

# Speed of sound of oxygen in supercritical states up to 500 K and 100 MPa

Frithjof H. Dubberke, Markus Riepold, Elmar Baumhögger, and Jadran Vrabec\*

*Thermodynamics and Energy Technology, University of Paderborn, Germany*

E-mail: jadran.vrabec@uni-paderborn.de

Phone: +49-5251/60-2421. Fax: +49-5251/60-3522

## Abstract

Oxygen is the second-most abundant element in the earth's atmosphere and plays an important role in various engineering applications. The precise knowledge of its thermophysical properties is thus important. As a fully fledged thermodynamic property, the speed of sound substantially contributes to the development and parameterization of equations of state. This work presents experimental speed of sound data for oxygen measured with an apparatus that is based on the pulse-echo technique with a double path-length. When working with pure oxygen at high temperatures and pressures, tight safety requirements have to be met, limiting the present measurements to 500 K and 100 MPa.

## Introduction

For optimizing industrial processes and for scientific applications the precise knowledge of thermodynamic properties is crucial. Oxygen, which is behind nitrogen the second-most abundant element in the earth's atmosphere, plays a major role in many industrial applications. The most accurate equation of state (EOS) for oxygen was established in the year 1985

by Schmidt and Wagner.<sup>1</sup> Highly accurate thermodynamic property data from experimental measurements are the basis for developing EOS<sup>2</sup> and speed of sound data are well suited for this purpose. However, there is a lack of speed of sound data in the supercritical region at elevated temperatures and moderate pressures, as illustrated in Fig. 1.

