

# Speeds of Sound in Dense Liquid and Vapor Pressures for 1,1-Difluoroethane

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Speeds of sound in the liquid phase of 1,1-difluoroethane, CHF<sub>2</sub>CH<sub>3</sub>, were measured by a sing-around technique operated at a frequency of 2 MHz. The results cover the temperature range along six isotherms from (243 to 333) K and pressures from near the saturation line to about 30 MPa. The combined uncertainty is estimated to be within  $\pm 0.2\%$  except for the region near the coexistence line in the upper temperature range. The vapor pressure was also measured with an uncertainty lower than  $\pm 20$  kPa by detecting the phase change using an acoustic absorption technique. The speeds of sound in the saturated liquid were estimated by the extrapolation to the vapor pressure from those in the compressed liquid. The temperature and/or pressure effects on the speed of sound are discussed and compared with data for some other hydrofluorocarbons reported elsewhere.

## Introduction

In previous work, we reported speeds of sound in the liquid phase of some hydrofluorocarbons (HFCs): difluoromethane, CH<sub>2</sub>F<sub>2</sub>,<sup>1</sup> 1,1,1,2-tetrafluoroethane, CF<sub>3</sub>CH<sub>2</sub>F,<sup>2</sup> pentafluoroethane, CF<sub>3</sub>CHF<sub>2</sub>,<sup>3</sup> and 1,1,1-trifluoroethane, CF<sub>3</sub>CH<sub>3</sub>.<sup>4</sup> These data covering wide temperature and pressure ranges give useful clues to use in investigating the characteristics of each substance. In this work, speeds of sound in the dense liquid and vapor pressures for 1,1-difluoroethane (HFC 152a), CHF<sub>2</sub>CH<sub>3</sub>, CASRN 75-37-6, were measured at temperatures from (243 to 333) K and from the coexistence line to about 30 MPa as part of the research series on the thermophysical properties of HFCs. This compound has comparatively high vapor pressure that is close to the vapor pressure of 1,1,1,2-tetrafluoroethane, CF<sub>3</sub>CH<sub>2</sub>F, a widely used alternative refrigerant that replaces dichlorodifluoromethane, CCl<sub>2</sub>F<sub>2</sub>, or chlorodifluoromethane, CHClF<sub>2</sub>. 1,1-Difluoroethane is inflammable. According to the third report of the Intergovernmental Panel on Climate Change (IPCC),<sup>5</sup> the lifetime and global warming potential, GWP, (100 year unit) of CF<sub>3</sub>CH<sub>2</sub>F are 13.8 years and 3300, and those for CHF<sub>2</sub>CH<sub>3</sub> are 1.4 years and 410, respectively. Thus, because the present compound is excellent according to environmental considerations, if the inflammability problem is solved, then the shift to CHF<sub>2</sub>CH<sub>3</sub> from CF<sub>3</sub>CH<sub>2</sub>F will be possible. There are few studies on the thermophysical properties of this substance; therefore, a study, especially under high pressure, is of great importance. With the present results, the temperature and pressure effects on the thermophysical properties may be compared with those for the HFC fluids reported elsewhere.

## Experimental Section

A sample of 1,1-difluoroethane, CHF<sub>2</sub>CH<sub>3</sub>, was supplied by Daikin Industrials Ltd. The purity was better than 99.96

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mol %, as measured by gas–liquid chromatography. Tetrachloromethane, CCl<sub>4</sub> (purity better than 99.9%), used for the check of the instrument was an HPLC-grade sample from Aldrich Co. The substances were used without further purification except for careful drying with molecular sieves (Wako Pure Chemicals Ind. Ltd.) ( $13 \times 1/16$  for CHF<sub>2</sub>CH<sub>3</sub> and  $4A \ 1/16$  for CCl<sub>4</sub>). Selected physical properties for CHF<sub>2</sub>CH<sub>3</sub> are listed in Table 1 together with those for several other ethane-based hydrofluorocarbons.

