Measurements of the Speed of Sound in Liquid and Supercritical Ethane

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Abstract

Comprehensive and accurate measurements of the speed of sound in pure ethane have been carried out in the liquid and supercritical regions by a double-path-length pulse-echo technique. The measured data cover the temperature range from 240 K to 420 K with pressures up to 100 MPa. The expanded measurement uncertainties *at the 95 % confidence level* amount to 2.1 mK for temperature, 0.007 % for pressure, and 0.01 % for speed of sound with the exception of a few state points in the vicinity of the critical point, where the uncertainty increases up to 0.016 %. The quality of the measurements is demonstrated by comparisons with literature data and the fundamental equation of state for ethane *by D. Bückner, W. Wagner* [J. Phys. Chem. Ref. Data 35 (2006) 205–266].

Keywords: ethane, high pressure, pulse-echo method, speed of sound

1. Introduction

Ethane is an important fluid with many industrial and scientific applications. For example, it is one of the most important basic substances in many production processes in the chemical industry, and it occurs as the second main component in natural gas beside methane. Moreover, it often serves as a reference fluid for developing *equations of state* or is used for validating models of intermolecular forces in molecular simulations. Therefore, precise knowledge of its thermodynamic properties is desirable.

Thermodynamic properties of a fluid are best represented by fundamental equations of state, from which all thermodynamic properties can be calculated. For developing and optimizing fundamental equation of state accurate *speed-of-sound* data sets in the liquid phase are very useful. *They* contribute to improving the description of the liquid region, the extrapolation behavior and the representation of caloric properties. For ethane, the most accurate fundamental equation of state was published by Bückner and Wagner [1]. For the optimization of the equation of state in the liquid phase, only one comprehensive *speed-of-sound* data set by Tsumura and Straty [2] was available. These data were measured with a sing-around pulse-echo technique, have an uncertainty of 0.05 % and cover the low temperature range between 100 K and 323 K with pressures up to 37 MPa. Besides, Trusler and Costa Gomez [3] measured a few data with a spherical resonator on the supercritical isotherm 350 K up to 20 MPa. At low pressures in the liquid phase, the Bückner and Wagner equation of state describes the speed of sound with an uncertainty of 0.15 %. At pressures above 40 MPa the uncertainties increase

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to 1 % up to 100 MPa, and even reach 5 % at higher pressures. With our *speed-of-sound* instrument [4, 5] very accurate *speed-of-sound* data with uncertainties well below 0.05 % were already measured for several pure fluids, e.g. [6, 7]. Thus, the aim of this work was to extend the measurement range for the speed of sound in liquid and supercritical ethane to higher pressures up to 100 MPa and higher temperatures up to 420 K. The new data can subsequently be used to improve the formulation of the Helmholtz energy for ethane.

2. Experimental Procedure

Our *speed-of-sound* instrument, the calibration procedure, and the analysis of measurements have been described in detail in refs. [4, 5]. The measurement principle of our *speed-of-sound* sensor is based on a double-path-length pulse-echo technique, which was first introduced by Muringer et al. [8]. A piezoelectric quartz crystal with a resonance frequency of 8 MHz is employed as a sound emitter and receiver. In the analysis of the *speed-of-sound* measurements, corrections for changes of the distances in the sensor with temperature, for compression of the sensor with pressure, and for diffraction effects are applied as described in ref. [4].

The *speed-of-sound* sensor is housed in a pressure vessel, which is thermostated in a circulating liquid-bath thermostat. The temperature inside the pressure vessel is kept constant within 0.5 mK during the course of one measurement. The temperature was measured by a *25-Ohm standard platinum resistance thermometer* in the wall of the pressure vessel. The *thermometer* was calibrated on the ITS-90, and the uncertainty of the temperature measurement is estimated to be 2.1 mK. The resistance of the thermometer was measured with an ASL-F18 bridge system with calibrated reference resistors. The pressure inside the pressure vessel was measured with a nitrogen-operated gas pressure balance. The pressure balance was coupled to the sample liquid via a differential pressure null indicator (Ruska membrane type cell). The uncertainty of the pressure measurement is *less* than 70 ppm. Both temperature and pressure measurement uncertainties are for a 95 % confidence level.