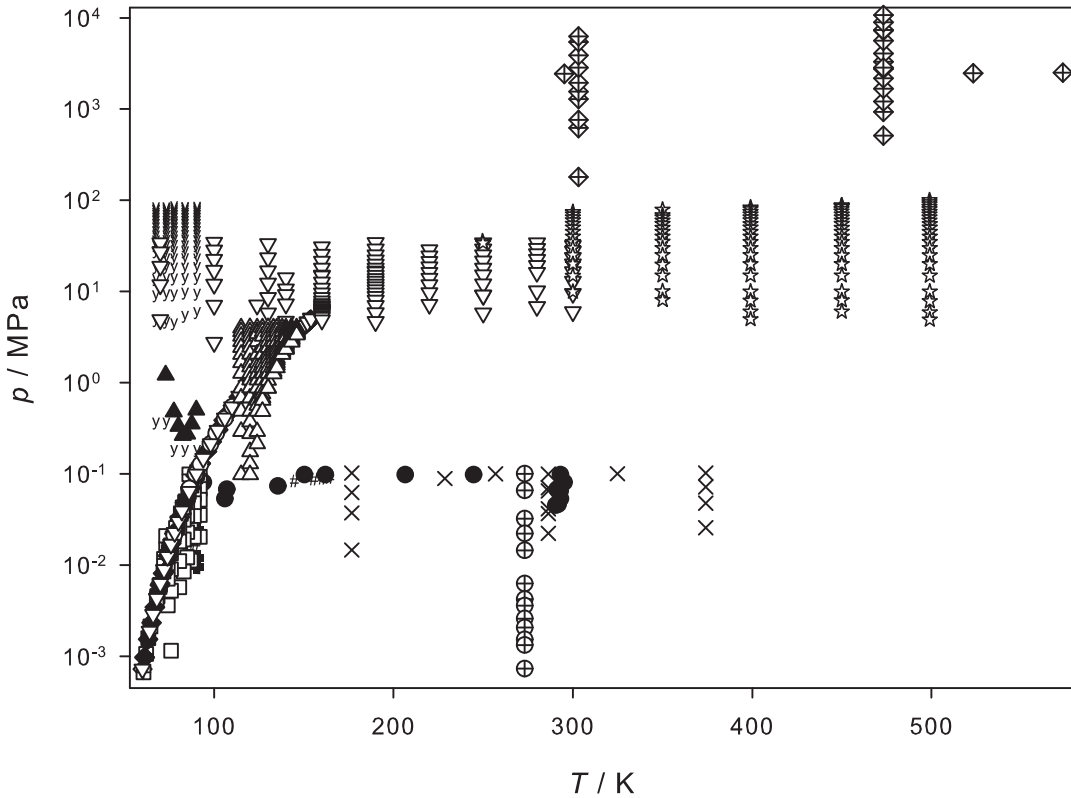


Figure 1: Experimental speed of sound data for oxygen: (●) Cook;<sup>3</sup> (#) Keesom et al.;<sup>4</sup> (▼) Bär;<sup>5</sup> (⊕) van Itterbeek and Mariëns;<sup>6</sup> (×) van Itterbeek and Mariëns;<sup>7</sup> (□) van Itterbeek and van Paemel;<sup>8</sup> (■) Liepmann;<sup>9</sup> (◇) Galt;<sup>10</sup> (▲) van Itterbeek and de Bock;<sup>11</sup> (⊕) Boyer;<sup>12</sup> (⊞) Verhaegen;<sup>13</sup> (y) van Itterbeek and van Dael;<sup>14</sup> (◆) van Dael et al.;<sup>15</sup> (○) Blagoi et al.;<sup>16</sup> (▽) Straty and Younglove;<sup>17</sup> (△) Baidakov and Kaverin;<sup>18</sup> (⊞) Abramson et al.;<sup>19</sup> (☆) this work.

Experiments with oxygen have been carried out by numerous authors and date back to the early 1900s, when Cook<sup>3</sup> used Kundt's tube<sup>20</sup> for speed of sound measurements of oxygen and air. First ultra-sonic measurements were accomplished in the 1930s, primarily in low pressure regions. Van Itterbeek and co-workers<sup>4,6-8,11,14,15</sup> established an acoustic interferometer,

enabling for measurements with uncertainties of about 0.1%. In 1938, Liepmann<sup>9</sup> determined data for liquid oxygen using a light diffraction method for measurements at low temperatures. In the middle of that century, Galt,<sup>10</sup> Boyer<sup>12</sup> and Verhaegen<sup>13</sup> contributed further data for low temperature and pressure regions. In 1962, van Itterbeek and van Dael<sup>14</sup> used the pulse-echo method in the liquid region between 64 K and 91 K and pressures of up to 92 MPa. Baidakov and Kaverin<sup>18</sup> determined data with an uncertainty of 0.17 % for superheated liquid oxygen for the first time in 1989, employing the pulse-echo technique by using an acoustic cell made out of glass. In 1999, Abramson et al.<sup>19</sup> reached extremely high pressures of up to 12.6 GPa with a diamond-anvil cell, attaining an overall uncertainty of 2 % in their measurements. An extensive study on the speed of sound of compressed liquid oxygen was presented by Straty and Younglove<sup>17</sup> in 1973, employing the pulse-echo technique. An overview of these data is given in Fig. 1. The present work follows up on these measurements in a poorly sampled region, i.e. for temperatures between 300 K and 500 K and pressures between 40 MPa and 100 MPa. This region intentionally overlaps for one state point at 250 K and 34 MPa and for the 300 K isotherm over a pressure range from 10 MPa to 32 MPa with data by Straty and Younglove,<sup>17</sup> cf. Fig. 2.

Speed of sound measurements of compressed oxygen in the supercritical state over a temperature range from 300 K to 500 K and a pressure of up to 100 MPa were carried out with the pulse-echo technique.<sup>21</sup> The measurement principle was based on a sample cell that has two known propagation path lengths  $l_1$  and  $l_2$ , where  $l_2 > l_1$ .<sup>22</sup> By emitting a modulated high frequency wave burst with a piezoelectric quartz crystal with a resonance frequency of 8 MHz, which was positioned between two reflectors in the fluid, the speed of sound  $c$  was determined by the time measurement of the wave propagation through the fluid. Applying a Fourier Transformation based digital filter on the sampled acoustic wave signals increased their signal-to-noise ratio and enhanced their time and amplitude resolutions, improving the overall measurement accuracy.<sup>23</sup> In addition, burst design led to technical advantages for determining the propagation time due to the associated conditioning of the echo. A

complete description of the method, apparatus and discussion of uncertainties has been published in preceding work.<sup>24,25</sup>

