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# Compressed Liquid Speed of Sound Measurements of *cis*-1,3,3,3-tetrafluoroprop-1-ene (R1234ze(Z))

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## Abstract

In this paper, 38 speed of sound measurements in the compressed liquid phase of a high purity sample of the novel alternative working fluid *cis*-1,3,3,3-tetrafluoroprop-1-ene (R-1234ze(Z)) are reported along five isotherms, ranging from 273.15 K to 333.15 K for pressures up to 25 MPa. The experimental technique is based on a *double pulse-echo* method resulting in an expanded uncertainty less than 0.05% at the 95% confidence level over the entire thermodynamic space.

*Keywords:* compressed liquid, high pressure, R1234ze(Z), speed of sound

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## 1. Introduction

Over the last 10 or so years, there has been increased interest in low Global Warming Potential (low-GWP) working fluids as propellants, solvents, foam blowing agents, refrigerants, and in high-temperature heat pumping applications and Organic Rankine Cycle (ORC) applications. This interest has been driven by regulations, legislation, taxing schemes, and a change in public perception. One family of working fluids that has received considerable interest and focus are halogenated olefins, particularly, fluorinated propene isomers (see, e.g., Brown, 2009a; Brown *et al.*, 2010; and other similar example papers too numerous to mention here.) One fluorinated propene isomer possessing a normal boiling point temperature appropriate for high-temperature heat pumping applications and low-temperature Organic Rankine Cycle applications is *cis*-1,3,3,3-tetrafluoroprop-1-ene, also indicated as R1234ze(Z), (see, e.g., Brown *et al.*, 2009). Akasaka *et al.* (2014) developed a high-accuracy fundamental Equation of State (EoS) for R1234ze(Z) valid for pressures less than 6 MPa, based on experimental values of vapour pressures, saturated liquid and vapor densities,  $pvT$  data in the liquid and vapor phases, and vapor phase sound speeds. The reader is referred to Akasaka *et al.* (2014) for references to the papers which report the above mentioned experimental measurements. To the best of the authors' knowledge, there are no experimental speed of sound measurements in the compressed liquid phase of R1234ze(Z) that have been reported in the publicly available literature. Therefore, this paper wishes to contribute to the characterization of R1234ze(Z) by reporting speed of sound measurements in the compressed liquid phase. The hope is that these data will prove useful for developing more refined and accurate formulations of EoS for R1234ze(Z),

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34 which will assist researchers and industry in further developing this alternative  
35 low-GWP working fluid.

## 36 2. Experimental section

37 The test sample of *cis*-1,3,3,3-tetrafluoroprop-1-ene (R1234ze(Z),  $\text{CF}_3\text{CH} =$   
38  $\text{CHF}$ ; CAS number 29118-25-0) was provided by Central Glass Co., Ltd. with a  
39 declared purity greater than 0.99 in mass fraction. Since the effects of impurities  
40 of this order of magnitude on speed of sound measurements are negligible when  
41 compared to other sources of uncertainties, no further analysis or purification  
42 were attempted on the sample.

### 43 2.1. Principle and apparatus for speed of sound measurements

44 In the present work, compressed liquid speed of sound measurements were  
45 taken by employing an advanced transient technique, in particular the double  
46 *pulse-echo* technique (Trusler 1991). This method is based on the determination  
47 of the time needed by an acoustic wave packet to travel a known distance in a  
48 fluid sample. In particular, an electric tone-burst is used to excite a piezoelec-  
49 tric (PZT) source generating two ultrasonic signals which propagate in opposite  
50 directions while spreading into the sample, which is maintained at a fixed ther-  
51 modynamic state. The electrical signal has the form of a five cycles repeated  
52 tone-burst with an amplitude of  $10 V_{\text{pp}}$ . A detailed description of the com-  
53 plete apparatus, and of the experimental technique, can be found in Lago *et al.*  
54 (2006).