The acoustic path length $\Delta l = 2(l_2 - l_1)$ at zero pressure and 273.15 K and the temperature depen-

Fig. 1. Relative deviations of measured speeds of sound in gaseous argon from the fundamental equation of state of Tegeler et al. after adjustment of the acoustic path length. Legend: X, This work; Δ, Estrada-Alexanders and Trusler.

dent thermal expansion coefficient of the sensor material were determined by calibration measurements in gaseous argon at pressures between 10 MPa and 13 MPa and temperatures between 240 K and 420 K. Argon was used as a calibration fluid instead of water because it enables to calibrate the sensor in a wider temperature range and to achieve a lower uncertainty of the calibration. With the *speed-of-sound* data of Estrada-Alexanders and Trusler [9], which have a relative uncertainty of 10 ppm, accurate references for the speed of sound in argon are available. The analysis of the calibration measurements was started with a calibration function from a previous measurement campaign. *Minimization of the deviations of our measurements from the reference data of Estrada-Alexanders and Trusler* was achieved by reducing the value of the acoustic path length at zero pressure and 273.15 K by about 0.014 %. The difference to the previous calibration is probably due to the fact that the sensor was disassembled and reassembled before the calibration measurements. *After the calibration two complete measurement campaigns with different ethane samples were carried out. These measurements had to be discarded because the samples were contaminated with air. Then the present ethane measurements were conducted, followed by a second calibration with argon which was also carried out and analyzed as described above. It was found that the acoustic path length had increased by 0.035 % since the first calibration. It is assumed that this difference is due to small movements of the crystal in the speed-of-sound sensor during temperature and pressure cycles. To check the reproducibility of the speed of sound after the second calibration, a few measurements at $T = 340$ K were repeated since this isotherm was measured first. These data deviated from the speeds of sound of the main measurement campaign by up to 55 ppm when evaluated with the same calibration function for the acoustic path length. This result provided high confidence that the speed-of-sound measurements for ethane are very consistent and are not affected by the rather large difference between the two calibrations. For this reason the ethane measurements were evaluated with the second calibration, and an additional allowance of 55 ppm was added as a systematic contribution to the combined uncertainty of the speed of sound. The observed difference of 55 ppm is probably also due to movements of the crystal during frequent temperature changes in the second calibration.*

Fig. 1 shows the deviations of our second series of calibration measurements and of the data of Estrada-Alexanders and Trusler from the *accurate* fundamental equation of state of Tegeler *et al.* for argon as a function of temperature after adjustment of the acoustic path length. *Our measurements agree with the data of Estrada-Alexanders and Trusler within 20 ppm with the exception of two points, which deviate by 35 ppm and 45 ppm from the data of Estrada-Alexanders and Trusler. These two points were discarded in the analysis of the calibration measurements. Their deviations are covered by the additional allowance of 55 ppm to the uncertainty of the speed of sound described above. The expanded uncertainty (confidence level 95 %) of the determination of the acoustic path length is estimated to be 40 ppm. It includes contributions from the time, temperature and pressure measurements, the uncertainty of the reference data, the deviation of the calibration measurements from the reference data, and the correction of the acoustic path length to zero pressure. Estrada-Alexanders and Trusler did not state whether the reported uncertainty of their speed of sound data is at the 68 % or 95 % confidence level. In our uncertainty analysis, it was considered as an expanded uncertainty at the 95 % confidence level. A detailed summary of all contributions to the measurement uncertainties is given in Table 1.*

For the measurements in ethane, the resolution of the time measurements is *less* than 2 ppm, while

Table 1. Summary of Uncertainty Budgets.