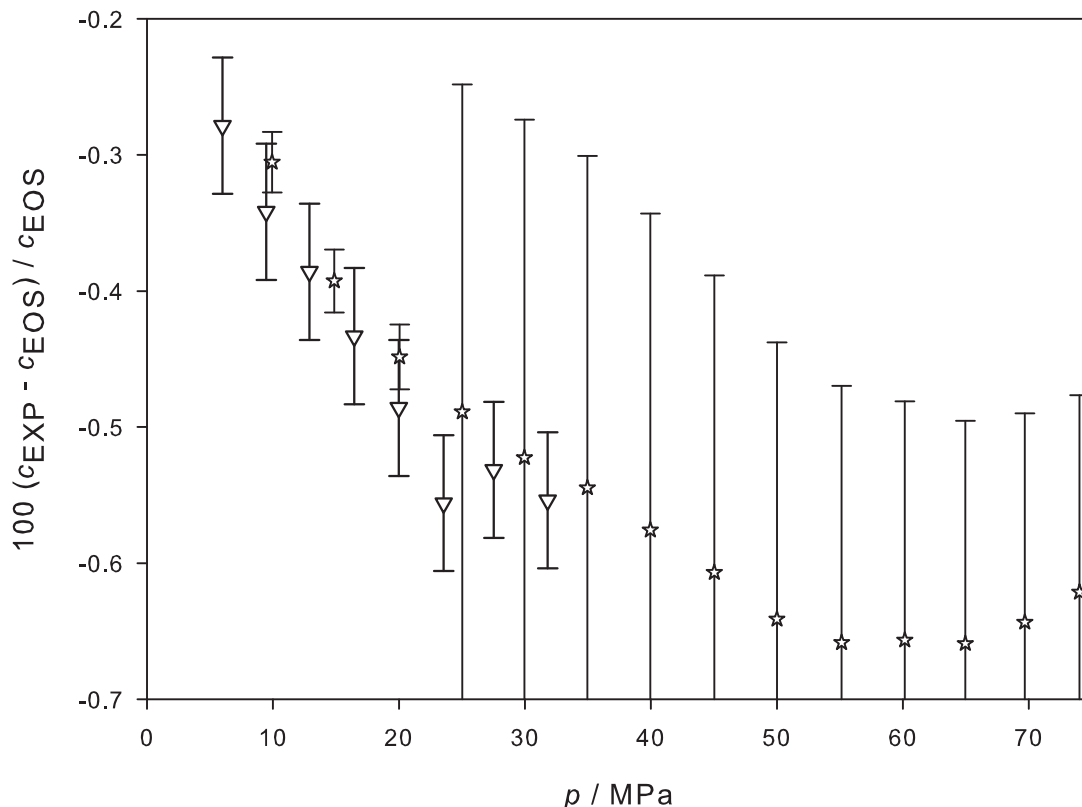


Figure 2: Comparison of speed of sound data for oxygen at 300 K measured by Straty and Younglove<sup>17</sup> ( $\nabla$ ) and in the present work ( $\star$ ) with the equation of state (EOS) by Schmidt and Wagner.<sup>1</sup>

## Safety requirements for handling oxygen

When working with pure oxygen, especially at high temperatures and pressures, tight safety requirements have to be met because it supports combustion and corrosion. Being highly oxidizing, it reacts vigorously with combustible materials and enhances fire or explosion, liberating large amounts of energy in a short time. A chemical reaction in an oxygen environment takes place, if the activation energy (i.e. ignition temperature) of a material is

exceeded. To prevent temperature peaks by adiabatic pressure surges, high fluid velocities through valves etc. of the apparatus should be avoided. Therefore, charging and discharging the measuring cell with oxygen through the piping system was done here very gently. Furthermore, the apparatus had to be free of welding beads and swarfs due to their sensitivity to pressure surges.<sup>26-28</sup>

The technical norm DIN EN 1797 introduces a method for testing the behavior of materials exposed to pressure surges, which can be caused by adiabatic compression or high gas velocities in pipes or components According to the recommendation BGR 500,<sup>26</sup> which demands an appropriate steel alloy with an accumulated mass fraction of chrome and nickel above 22%, the measurement cell was made out of highly corrosion resistant stainless steel (1.4571) and the cylindrical pressure vessel (sealed with a copper gasket) out of highly tensile steel (1.4462) that are both suitable for applications with pure oxygen

Pure copper has an ignition temperature of 1338 K in pure oxygen at 70 MPa.<sup>29</sup> It is even harder to ignite than stainless steel<sup>30</sup> and is recommended in the literature as "particularly useful for resisting ignition by particle impact and therefore can be used in high-velocity gas applications for which burn-resistant alloys are required".<sup>28</sup>