55 The experimental apparatus was an improved version of the system described  
56 previously in Benedetto *et al.* (2005) and in Giuliano Albo *et. al.* (2014). In  
57 particular, for measurements made in a compressed liquid (therefore with sound  
58 speeds typically below  $1000 \text{ m}\cdot\text{s}^{-1}$ ), it is of fundamental importance to carefully  
59 choose the dimensions of the sensor. In this work, the sensor was constructed  
60 from 316L stainless steel with two spacer tubes with nominal lengths of 67 mm  
61 and 45 mm, with inside and outside diameters of 25 mm and 33 mm, respec-  
62 tively (see Figure 1). Acoustic path lengths were chosen in combination with the  
63 source diameter of 7 mm and the tone-burst carrier frequency of 4 MHz. Using  
64 this combination, *near-field* effects are avoided and time-of-flight measurements  
65 are independent from the chosen frequency up to 5 MHz. By using 4 MHz, it is  
66 possible to measure speeds of sound down to  $500 \text{ m}\cdot\text{s}^{-1}$ . Furthermore, the cho-  
67 sen lengths represent an acceptable trade-off between shorter distances, which  
68 reduce wave damping and accuracy, and longer trajectories, which increase wave  
69 damping and accuracy. Shorter cells are not recommended for measurements  
70 in compressed liquids because, depending on the source diameter, it is possible  
71 to fall into geometrical configurations in which wrong, but repeatable, time-of-  
72 flight evaluations are possible. The acoustic path length difference of the cell  
73 was determined in ambient conditions by calibration with degassed Millipore  
74 ultra-quality water at  $T = 298.15 \text{ K}$  and  $p = 0.1 \text{ MPa}$  against the speed of  
75 sound given by the 1995 EoS formulation of the International Association for  
76 the Properties of Water and Steam (IAPWS-95) which, for this particular state  
77 point, has an uncertainty of 0.005% as declared in Wagner and Pruss (2002),  
78 according to the procedure described in Lago *et al.* (2006).

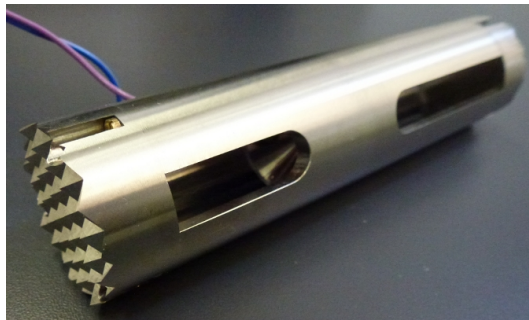


Figure 1: Sensor used for speed of sound measurements in compressed liquids. Different path lengths are revealed by the asymmetry of the loops. Pyramids, on the outer surfaces of the reflectors, prevent the transmitted signal to return to the receiver, interfering with the main signal.

### 79 3. Experimental results

80 Speed of sound,  $w_{\text{exp}}$ , measurements of R1234ze(Z) in the compressed liquid  
 81 state were taken for five isotherms (273.15 K, 283.15 K, 293.15 K, 313.15 K,  
 82 333.15 K) and for seven different pressures (0.1 MPa, 1.0 MPa, 5.0 MPa,  
 83 10.0 MPa, 15.0 MPa, 20.0 MPa, 25.0 MPa).

84 Since the experimental pressures can differ from the desired values up to  
 85 about  $\pm 0.15$  MPa, in order to be able to produce a regular grid of speed of  
 86 sound data, the experimental results have been fitted using the following bi-  
 87 dimensional polynomial

$$w(p, T) = \sum_{i=0}^M \sum_{j=0}^N a_{ij} (p - p_0)^i (T - T_0)^j, \quad (1)$$

88 where  $a_{ij}$  are experimentally determined coefficients, and  $p_0$  and  $T_0$  are refer-  
 89 ence pressure and temperature values, respectively. The "realigned" values are  
 90 calculated in order to have them match the desired thermodynamic state points.  
 91 The degree of the bi-dimensional polynomial,  $M = 3$  and  $N = 4$ , has been cho-  
 92 sen so that the differences between the experimental values and those calculated  
 93 using eq. 1 are less than 10% of the experimental uncertainty in the speed of  
 94 sound measurements. Table 1 provides the experimental speed of sound,  $w_{\text{exp}}$ ,  
 95 measurements together with the corresponding thermodynamic state points de-  
 96 termined by the measured temperature and pressure values. Table 2 lists speed  
 97 of sound data on the regular mesh obtained by eq. 1, while Table 3 reports the  
 98 matrix of experimentally determined coefficients,  $a_{ij}$  (see Eq. (1)).