Source of uncertainty	Value (confidence level=95 %)	Influence
Temperature measurement:		
SPRT calibration	2.0 mK	random
Calibration of reference resistance	0.1 mK	random
ASL F18 bridge	0.1 mK	random
Temperature variation in pressure vessel	0.5 mK	random
Total uncertainty	2.1 mK	
Pressure measurement:		
Calibration of pressure balance	$10^{-4} \text{ MPa} + 4.3 \cdot 10^{-5} \cdot p + 2.8 \cdot 10^{-7} \cdot p^2 / \text{MPa}$	random
Differential pressure indicator	$5 \cdot 10^{-6} \cdot p$	random
Hydrostatic pressure correction	$2 \cdot 10^{-6} \cdot p$	random
Ambient pressure measurement	20 Pa	random
Total uncertainty	$< 70 \cdot 10^{-6} \cdot p$	
Determination of acoustic path length with measurements in argon:		
Time difference	$2 \cdot 10^{-6} \cdot \Delta L$	random
Temperature measurement	$6 \cdot 10^{-6} \cdot \Delta L$	random
Pressure measurement	$6 \cdot 10^{-6} \cdot \Delta L$	random
Correction of ΔL to ambient pressure	$3 \cdot 10^{-6} \cdot \Delta L$	systematic
Diffraction correction	$2 \cdot 10^{-6} \cdot \Delta L$	systematic
Uncertainty of reference data	$10 \cdot 10^{-6} \cdot \Delta L$	random
Deviation of calibration measurements from reference data	$20 \cdot 10^{-6} \cdot \Delta L$	systematic
Total uncertainty	$40 \cdot 10^{-6} \cdot \Delta L$	
<i>Speed-of-sound</i> measurement:		
Acoustic path length	$40 \cdot 10^{-6} \cdot c$	random
Pressure dependence of acoustic path length	$(25 \cdot 10^{-8} \cdot p / \text{MPa}) \cdot c$	systematic
Time difference	$2 \cdot 10^{-6} \cdot c$	random
Diffraction correction	$3 \cdot 10^{-6} \cdot c$	random
Total uncertainty	$(45 \cdot 10^{-6} + 25 \cdot 10^{-8} \cdot p / \text{MPa}) \cdot c$	

the reproducibility of the speed of sound after temperature and pressure cycles during the measurement campaign is *less* than 25 ppm, at high pressures it is even *less* than 10 ppm. It is assumed that the reproducibility of the time measurements is limited by the reproducibility with which the temperature and pressure of a state point can be set in the pressure vessel. The uncertainty of the *speed-of-sound* measurement is 45 ppm at the 95 % confidence level, excluding contributions from sample impurities, from temperature and pressure measurement uncertainties and the reproducibility after the second calibration.

The ethane sample was purchased from Westfalen, Germany, had a manufacturer specified volume purity better than 99.999 % and was used as delivered. According to the manufacturer's specification the volume purity is as follows: other hydrocarbons (CH_4 , C_2H_4 , C_2H_2 , C_3H_8 , and C_{4+}): ≤ 6 ppm,

nitrogen: ≤ 3 ppm, carbon dioxide: ≤ 2 ppm, oxygen: ≤ 1 ppm, and water: ≤ 1 ppm. To account for sample impurities, an additional allowance of 10 ppm was added to the combined uncertainty of the speed of sound.

3. Results

Our measurements cover the liquid and supercritical region between $T = 240$ K and $T = 420$ K with pressures up to 100 MPa and were conducted along 10 isotherms in steps of 20 K. Additionally, measurements on the critical isotherm at $T_{\text{crit}} = 305.32$ K were carried out. In order to compare our measurements with the spherical resonator data of Trusler and Costa Gomez, some data were measured between 13 MPa and 25 MPa at $T = 350$ K. On subcritical isotherms the lowest pressure was chosen slightly above the vapor pressure of ethane at ambient temperature of about 3.75 MPa, while on supercritical isotherms measurements were started at the lowest pressure where a clear signal cancellation could be observed on the oscilloscope. The measurement results are listed in Table 2. Our *speed-of-sound* data on the eleven completely measured isotherms are shown in Fig. 2 as a function of pressure. In the region of our measurements, the speed of sound ranges from $350 \text{ m}\cdot\text{s}^{-1}$ to $1600 \text{ m}\cdot\text{s}^{-1}$.

Table 2. Results for the speed of sound in ethane.