The piezoelectric quartz crystal was connected by circular gold electrodes that do not hold any risks. The teflon coated cables were mechanically connected to the gold electrodes and on the other end soldered, without using any flux, to the electrical feed through.<sup>24</sup> Upon combustion even small amounts of material may liberate large quantities of energy, resulting into an increasing temperature. This may lead to a chain reaction if the ignition temperature of other materials is attained. Thus, the lowest ignition temperature of all materials in the apparatus must not be exceeded Before use, the apparatus was very carefully cleaned and freed from impurities, especially of oily and greasy contaminants, which can induce a high risk due to their low ignition temperature.<sup>26,28</sup>

Before assembling all internal surfaces of the piping system including valves, both pressure sensors and the pressure cylinder were cleaned with acetone. After assembling, the system

was evacuated and then flushed about five times with argon at a temperature of 400 K. After a final evacuation, the system was flushed with oxygen for about one hour to minimize contamination by argon.

## Results and discussion

The measuring cell was filled at low temperatures of around 250 K, closed and then heated up to each studied isotherm. This isochoric pressurizing has a low risk of an increase of temperature through adiabatic compression by a feed pump or by a pressure surge in the piping system. Measurements were carried out from high to low pressure by releasing fluid to the ambient through a valve. Below a pressure of 5 MPa, measurements were not feasible due to the usual limitations of the pulse-echo technique, such as acoustic impedance and attenuation. These effects predominantly play a role in low density fluids, i.e., gases up to the critical region and other highly attenuating liquids, and impede the readability of the echoes due to their distortion, temporal extension and low amplitude.<sup>25</sup>

The first measurement was performed for a data point at 250 K and 34 MPa and showed a good agreement in a range of 0.07 % with the data by Straty and Younglove,<sup>17</sup> which is within the stated uncertainty. The overall uncertainty of the temperature measurement with a Pt 100 thermometer (Rössel Messtechnik R.M-type) was less than  $u_{c,\Delta T} = 30$  mK. The pressure was measured with two transducers (Honeywell TJE), one with a measuring range from 0 to 20 MPa and the second one with a measuring range up to 200 MPa. The first one had an uncertainty of  $\pm 0.05$  % and the second one of  $\pm 0.1$  % with respect to their full scale and therefore had a maximum absolute uncertainty of  $\pm 0.2$  MPa above 20 MPa, which had the largest impact at low temperatures. This is a consequence of the pressure uncertainty, combined with the high isothermal compressibility of the fluid at such thermodynamic states. The propagation path lengths were referenced at the two isotherms 300 K and 350 K up to a pressure of 40 MPa with pure argon (cf. table 1.) using values calculated from the EOS

by Tegeler et al.<sup>31</sup> with an uncertainty  $u_{\text{EOS}} = 0.02\%$ . Here, the temperature was measured with the same Pt 100 thermometer which was used during the present oxygen measurements and the pressure was measured with a dead weight tester (DH-Budenberg 580 EHX) with an overall absolute uncertainty  $u_{c,\Delta p,\text{REF}} = 0.02\%$ .

Table 1: Sample table.

<i>Chemical Name</i>	<i>Source</i>	<i>Impurity</i>	<i>Purification Method</i>
Argon	Air Liquide	≤ 10 ppm	none
Oxygen	Air Liquide	≤ 15 ppm	none

According to the error propagation law, the combined speed of sound measurement uncertainty  $u_c$  is composed of the relevant contributions due to uncertainties of temperature (in this case twice, i.e. for referencing and measuring) and pressure measurements, as well as the uncertainties of the referencing procedure

$$u_c = \sqrt{2 \cdot (u_{c,\Delta T})^2 + (u_{c,\Delta p})^2 + (u_{\text{EOS}})^2 + (u_{c,\Delta p,\text{REF}})^2}. \quad (1)$$

The uncertainty of the operation procedure was limited by the internal time reference of the function generator and was thus neglected. Likewise the uncertainty of the very low impurity of oxygen (cf. table 1.) was not considered. Numerical experimental data together with their uncertainties are listed in table 2.