99 Figures 2 and 3 show the compressed liquid speed of sound measurements  
 100 of R1234ze(Z) as a function of pressure and temperature, respectively. The  
 101 behavior of the experimental results as shown in Figures 2 and 3 are typical  
 102 of refrigerants previously measured by the authors and show consistent and  
 103 expected functional forms, confirming the validity and accuracy of the measure-  
 104 ments. To the best of the authors' knowledge there are no other experimental  
 105 data available in the public literature for compressed liquid speeds of sound of  
 106 R1234ze(Z). Akasaka *et al.* (2014) developed a high-accuracy fundamental EoS  
 107 for R1234ze(Z) for pressures less than 6 MPa based on experimental values of

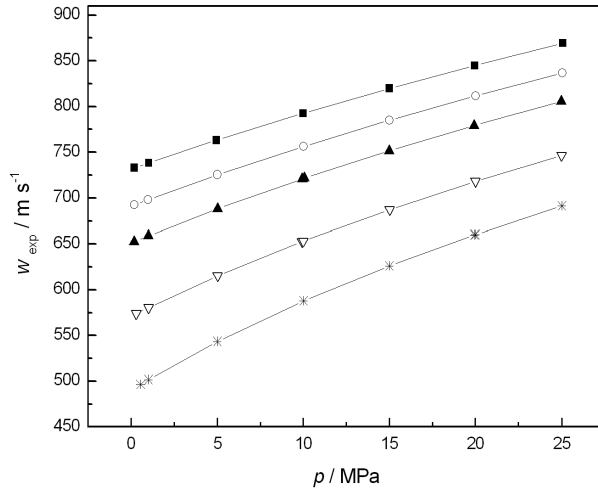


Figure 2: Experimental speed of sound measurements as a function of pressure in R1234ze(Z). Symbols show values for each isotherm: (■),  $T = 273.15$  K; (○),  $T = 283.15$  K; (▲),  $T = 293.15$  K; (▽),  $T = 313.15$  K; (\*),  $T = 333.15$  K.

108 vapor pressures, saturated liquid and vapor densities,  $pvT$  data in the liquid  
 109 and vapor phases, and vapor phase sound speeds. While not developed from  
 110 compressed liquid speed of sound data, Akasaka's EoS also could be used to  
 111 estimate these values. If this is carried out for the experimental results reported  
 112 in Table 1, the deviations of the measured data from Akasaka's EoS estimates  
 113 vary from being 1.3% to 7.0% greater, with a mean of 4.1%. While these devi-  
 114 ations are significant, they are considered to be acceptable since the EoS was  
 115 developed without access to this type of data and the fact that compressed liq-  
 116 uid speed of sound data are generally sensitive. Thus, the authors recommend  
 117 that Akasaka's EoS be updated using the experimental compressed liquid speed  
 118 of sound data reported herein.

#### 119 4. Assessment of measurement uncertainty

120 From a metrological point of view, the double *pulse-echo* technique for sound  
 121 speed determination, as described above, is an indirect measurement method  
 122 represented by the following model:

$$w_{\text{exp}} = w(\Delta L, \tau, T, p) = \frac{2\Delta L}{\tau_{\text{exp}}} \quad (2)$$

123 where  $\Delta L$ , the difference in acoustic path lengths, and  $\tau_{\text{exp}}$ , the measured time  
 124 of flight, are independent measurements, and temperature  $T$  and pressure  $p$   
 125 are measured state variables. Applying a standard uncertainty propagation