T / K	p / MPa	$c / \text{m}\cdot\text{s}^{-1}$	$U_c(c) / \text{m}\cdot\text{s}^{-1}$	T / K	p / MPa	$c / \text{m}\cdot\text{s}^{-1}$	$U_c(c) / \text{m}\cdot\text{s}^{-1}$
$T = 240 \text{ K}$							
240.0012	4.10593	926.064	0.084	239.9997	25.1199	1166.32	0.10
239.9981	5.10652	941.251	0.085	240.0001	30.1231	1209.20	0.11
239.9980	6.10717	955.831	0.086	240.0001	35.1264	1248.93	0.11
239.9978	7.10781	969.878	0.087	240.0001	40.1303	1286.06	0.12
239.9978	8.10848	983.446	0.088	240.0003	45.1335	1320.97	0.12
239.9977	9.10914	996.573	0.089	240.0008	50.1368	1353.97	0.12
239.9985	10.1100	1009.31	0.09	240.0010	60.1434	1415.23	0.13
240.0013	10.1098	1009.29	0.09	240.0011	70.1499	1471.28	0.14
239.9988	12.6117	1039.51	0.09	240.0000	80.1574	1523.13	0.14
239.9990	15.1133	1067.76	0.09	240.0000	90.1641	1571.51	0.15
239.9994	17.6150	1094.36	0.10	240.0003	100.171	1616.94	0.16
239.9993	20.1166	1119.53	0.10				
$T = 260 \text{ K}$							
259.9961	4.10520	758.654	0.073	259.9974	25.1182	1055.06	0.10
259.9963	4.10521	758.657	0.073	259.9973	30.1216	1103.48	0.10
259.9964	5.10587	779.780	0.074	259.9972	35.1250	1147.75	0.10
259.9964	6.10658	799.566	0.075	259.9969	40.1292	1188.69	0.11
259.9962	7.10727	818.209	0.076	259.9969	45.1326	1226.87	0.11

Table 2. (*continued*)

T / K	p / MPa	c / m·s ⁻¹	$U_c(c)$ / m·s ⁻¹	T / K	p / MPa	c / m·s ⁻¹	$U_c(c)$ / m·s ⁻¹
259.9963	8.10795	835.879	0.078	259.9971	50.1361	1262.73	0.12
259.9959	9.10859	852.699	0.079	259.9969	60.1429	1328.74	0.12
259.9985	10.1088	868.730	0.080	259.9992	60.1429	1328.72	0.12
259.9959	10.1092	868.763	0.080	259.9994	60.1429	1328.72	0.12
259.9970	12.6096	906.138	0.083	259.9969	70.1498	1388.63	0.13
259.9971	15.1113	940.293	0.085	259.9969	80.1567	1443.69	0.14
259.9974	17.6130	971.860	0.088	259.9968	90.1636	1494.80	0.15
259.9971	20.1147	1001.30	0.09	259.9996	100.170	1542.59	0.15
$T = 280$ K							
280.0052	4.10515	566.797	0.064	280.0055	25.1195	949.349	0.088
280.0052	5.10580	601.255	0.064	280.0058	30.1229	1003.67	0.09
280.0053	6.10650	631.325	0.065	280.0057	35.1263	1052.61	0.10
280.0055	7.10721	658.247	0.066	280.0061	40.1297	1097.38	0.10
280.0054	8.10789	682.772	0.068	280.0058	45.1329	1138.77	0.11
280.0049	9.10855	705.402	0.069	280.0059	50.1362	1177.40	0.11
280.0054	10.1092	726.480	0.070	280.0057	60.1429	1247.95	0.12
280.0051	12.6109	773.922	0.073	279.9958	70.1496	1311.50	0.13
280.0057	15.1126	815.712	0.077	279.9965	80.1563	1369.52	0.13
280.0058	17.6144	853.356	0.080	279.9967	90.1630	1423.14	0.14
280.0057	20.1161	887.783	0.082	279.9968	100.169	1473.10	0.15
$T = 300$ K							
299.9958	5.10486	368.914	0.067	299.9981	30.1220	910.875	0.086
299.9955	6.10563	434.503	0.060	299.9985	35.1255	964.446	0.091
299.9953	7.10643	481.738	0.059	299.9981	40.1289	1012.92	0.10
299.9955	8.10714	520.103	0.060	299.9983	45.1326	1057.39	0.10
299.9960	9.10782	553.015	0.061	299.9986	50.1359	1098.61	0.11
299.9959	10.1085	582.153	0.062	299.9986	60.1428	1173.35	0.11
299.9960	12.6102	644.019	0.065	299.9984	70.1495	1240.16	0.12
299.9959	15.1119	695.622	0.069	299.9992	80.1563	1300.86	0.13
299.9963	17.6133	740.509	0.072	299.9992	90.1631	1356.74	0.14
299.9981	20.1151	780.577	0.075	299.9993	100.170	1408.64	0.14
299.9981	25.1186	850.525	0.081				
$T = 305.32$ K							
305.3173	6.10496	370.857	0.062	305.3188	30.1222	887.499	0.085
305.3176	7.10578	429.831	0.059	305.3189	35.1254	942.256	0.090
305.3174	8.10655	474.477	0.058	305.3189	40.129	991.671	0.095