## Conclusion

The speed of sound of oxygen was measured in the supercritical region along five isotherms from 300 K to 500 K and from somewhat above 5 MPa up to 100 MPa. The measured speed of sound data for oxygen were compared with the EOS by Schmidt and Wagner.<sup>1</sup> The uncertainties of the EOS which is valid in the temperature range from the triple point to

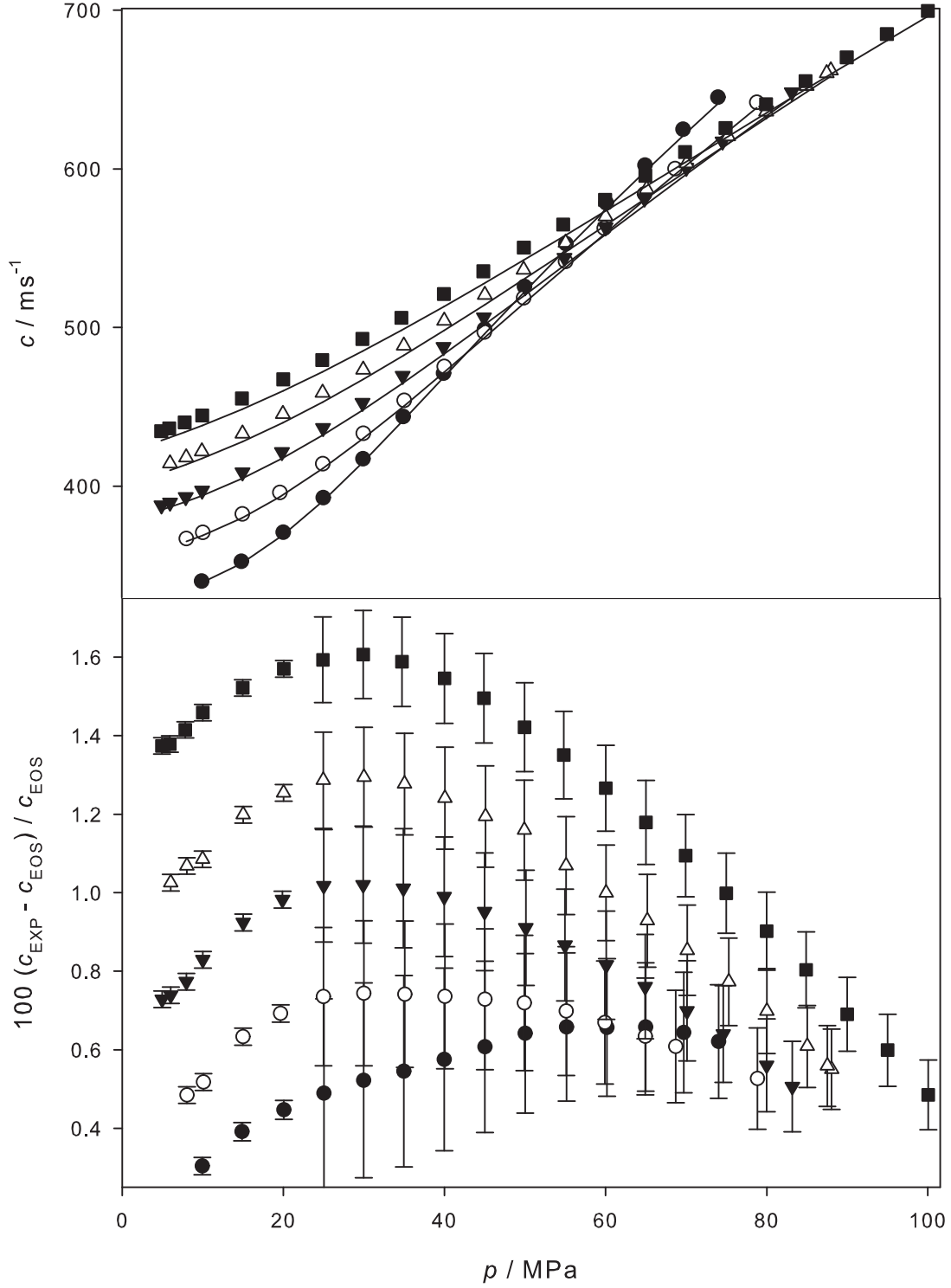


Figure 3: Absolute values (top) and deviations (bottom) of present experimental speed of sound data from the equation of state (EOS) for oxygen by Schmidt and Wagner<sup>1</sup> at (●) 300 K, (○) 350 K, (▼) 400 K, (△) 450 K and (■) 500 K.