The speeds of sound were measured using the sing-around technique employing a fixed-path interferometer operated at a frequency of 2 MHz, similar to that described previously.<sup>1,2</sup> The fixed-path acoustic interferometer was immersed in a liquid thermostat filled with the mixture ethylene glycol + water and controlled to within  $\pm 20$  mK. Temperature was measured by a quartz thermometer calibrated (ITS-90) within  $\pm 5$  mK using a standard platinum thermometer. Pressure was measured by two precision strain gauges (Nagano Keiki Co., KH15) of maximum pressure ( $5 \pm 0.003$ ) MPa calibrated by a quartz crystal pressure transducer (Paroscientific Inc., 730-31K-101) and ( $35 \pm 0.005$ ) MPa calibrated by a precision manometer (Tsukasa Sokken Co., PH-22-G). Ultrasonic speed,  $u \{= 2L/(t_2 - t_1)\}$  was obtained by measuring the period between the first,  $t_1$ , and second,  $t_2$ , echoes of a short acoustic pulse traveling a known distance,  $L$ , between the transducer and reflector. The value of  $\{L = (23.801 \pm 0.002)$  mm at 298.15 K and 0.1 MPa $\}$  was determined by measuring the period in pure tetrachloromethane, CCl<sub>4</sub>, at 298.15 K and 0.1 MPa and using the speed of sound ( $921.11 \pm 0.07$ ) m·s<sup>-1</sup> reported by Tamura et al.<sup>7</sup> The difference between both echoes,  $(t_2 - t_1)$ , was recorded by a universal counter with a resolution of 0.1 ns as the average value of 1000 periods.

The acoustic wave generated for the speed of sound measurement exhibits large absorption in the gas phase compared to that in the liquid phase. In this work, the existence of a vapor phase in the sample chamber was observed by monitoring and analyzing the acoustic signal.<sup>8</sup>

**Table 1. Physical Properties for Several Ethane-Based Hydrofluorocarbons<sup>a</sup>**

substance	$T_c^b$ /K	$p_c^b$ /MPa	$\rho_c^b$ /kg·m <sup>-3</sup>	$\mu^c$ /D	$\rho^b$ /kg·m <sup>-3</sup>	$u$ /m·s <sup>-1</sup>	$\kappa_S$ /GPa <sup>-1</sup>	$L_f^e$ /nm
CF <sub>3</sub> CHF <sub>2</sub>	339.17	3.618	568	3.481	1328	464.3 <sup>d</sup>	3.493	7.24
CF <sub>3</sub> CH <sub>2</sub> F	374.27	4.606	511	3.338	1202	500.6 <sup>e</sup>	3.320	7.09
CF <sub>3</sub> CH <sub>3</sub>	345.97	3.769	429	3.602	1013	523.3 <sup>f</sup>	3.605	7.04
CHF <sub>2</sub> CH <sub>3</sub>	386.41	4.517	368	3.264	870.7	592.3 <sup>g</sup>	3.274	6.60

<sup>a</sup> Critical temperature,  $T_c$ , critical pressure,  $p_c$ , critical density,  $\rho_c$ , dipole moment,  $\mu$ , density,  $\rho$ , speed of sound,  $u$ , isentropic compressibility,  $\kappa_S$ , and intermolecular free length,  $L_f$ , at reduced temperature  $T_r = T/T_c = 0.8$ . <sup>b</sup> Reference 5. <sup>c</sup> Reference 6. <sup>d</sup> Reference 3. <sup>e</sup> Reference 2. <sup>f</sup> Reference 4. <sup>g</sup> This work.

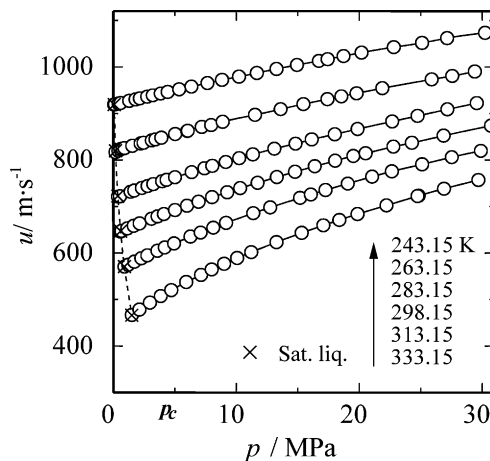
**Table 2. Experimental Speeds of Sound,  $u$ , in the Liquid Phase of 1,1-Difluoroethane at Various Temperatures,  $T$ , and Pressures,  $p$** 