Table 2. (*continued*)

T / K	p / MPa	$c / \text{m}\cdot\text{s}^{-1}$	$U_c(c) / \text{m}\cdot\text{s}^{-1}$	T / K	p / MPa	$c / \text{m}\cdot\text{s}^{-1}$	$U_c(c) / \text{m}\cdot\text{s}^{-1}$
305.3172	9.10732	511.481	0.059	305.3192	45.1323	1036.91	0.10
305.3175	10.108	543.524	0.060	305.3196	50.1357	1078.77	0.10
305.3176	12.6098	610.162	0.063	305.3194	60.1424	1154.56	0.11
305.3175	15.1116	664.739	0.067	305.3197	70.1489	1222.17	0.12
305.3175	17.6134	711.717	0.070	305.3200	80.1554	1283.54	0.13
305.3175	20.1152	753.370	0.073	305.3202	90.1618	1339.96	0.14
305.3173	25.1187	825.573	0.079	305.3202	100.168	1392.33	0.14
305.3185	25.1190	825.573	0.079				
$T = 320 \text{ K}$							
320.0042	8.10853	346.325	0.055	320.0047	20.1171	681.812	0.069
320.0043	9.10928	397.386	0.055	320.0049	25.1205	760.047	0.075
319.9967	9.10820	397.392	0.055	320.0048	30.1239	826.137	0.081
319.9969	9.10822	397.386	0.055	320.0050	35.1273	884.000	0.086
320.0044	10.1100	438.915	0.056	320.0049	40.1308	935.854	0.091
320.0044	11.1107	474.377	0.057	320.0046	45.1341	983.085	0.096
320.0044	12.1114	505.620	0.058	320.0048	50.1375	1026.62	0.10
319.9971	12.1104	505.627	0.058	320.0047	60.1443	1105.08	0.11
320.0047	13.1121	533.741	0.059	320.0047	70.1514	1174.77	0.12
320.0045	14.1128	559.399	0.061	320.0048	80.1582	1237.82	0.12
320.0043	15.1135	583.107	0.062	320.0049	90.1650	1295.66	0.13
319.9970	15.1124	583.116	0.062	320.0051	100.172	1349.23	0.14
320.0044	17.6152	635.895	0.066				
$T = 340 \text{ K}$							
340.0030	10.1090	324.097	0.045	340.0044	25.1188	679.706	0.070
340.0038	10.1090	324.083	0.045	340.0048	30.1222	750.561	0.076
340.0029	11.1097	362.179	0.049	340.0044	35.1256	812.002	0.081
340.0026	12.1104	397.205	0.051	340.0043	40.1289	866.676	0.086
340.0027	13.1110	429.062	0.053	340.0045	45.1322	916.206	0.091
340.0036	14.1114	458.141	0.054	340.0043	50.1369	961.680	0.096
340.0034	15.1120	484.909	0.056	340.0041	60.1439	1043.25	0.10
340.0040	15.1125	484.913	0.056	340.0043	70.1508	1115.34	0.11
340.0039	17.6137	543.915	0.060	340.0043	80.1578	1180.36	0.12
340.0042	17.6142	543.923	0.060	340.0041	90.1647	1239.84	0.13
340.0040	20.1154	594.616	0.063	340.0040	100.172	1294.82	0.14
$T = 350 \text{ K}$							
350.0020	13.1114	388.893	0.049	350.0024	17.1142	493.336	0.056