300 K and a pressure of up to 80 MPa were stated as 1% for the speed of sound, except for the critical region. The present measurements confirm this uncertainty and show that for temperatures above 400 K the maximum deviation increases to about 1.6 %, cf. Fig. 3.

Steeper slopes of the isotherms at lower temperatures for the speed of sound as a function of pressure in the supercritical region can also be observed for other diatomic fluids like nitrogen (measurements by Costa Gomez et al.<sup>32</sup>) or hydrogen (equation of state by Leachman et al.<sup>33</sup>) at comparable states (cf. Fig. 3 (top)). Due to the large contribution of the pressure uncertainty (for measurements above 20 MPa around 95 % and below 20 MPa around 40 %) to the overall uncertainty,  $u_c$  has its maximum of almost 0.25 % for the data point at 300 K and 30 MPa, cf. Fig. 3 (bottom).

This work covered a wide range of temperature and pressure in the supercritical state for which no experimental data were available for oxygen. The present results show that the pulse-echo technique is a reliable and accurate method for the measurement of the speed of sound of supercritical oxygen.

Table 2: Experimental data for the speed of sound of oxygen

$T$ [K]	$p$ [MPa]	$c$ [m/s]	$\pm u_c$ [m/s]	$T$ [K]	$p$ [MPa]	$c$ [m/s]	$\pm u_c$ [m/s]
299.997	74.03	645.07	0.93	399.090	7.95	393.26	0.08
299.966	69.69	624.95	0.95	399.091	6.02	389.77	0.08
299.966	64.96	602.28	0.98	399.092	4.96	388.03	0.08
299.968	60.16	578.47	1.01				
299.966	55.14	552.86	1.04	449.950	88.05	662.01	0.67
299.966	50.01	525.82	1.06	449.794	87.52	660.32	0.68
299.967	45.03	498.92	1.08	449.883	85.02	652.33	0.68
299.969	39.96	471.20	1.09	449.867	80.01	636.12	0.68
299.972	34.96	443.87	1.08	449.877	75.27	620.61	0.69
299.971	29.96	417.33	1.03	449.887	70.12	603.58	0.69
299.970	25.03	392.82	0.94	449.888	65.18	587.16	0.69
299.969	20.05	370.99	0.09	449.896	60.07	570.12	0.69
299.965	14.86	352.65	0.08	449.896	55.09	553.54	0.68
299.967	9.92	340.22	0.08	449.939	49.91	536.52	0.67
				449.940	45.09	520.58	0.66
349.976	78.85	641.85	0.82	449.934	40.05	504.35	0.65
349.987	68.69	600.07	0.85	449.934	35.03	488.60	0.62
350.030	64.93	584.11	0.86	449.935	30.00	473.40	0.59
349.988	59.91	562.59	0.88	449.938	24.94	458.85	0.56
349.985	55.11	541.66	0.88	449.943	20.01	445.60	0.09
349.983	49.90	518.73	0.89	449.944	15.00	433.26	0.09
349.986	45.02	497.15	0.88	449.936	9.97	422.01	0.09
350.033	40.05	475.39	0.87	449.948	8.01	418.16	0.09
349.987	35.08	454.09	0.84	449.941	6.01	414.33	0.09
349.977	29.99	433.29	0.79				
349.988	24.98	414.20	0.72	498.908	100.06	699.53	0.62
349.988	19.64	396.03	0.09	498.901	95.00	684.96	0.62
349.990	14.98	382.53	0.08	498.906	90.00	670.28	0.63
349.988	10.07	370.90	0.08	498.925	84.89	655.27	0.63
349.978	8.03	367.01	0.08	498.918	79.99	640.74	0.63
				498.908	74.96	625.69	0.63
399.051	83.18	648.15	0.74	498.833	69.94	610.55	0.63
399.066	79.99	636.78	0.75	498.895	65.00	595.63	0.63
399.072	74.59	617.20	0.76	498.888	60.01	580.54	0.63
399.083	70.10	600.65	0.76	499.030	54.81	564.89	0.62
399.082	64.90	581.28	0.77	499.026	49.93	550.29	0.61
399.077	60.07	563.14	0.77	499.004	44.90	535.41	0.60
399.080	54.97	543.88	0.77	498.990	40.01	521.13	0.59
399.086	50.09	525.43	0.76	499.000	34.73	506.11	0.57
399.083	44.98	506.29	0.75	498.999	29.91	492.81	0.54
399.081	39.97	487.82	0.73	499.014	24.90	479.52	0.52
399.084	34.89	469.60	0.71	499.037	20.07	467.39	0.10
399.089	29.90	452.47	0.67	499.016	14.94	455.31	0.09
399.092	25.01	436.72	0.62	498.943	10.00	444.64	0.09
399.064	19.90	421.58	0.09	499.026	7.82	440.23	0.09
399.095	15.01	408.72	0.09	499.031	5.91	436.52	0.09
399.109	9.98	397.34	0.08	499.027	4.92	434.71	0.09