$p$ /MPa	$u$ /(m·s <sup>-1</sup> )	$p$ /MPa	$u$ /(m·s <sup>-1</sup> )	$p$ /MPa	$u$ /(m·s <sup>-1</sup> )	$p$ /MPa	$u$ /(m·s <sup>-1</sup> )
$T = 243.15$ K							
0.138	920.2	3.217	939.9	8.846	973.1	18.731	1026.3
0.442	922.3	3.854	943.7	10.231	981.0	18.731	1026.3
0.595	923.2	4.428	947.1	11.681	989.0	20.194	1033.7
1.302	927.8	5.359	952.7	13.279	997.6	22.819	1046.4
1.815	931.0	6.355	958.6	14.943	1005.5	25.117	1058.6
2.160	933.1	7.657	966.2	16.723	1015.9	27.154	1068.9
2.762	936.9	8.846	973.1	17.442	1019.5	30.242	1084.3
$T = 263.15$ K							
0.407	822.3	3.130	842.9	7.967	876.3	18.552	941.0
0.581	823.3	3.429	844.7	8.899	881.9	19.791	947.4
0.759	824.6	3.914	848.6	9.893	888.5	21.881	959.5
0.928	825.5	5.038	856.2	11.531	898.7	25.895	980.9
1.550	831.3	5.789	861.4	13.616	912.0	27.572	989.5
2.228	835.9	6.568	866.7	15.466	922.7	29.409	998.8
2.461	837.6	7.201	871.0	17.421	934.4		
$T = 283.15$ K							
0.547	722.7	3.256	747.8	9.151	795.4	19.869	868.3
0.750	724.6	3.975	754.0	10.246	803.6	22.681	885.6
1.038	727.4	4.329	756.9	11.356	811.6	24.751	897.6
1.402	731.2	5.020	762.5	13.100	824.0	27.174	911.6
1.697	733.8	6.373	773.5	14.824	835.9	29.569	925.1
2.322	739.5	7.420	781.9	16.147	844.8		
2.793	743.7	8.061	787.0	18.020	857.0		
$T = 298.15$ K							
0.660	648.0	4.115	684.3	10.321	740.1	19.521	809.3
1.153	653.4	5.023	692.9	11.735	751.5	20.530	816.2
1.656	658.8	5.998	702.2	13.300	763.9	22.781	831.1
2.142	663.6	6.939	710.9	14.789	775.3	24.289	840.6
3.104	674.1	8.037	720.6	16.388	787.1	26.870	856.4
3.609	679.2	9.271	731.2	18.041	799.0	30.717	878.8
$T = 313.15$ K							
1.222	575.1	4.942	621.0	11.390	686.3	21.055	764.7
1.721	581.7	6.282	635.8	12.765	698.6	22.659	776.2
2.288	589.2	7.106	644.5	15.195	719.2	25.122	793.3
2.776	595.3	8.134	655.1	16.072	726.4	27.530	808.2
3.587	605.3	9.180	665.6	17.264	736.0	29.895	822.3
4.184	612.4	9.927	672.7	19.072	749.8		
$T = 333.15$ K							
2.129	478.7	7.142	552.1	13.279	623.8	22.222	702.8
2.606	487.2	8.008	565.1	15.330	643.8	24.836	723.7
3.860	507.8	9.016	577.2	17.092	660.1	24.752	723.7
4.725	520.6	10.079	589.7	18.393	671.6	26.902	738.8
5.932	538.0	11.228	602.3	19.875	684.3	29.698	758.6

The pressure under the condition when large absorption appeared was regarded as the saturated vapor pressure and was measured by a precision strain gauge with an uncertainty of  $\pm 10$  kPa.