Table 2. (*continued*)

T / K	p / MPa	$c / \text{m}\cdot\text{s}^{-1}$	$U_c(c) / \text{m}\cdot\text{s}^{-1}$	T / K	p / MPa	$c / \text{m}\cdot\text{s}^{-1}$	$U_c(c) / \text{m}\cdot\text{s}^{-1}$
350.0020	14.1120	417.627	0.051	350.0023	18.1149	515.598	0.058
350.0033	15.1124	444.518	0.053	350.0021	19.1156	536.645	0.059
350.0027	15.1124	444.518	0.053	350.0023	20.1162	556.623	0.061
350.0020	15.1127	444.535	0.053	350.0019	22.6180	602.591	0.064
350.0023	16.1135	469.707	0.055	350.0025	25.1197	643.969	0.067
$T = 360 \text{ K}$							
360.0045	11.1091	308.749	0.035	359.9966	30.1216	685.231	0.071
360.0049	11.1089	308.751	0.035	359.9960	35.1260	749.097	0.077
360.0048	12.1098	333.419	0.040	359.9959	40.1295	805.780	0.082
360.0053	13.1104	359.771	0.044	359.9959	45.1330	856.995	0.087
360.0049	14.1111	386.181	0.047	359.9959	50.1364	903.907	0.092
360.0053	15.1118	411.730	0.049	359.9957	60.1432	987.833	0.101
360.0058	17.6135	470.763	0.054	359.9959	70.1501	1061.82	0.11
360.0059	20.1151	522.916	0.058	359.9959	80.1569	1128.38	0.12
359.9961	20.1155	522.955	0.058	359.9960	90.1635	1189.16	0.12
359.9966	22.6167	569.439	0.062	359.9963	100.170	1245.27	0.13
359.9967	25.1184	611.431	0.065				
$T = 380 \text{ K}$							
379.9982	15.1122	370.700	0.042	379.9964	35.1260	695.570	0.073
379.9983	16.1129	390.923	0.045	379.9962	40.1295	753.227	0.078
379.9982	17.1137	411.213	0.047	379.9962	45.1329	805.392	0.084
379.9984	18.1144	431.245	0.049	379.9966	50.1363	853.187	0.088
379.9984	19.1152	450.840	0.051	379.9968	60.1431	938.665	0.097
379.9972	20.1158	469.906	0.053	379.9965	70.1498	1013.96	0.11
379.9970	22.6176	515.025	0.057	379.9993	80.1574	1081.64	0.11
379.9971	25.1193	556.627	0.061	379.9993	90.1643	1143.40	0.12
379.9968	27.6209	595.084	0.064	379.9990	100.171	1200.37	0.13
379.9968	30.1226	630.815	0.067				
$T = 400 \text{ K}$							
400.0010	15.1122	355.737	0.036	399.9986	35.1258	651.397	0.070
400.0009	16.1130	370.546	0.039	399.9988	40.1288	708.909	0.075
399.9986	17.1138	386.281	0.042	399.9992	45.1323	761.231	0.080
399.9990	18.1144	402.564	0.044	399.9993	50.1356	809.310	0.085
399.9985	19.1151	419.112	0.046	399.9990	60.1425	895.499	0.094
399.9988	20.1157	435.709	0.048	399.9992	70.1493	971.531	0.103
399.9987	22.6174	476.551	0.053	399.9998	80.1560	1039.913	0.11

Table 2. (*continued*)

