sup> because it does not appear to converge at the highest pressures studied in this work. On the other hand, both eqs 8 and 9 appear to converge to this order to within 0.01%, as judged by the difference between truncation after  $n = 6$  and after  $n = 7$ . Furthermore, the uncertainties of the virial coefficients as reported by Gokul et al.<sup>41</sup> give rise to uncertainties in  $Z$  or  $Z_a$  which are smaller than 0.015%. Figure 5 compares our experimental speeds of sound with those calculated from the virial EOS and, remarkably, the agreement is within the experimental uncertainty over the entire pressure range. Also plotted in Figure 5 are the values at  $p = 100$  MPa reported by Vidal et al.<sup>22</sup> and by Kortbeek et al.;<sup>24</sup> the former also showing excellent agreement with the acoustic virial EOS.

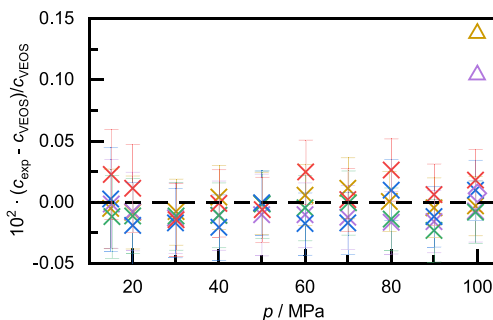


**Figure 5.** Relative deviations of the experimentally determined speeds of sound  $c_{\text{exp}}$  in helium from the values calculated with the *ab initio* VEOS by Gokul et al. (dashed line).<sup>41</sup> ×, this work; ◇, Vidal et al.,<sup>22</sup> △, Kortbeek et al.<sup>24</sup> Colors denote temperature: red = 373 K; blue = 348 K; green = 323 K; purple = 298 K; brown = 273 K.

#### 4. CONCLUSIONS

The speed of sound in gaseous helium was measured along five isotherms from (273 to 373) K and in a pressure range from (15 to 100) MPa using the dual-path pulse-echo technique. This new data set fills a significant gap in the database of

thermodynamic properties of helium. The expanded uncertainty of the speed of sound measurements ranges from (0.30 to 0.49) m·s<sup>-1</sup>, fractionally (0.02 to 0.04)%. At pressures up to 50 MPa, the data agree within the experimental uncertainty with the *de facto* reference EOS, the unpublished equation of Ortiz Vega et al.,<sup>14</sup> implemented in common thermophysical property software such as REFPROP 10 and TREND 5.0. At higher pressures, negative deviations of increasing magnitude are consistently observed, with the worst case being a relative deviation of -0.26% at  $T = 273$  K and  $p = 100$  MPa. Since Ortiz Vega et al.<sup>14</sup> considered data only up to 15 MPa, the EOS was not previously validated for higher pressures. It can now be concluded that the uncertainty of the Ortiz Vega et al. EOS at pressures above 60 MPa is significantly greater than the estimates of 0.01% given in REFPROP 10 and TREND 5.0. The new experimental data may be an important contribution in the future to the optimization of a new wide-ranging EOS for helium. Remarkably, the present results agree with the predictions of the virial EOS, with the ordinary and acoustic virial coefficients reported by Gokul et al.,<sup>41</sup> at all investigated state points.

## AUTHOR INFORMATION

### Corresponding Author

J. P. Martin Trusler – Department of Chemical Engineering,  
Imperial College London, London SW7 2AZ, U.K.;  
orcid.org/0000-0002-6403-2488; Email: m.trusler@imperial.ac.uk

### Author

Carsten Wedler – Department of Chemical Engineering,  
Imperial College London, London SW7 2AZ, U.K.;  
orcid.org/0000-0002-8275-912X

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acs.jced.3c00083>

### Notes

The authors declare no competing financial interest.

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