Standard uncertainties  $u$  are  $u(T) = 0.03$  K,  $u(p) = 0.2$  MPa for  $p \geq 20$  MPa and  $u(p) = 0.01$  MPa for  $p \leq 20$  MPa where  $u(p)$  contributed around 95 % above 20 MPa and around 40 % below 20 MPa to the combined uncertainty  $u_c$ .

## Acknowledgement

The authors thank Christian Binder, Thomas Kasch and Siegfried Lehné of the Bundesamt für Materialforschung (BAM) in Berlin for consultancy about safety issues with respect to pure oxygen.

## Literature Cited

- (1) Schmidt, R.; Wagner, W. A New Form of the Equation of State for Pure Substances and its Application to Oxygen. *Fluid Phase Equilib.* **1985**, *19*, 175–200.
- (2) Span, R. *Multiparameter Equations of State: An accurate Source of Thermodynamic Property Data*; Springer, Berlin, 2000.
- (3) Cook, S. R. On the velocity of sound in gases, and the ratio of the specific heats, at the temperature of liquid air. *Phys. Rev. (Series I)* **1906**, *23*, 212–237.
- (4) Keesom, W. H.; van Itterbeek, A.; Lammeren, J. A. Measurements about the velocity of sound in oxygen gas. *Commun. Phys. Lab. Leiden* **1931**, *216*, 996–1003.
- (5) Bär, R. Velocity of sound in liquid oxygen. *Nature* **1935**, *135*, 153.
- (6) van Itterbeek, A.; Mariëns, P. Measurement with ultra-sonics on the velocity and absorption of sound at ordinary and at low temperatures. *Physica* **1937**, *4*, 207–215.
- (7) van Itterbeek, A.; Mariëns, P. Measurements on the velocity and absorption of sound in various gases between +100°C and –100°C - Influence of pressure on the absorption. *Physica* **1937**, *4*, 609–616.
- (8) van Itterbeek, A.; van Paemel, O. Measurements on the velocity of sound as a function of pressure in oxygen gas at liquid oxygen temperatures. Calculation of the second virial coefficient and the specific heats. *Physica* **1938**, *5*, 593–604.

- (9) Liepmann, H. W. Die Schallgeschwindigkeit in flüssigem Sauerstoff als Funktion der Siedetemperatur bei Frequenzen von 7.5 und  $1,5 \times 10^6$  Hz. *Helv. Phys. Acta* **1938**, *11*, 381–396.
- (10) Galt, J. K. Sound absorption and velocity in liquefied argon, oxygen, nitrogen, and hydrogen. *Technical report, Massachusetts Institute of Technology* **1947**, *46*.
- (11) van Itterbeek, A.; de Bock, A. Velocity of sound in liquid oxygen. *Physica* **1948**, *14*, 542–544.
- (12) Boyer, R. Velocity of sound in liquid oxygen. *J. Acoust. Soc. Am.* **1950**, *23*, 176–178.
- (13) Verhaegen, L. Metingen over de voortplantingssnelheid van het geluid in enkele vloeibaar gemaakte gassen. *Verhandelingen van de KVAB voor Wetenschappen* **1952**, *38*, 1–65.
- (14) van Itterbeek, A.; van Dael, W. Velocity of sound in liquid oxygen and liquid nitrogen as a function of temperature and pressure. *Physica* **1962**, *28*, 861–870.
- (15) van Dael, W.; van Itterbeek, A.; Cops, A.; Thoen, J. Sound velocity measurements in liquid argon, oxygen and nitrogen. *Physica* **1966**, *32*, 611–620.
- (16) Blagoi, Y. P.; Butko, A. E.; Mikhailenko, S. A.; Yakuba, V. V. Sound velocity in liquid nitrogen, oxygen and argon in the region above normal boiling temperature. *Akusticheskij Zhurnal* **1966**, *12*, 405–410.
- (17) Straty, G. C.; Younglove, B. A. Velocity of sound in saturated and compressed fluid oxygen. *J. Chem. Thermodyn.* **1973**, *5*, 305–312.
- (18) Baidakov, V. G.; Kaverin, A. M. Ultrasonic speed in superheated liquid oxygen. *J. Chem. Thermodyn.* **1989**, *21*, 1159–1167.
- (19) Abramson, E. H.; Slutsky, L. J.; Harrell, M. D.; Brown, J. M. Speed of sound and equation of state for fluid oxygen to 10 GPa. *J. Chem. Phys.* **1999**, *110*, 10493–10497.