T / K	p / MPa	$c / \text{m}\cdot\text{s}^{-1}$	$U_c(c) / \text{m}\cdot\text{s}^{-1}$	T / K	p / MPa	$c / \text{m}\cdot\text{s}^{-1}$	$U_c(c) / \text{m}\cdot\text{s}^{-1}$
399.9986	25.1191	515.631	0.057	399.9998	90.1626	1102.310	0.12
399.9987	27.6208	552.587	0.060	400.0003	100.169	1159.871	0.13
399.9984	30.1224	587.434	0.064				
$T = 420 \text{ K}$							
420.0020	15.1106	355.162	0.034	420.0030	35.1249	615.947	0.066
420.0021	16.1113	365.770	0.036	420.0036	40.1284	672.253	0.072
420.0023	17.1125	377.505	0.038	420.0033	45.1318	723.939	0.077
420.0025	18.1132	390.104	0.040	420.0034	50.1352	771.705	0.082
420.0027	19.1139	403.343	0.042	420.0034	60.1421	857.752	0.091
420.0027	20.1146	417.021	0.044	420.0032	70.1495	933.942	0.100
420.0028	22.6163	452.115	0.049	420.0036	80.1565	1002.60	0.11
420.0027	25.1181	487.213	0.053	420.0035	90.1635	1065.31	0.12
420.0029	27.6198	521.412	0.057	420.0035	100.170	1123.20	0.12
420.0030	30.1215	554.325	0.060				

^a Uncertainty of temperature: $u(T) = 2.1 \text{ mK}$; relative uncertainty of pressure: $u_r(p) = 0.008 \%$ (all uncertainties refer to a level of confidence = 95 %).

Fig. 2. The speed of sound in ethane as a function of pressure for all measured isotherms. Legend: $\diamond$, 240 K; $\blacklozenge$, 260 K; ∇ , 280 K; $\blacktriangledown$, 300 K; $\triangle$, 305.32 K (critical isotherm); $\blacktriangle$, 320 K; $\square$, 340 K; $\blacksquare$, 350 K; $\circ$, 360 K; $\bullet$, 380 K; $\otimes$, 400 K; $\times$, 420 K and ----, saturated liquid speed of sound calculated from the fundamental equation of state of Bucker and Wagner.

For each measured state point a detailed analysis of the combined uncertainty of the *speed-of-sound* measurement was carried out. The uncertainty contributions to the speed of sound due to the uncertainties of temperature and pressure measurements were estimated by the equation of state of Bückner and Wagner [1]. The combined uncertainty is generally *less* than 0.01 %, including the uncertainties of the temperature and pressure measurement and the influences due to sample impurities. Only at low pressures in the critical region it is larger, increasing up to 0.016 %. These uncertainty estimates are for a 95 % confidence level. For each measured state point the combined uncertainty of the speed of sound is reported in Table 2. The combined uncertainties were rounded to the same number of digits as the *speed-of-sound* data.

4. Discussion

Fig. 3. Distribution of our measurements and literature data for the speed of sound in ethane in the p,T -plane. The grey area is the region of our measurements. Legend: $\times$, This work; O , Tsumura and Straty; Δ , Trusler and Costa Gomez; $\otimes$, Lemming; $\diamond$, Boyes; $\square$, Estrada-Alexanders and Trusler; ∇ , Noury; $+$, Terres et al.; $\blacklozenge$, critical point and $----$, vapor pressure calculated from the fundamental equation of state of Bückner and Wagner.

Experimental data for the speed of sound in ethane were published by several groups. Fig. 3 depicts the distribution of our data and literature data sets in the pressure-temperature plane. Lemming [10], Boyes [11], Colgate et al. [12], and Estrada-Alexanders and Trusler [9] measured speeds of sound in the gas region with a spherical resonator. The data sets of Trusler and Costa Gomez [3] and Terres et al. [13] also cover parts of the gas region and overlap with our data at low pressures at supercritical temperatures. Noury [14] measured the speed of sound in the critical region of ethane. Speeds of

sound in saturated liquid ethane were measured by Poole and Aziz [15], Vangeel [16], and Tsumura and Straty [2]. Only the data set of Tsumura and Straty [2] covers a large part of the liquid region.

Fundamental equations of state for ethane in terms of the Helmholtz free energy were developed by Friend et al. [17], Span and Wagner [18], Bückner and Wagner [1], and Kunz and Wagner [19]. Younglove and Ely [20] published a thermal equation of state of the MBWR-type, which together with an equation for the isochoric ideal gas heat capacity can be represented as a fundamental equation of state. Since the Bückner and Wagner equation is the most accurate fundamental equation of state for ethane, it is chosen as the reference for the following discussion. In the remainder of this section, our data are compared with the equation of state of Bückner and Wagner [1], the data of Tsumura and Straty [2], and the data of Trusler and Costa Gomez [3].