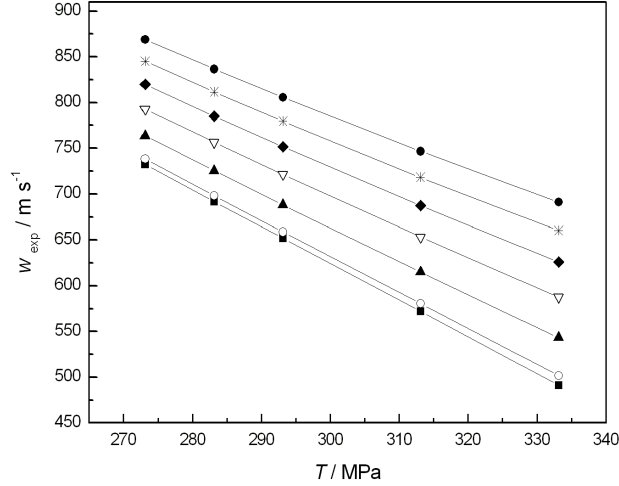


Figure 3: Experimental speed of sound measurements as a function of temperature in R1234ze(Z). Symbols show values for each isobar: (■),  $p = 0.1$  MPa; (○),  $p = 1.0$  MPa; (▲),  $p = 5.0$  MPa; (▽),  $p = 10.0$  MPa; (◆),  $p = 15.0$  MPa; (\*),  $p = 20.0$  MPa; (●),  $p = 25.0$  MPa.

126 procedure to Eq. (2), the following expression for  $u(w_{\text{exp}})/w_{\text{exp}}$  is obtained:

$$\left[ \frac{u(w_{\text{exp}})}{w_{\text{exp}}} \right]^2 = \left[ \frac{u(\Delta L)}{\Delta L} \right]^2 + \left[ \frac{u(\tau)}{\tau} \right]^2 + \left[ \frac{T}{w_{\text{exp}}} \left( \frac{\partial w}{\partial T} \right)_p \frac{u(T)}{T} \right]^2 + \left[ \frac{p}{w_{\text{exp}}} \left( \frac{\partial w}{\partial p} \right)_T \frac{u(p)}{p} \right]^2. \quad (3)$$

127 Table 4 lists the contributions to the overall uncertainty from the measured  
 128 quantities of Eq. (3). As can be seen, the largest contribution comes from  
 129 the pressure determination while that of temporal delay and repeatability can  
 130 be considered negligible. The uncertainty contribution due to the temperature  
 131 measurement is approximately 50% higher than ones measured in liquid hydro-  
 132 carbons, such as  $n$ -alkanes, because of the smaller value of the speed of sound in  
 133 R1234ze(Z), despite the fact that,  $(\partial w/\partial T)_p$  is almost the same for both fluids.

## 134 5. Conclusions

135 In this work, we report 38 compressed liquid speed of sound measurements  
 136 and their associated uncertainties for a novel alternative working fluid, R1234ze(Z)  
 137 (*cis*-1,3,3,3-tetrafluoroprop-1-ene), by means of a *double pulse-echo* technique.  
 138 These results should prove useful for developing more refined and accurate for-  
 139 mulations of equations of state for R1234ze(Z), which will assist researchers and  
 140 industry in further developing this low-GWP working fluid as a propellant, sol-  
 141 vent, and foam blowing agent, and for refrigeration, heat pumping, and Organic  
 142 Rankine Cycle applications.

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R1234ze(Z)		
$T_{\text{exp}} / \text{K}$	$p_{\text{exp}} / \text{MPa}$	$w_{\text{exp}} / (\text{m} \cdot \text{s}^{-1})$
273.148	0.192	733.01
273.147	1.017	738.46
273.146	4.940	763.22
273.152	9.982	792.63
273.151	15.012	819.86
273.151	19.968	844.97
273.158	25.059	869.25
283.146	0.194	692.40
283.144	0.979	698.01
283.144	5.005	725.37
283.148	10.017	756.50
283.145	15.005	785.05
283.148	20.019	811.73
283.143	25.023	836.72
293.151	0.198	652.56
293.148	1.001	658.82
293.149	5.029	688.26
293.149	10.065	721.69
293.147	9.940	720.93
293.149	15.001	751.59
293.148	19.929	779.17
293.147	24.979	805.49
313.152	0.320	574.19
313.153	1.010	580.61
313.152	5.026	615.30
313.151	9.998	653.18
313.150	9.927	652.68
313.152	15.023	687.34
313.151	20.004	718.15
313.153	24.987	746.57
333.150	0.554	496.55
333.151	1.002	501.61
333.150	4.999	543.43
333.146	10.015	587.78
333.149	15.006	626.08
333.149	20.009	660.13
333.148	19.956	659.78
333.150	25.005	691.19