- (20) Kundt, A. Ueber eine neue Art akustischer Staubfiguren und über die Anwendung derselben zur Bestimmung der Schallgeschwindigkeit in festen Körpern und Gasen. *Annalen der Physik und Chemie* **1866**, *127*, 497–523.
- (21) Kortbeek, P.; Muringer, M.; Trappeniers, N.; Biswas, S. Apparatus for sound velocity measurements in gases up to 10 kbar: Experimental data for argon. *Rev. Sci. Instrum.* **1985**, *56*, 1269–1273.
- (22) Lin, C.-W.; Trusler, J. P. M. The speed of sound and derived thermodynamic properties of pure water at temperatures between (253 and 473) K and at pressures up to 400 MPa. *J. Chem. Phys.* **2012**, *136*, 094511.
- (23) Benedetto, G.; Gavioso, R.; Albo, P. G.; Lago, S.; Ripa, D. M.; Spagnolo, R. Speed of sound in pure water at temperatures between 274 and 394 K and at pressures up to 90 MPa. *Int. J. Thermophys.* **2005**, *26*, 1667–1680.
- (24) Dubberke, F. H.; Rasche, D. B.; Baumhögger, E.; Vrabec, J. Apparatus for the measurement of the speed of sound of ammonia up to high temperatures and pressures. *Rev. Sci. Instrum.* **2014**, *85*, 084901.
- (25) Dubberke, F. H.; Baumhögger, E.; Vrabec, J. Burst design and signal processing for the speed of sound measurement of fluids with the pulse-echo technique. *Rev. Sci. Instrum.* **2015**, *86*, 054903.
- (26) Deutsche Gesetzliche Unfallversicherung, BGR 500. *Betreiben von Arbeitsmitteln* **2008**, *500*.
- (27) Grunewald, T.; Finke, R.; Grätz, R. Untersuchungen zur Zündwahrscheinlichkeit und Datenanalyse zur Erfassung der Einflussgrößen mechanisch erzeugter Stahl-Schlagfunken in explosionsfähigen Brenngas/Luft-Gemischen. *Forschungsbericht* **2010**, *292*.

- (28) Beesom, H. D.; Smith, S. R.; Stewart, W. F. *Safe Use of Oxygen and Oxygen Systems: Handbook for Design, Operation, and Maintenance*; ASTM International, 2007.
- (29) Bolobov, V. I.; Berezin, A. Y. Conditions for Ignition of Copper and Copper Alloys in Oxygen. *Combustion, Explosion, and Shock Waves* **1998**, *34*, 47–50.
- (30) Emerson Process Management, Material Guidelines for Gaseous Oxygen Service. *Product Bulletin* **2006**, *59:045*.
- (31) Tegeler, C.; Span, R.; Wagner, W. A New Equation of State for Argon Covering the Fluid Region for Temperatures From the Melting Line to 700 K at Pressures up to 1000 MPa. *J. Phys. Chem. Ref. Data* **1999**, *28*, 779–850.
- (32) Costa Gomes, M.; Trusler, J. The speed of sound in nitrogen at temperatures between  $T=250\text{K}$  and  $T=350\text{K}$  and at pressures up to 30 MPa. *J. Chem. Thermodyn.* **1998**, *30*, 527–534.
- (33) Leachman, J.; Jacobsen, R.; Penoncello, S.; Lemmon, E. Fundamental Equations of State for Parahydrogen, Normal Hydrogen, and Orthohydrogen. *J. Phys. Chem. Ref. Data* **2009**, *38*, 721–748.