In Figs. 4 to 6, the relative deviations of our data, the data of Tsumura and Straty [2] and Trusler and Costa Gomez [3] from the fundamental equation of state of Bückner and Wagner are plotted versus pressure for all measured isotherms. Since the deviations of speeds of sound calculated from the other fundamental equations of state and of the data of Terres et al. [13] and Noury [14] from the fundamental equation of state of Bückner and Wagner are in large parts much larger than the chosen scale of the figures, they have not been included in the deviation plots.

Our data agree with the fundamental equation of state within 0.1 % with the exception of a few points at high pressures on the six isotherms up to $T = 320$ K, where deviations up to 0.3 % are observed. They generally show the same systematic deviation pattern as the data of Tsumura and Straty, and agree with them mostly within 0.03 %. Our data are very consistent, while the data of Tsumura and Straty scatter within their uncertainty of about 0.05 %. At $T = 260$ K our data are up to 0.04 % higher than the Tsumura and Straty data, and at low pressures on the critical isotherm deviations up to 0.05 % are found. Tsumura and Straty estimated the uncertainty of their data generally to 0.05 %. Only close to the critical point, that is at the lowest pressures at $T = 300$ K and on the critical isotherm $T = 305.32$ K the uncertainty is 0.1 %. Thus, the agreement between the two data sets is within the uncertainty the data of Tsumura and Straty.

At $T = 350$ K, we compare our data with five spherical resonator data of Trusler and Costa Gomez in the pressure range between 10 MPa and 20 MPa where the two different measurement techniques overlap. The uncertainty of these data is 0.025 %. Again, both data sets show the same deviation pattern with a small maximum between 10 MPa and 20 MPa. *Our data are 0.03 % higher than the data of Trusler and Costa Gomez. Thus, the agreement is within their mutual uncertainties.* The maximum of the deviations is also observed on all other supercritical isotherms, being shifted to higher pressures with increasing temperature. This systematic deviation pattern may result from certain terms in the fundamental equation of state. This conclusion is warranted because of the low uncertainty of our experimental data. Conversely, the present experimental data should result in future formulations of the Helmholtz energy of ethane with different terms.

5. Conclusions

We have measured the speed of sound in liquid and supercritical ethane between 240 K and 420 K up to 100 MPa with high accuracy. This range exceeds the previously available speed of sound data for ethane considerably as does the accuracy. Therefore, this data set provides significant leverage to

improve the formulation of the Helmholtz energy for ethane.

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List of Symbols

c	speed of sound ($\text{m}\cdot\text{s}^{-1}$)
l	distance between quartz crystal and reflector (m)
Δl	acoustic path length (m)
p	pressure (MPa)
T	temperature (K)
U_c	combined uncertainty (at the 95 % confidence level)
u	expanded uncertainty (at the 95 % confidence level)

Fig. 4. Relative deviations $\Delta c = c(\text{expt.}) - c(\text{calc.})$ of experimental speeds of sound $c(\text{expt.})$ in ethane and literature data from values $c(\text{calc.})$ calculated from the fundamental equation of state of Bückner and Wagner as a function of pressure at 240 K, 260 K, 280 K and 300 K. Legend: $\times$, This work; $\circ$, Tsumura and Straty.

Fig. 5. Relative deviations $\Delta c = c(\text{expt.}) - c(\text{calc.})$ of experimental speeds of sound $c(\text{expt.})$ in ethane and literature data from values $c(\text{calc.})$ calculated from the fundamental equation of state of Bückner and Wagner as a function of pressure at 305.32 K, 320 K, 340 K and 360 K. Legend: $\times$, This work; $\circ$, Tsumura and Straty; $\triangle$, Trusler and Costa Gomez at 350 K.

Fig. 6. Relative deviations $\Delta c = c(\text{expt.}) - c(\text{calc.})$ of experimental speeds of sound $c(\text{expt.})$ in ethane and literature data from values $c(\text{calc.})$ calculated from the fundamental equation of state of Bückner and Wagner as a function of pressure at 360 K, 380 K, 400 K and 420 K. Legend: $\times$, This work; Δ , Trusler and Costa Gomez at 350 K.

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