Table 1: Experimental measurements of the speed of sound,  $w_{\text{exp}}$ , of R1234ze(Z) as function of temperature,  $T_{\text{exp}}$ , and pressure,  $p_{\text{exp}}$ .



$p$ (MPa)	$w$ (m · s <sup>-1</sup> )	$p$ (MPa)	$w$ (m · s <sup>-1</sup> )	$p$ (MPa)	$w$ (m · s <sup>-1</sup> )	$p$ (MPa)	$w$ (m · s <sup>-1</sup> )	$p$ (MPa)	$w$ (m · s <sup>-1</sup> )	$p$ (MPa)	$w$ (m · s <sup>-1</sup> )	$p$ (MPa)	$w$ (m · s <sup>-1</sup> )
							$T = 273.15$ K						
0.1	732.41	1.0	738.33	5.0	763.54	10.0	792.76	15.0	819.82	20.0	845.10	25.0	870.18
							$T = 283.15$ K						
0.1	691.75	1.0	698.15	5.0	725.27	10.0	756.43	15.0	785.04	20.0	811.59	25.0	838.18
							$T = 293.15$ K						
0.1	651.84	1.0	658.77	5.0	688.01	10.0	721.32	15.0	751.60	20.0	779.50	25.0	806.87
							$T = 313.15$ K						
0.1	572.22	1.0	580.51	5.0	614.99	10.0	653.28	15.0	687.26	20.0	718.04	25.0	751.72
							$T = 333.15$ K						
0.1	491.51	1.0	501.68	5.0	543.23	10.0	587.84	15.0	626.10	20.0	659.94	25.0	692.49

Table 2: R1234ze(Z) speed of sound measurements as a function of temperature,  $T$ , and pressure,  $p$ , on a regular grid (see Eq. (1)).

$a_{ij}$ with $N = 3$ ( $i = 0, 1, 2, 3$ ); $M = 4$ ( $j = 0, 1, 2, 3, 4$ ) and $p_0 = 15$ MPa, $T_0 = 298.15$ K					
	$j = 0$	$j = 1$	$j = 2$	$j = 3$	$j = 4$
$i = 0$	735.247	-3.25144	0.00379791	-3.40437 · 10 <sup>-5</sup>	9.75196 · 10 <sup>-7</sup>
$i = 1$	5.9522	0.0314215	7.30976 · 10 <sup>-5</sup>	-2.71137 · 10 <sup>-7</sup>	1.03969 · 10 <sup>-8</sup>
$i = 2$	-0.051567	-0.000762512	-3.88632 · 10 <sup>-6</sup>	-3.51627 · 10 <sup>-8</sup>	-2.63479 · 10 <sup>-9</sup>
$i = 3$	0.00094674	2.48165 · 10 <sup>-5</sup>	6.09387 · 10 <sup>-7</sup>	6.56473 · 10 <sup>-9</sup>	-1.84995 · 10 <sup>-10</sup>

Table 3: Matrix of coefficients,  $a_{ij}$ , of the speed of sound function (see Eq. (1)) for R1234ze(Z).

Uncertainty source		Relative magnitude
determination of the acoustic path	$u(\Delta L)/\Delta L$	0.012%
determination of temporal delay	$u(\tau)/\tau$	0.002%
temperature measurements	$\left(\frac{\partial w}{\partial T}\right) \frac{u(T)}{w}$	0.015%
pressure measurements	$\left(\frac{\partial w}{\partial p}\right) \frac{u(p)}{w}$	0.042%
repeatability		0.001%
Estimated Overall Uncertainty		0.046%

Table 4: Uncertainties budget. All uncertainties are reported at a 95 % confidence level.