## Results and Discussion

**Speeds of Sound in Liquid CHF<sub>2</sub>CH<sub>3</sub>.** Experimental results of the speeds of sound,  $u$ , in the liquid phase of 1,1-difluoroethane at several temperatures  $T$  and pressures  $p$  are presented in Table 2. The critical temperature,  $T_c$  (386.41 K), and pressure,  $p_c$  (4.512 MPa), of 1,1-difluoroethane are comparatively higher than those of some other hydrofluorocarbons (Table 1), and the obtained values of the speed of sound increase monotonically with increasing

**Figure 1.** Experimental speeds of sound,  $u$ , in liquid 1,1-difluoroethane as a function of temperature and pressure.

pressure over the whole experimental range, as illustrated graphically in Figure 1. The results are represented as a function of the reduced temperature,  $T_r (= T/T_c)$ , and reduced pressure,  $p_r (= p/p_c)$ , by the polynomial equation

$$\frac{u_{T,p}}{u_0} = \frac{\sum_{i=0}^3 a_i (1 - T_r)^i + \sum_{j=1}^2 b_j p_r^j}{A + \sum_{j=3}^5 b_j p_r^{(j-2)}} \quad (1)$$

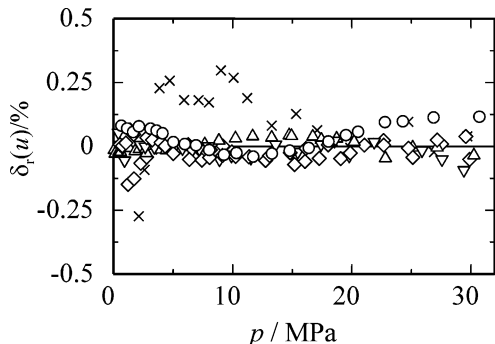
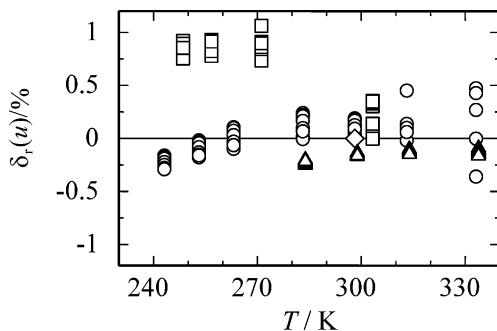
where  $u_{T,p}$  is the speed of sound at temperature  $T$  and pressure  $p$ ,  $u_0 (= 646.6 \text{ m}\cdot\text{s}^{-1})$  is the value in the saturated liquid at 298.15 K, and  $A = 1 + a_4(1 - T_r)$ . The values of coefficients  $a_i$  and  $b_j$  were calculated by a least-squares analysis of all 145 experimental data points weighted equally and are listed in Table 3. Figure 2 shows the deviations of the experimental data from eq 1 for each of the six isotherms. Equation 1 reproduces the experimental values with a mean deviation  $\delta_{\text{mean}}$  of  $0.102 \text{ m}\cdot\text{s}^{-1}$ . Larger deviations (maximum  $\pm 0.3\%$ ) occur mainly near the saturation line in the upper temperature range.

The available information about the speed of sound in the compressed liquid 1,1-difluoroethane is scarce. Only two independent sets measurements and an additional reference reporting correlation work were found in the literature. Beliajeva et al.<sup>9</sup> reported the speeds of sound in the liquid phase of 1,1-difluoroethane measured by an impulse method at a frequency of 1 MHz in the temperature range from (230 to 302) K and at pressures up to 13 MPa. Their instrument was calibrated by measuring the speed of sound in water and toluene with a standard error within  $\pm 0.07\%$ . However, the reported values show large differences from our results represented by eq 1, especially in the lower-temperature region as shown in Figure 3. For example, their experimental value at 248.43 K and 1 MPa ( $907.5 \text{ m}\cdot\text{s}^{-1}$ ) is higher than our value by about 0.9% ( $8.2 \text{ m}\cdot\text{s}^{-1}$ ).

**Table 3.** Coefficients  $a_i$  and  $b_j$  of Equation 1 and Maximum,  $\delta_{\max}$ , and Mean,  $\delta_{\text{mean}}$ , Deviations

	$i, j = 0$	1	2	3	4	5
$a_i$	3.6640	-7.5028	4.9712	-1.1382		-0.888781
$b_j$		$3.7057 \times 10^{-2}$	$-2.8047 \times 10^{-3}$	$1.1986 \times 10^{-2}$	$-1.7264 \times 10^{-3}$	$9.8606 \times 10^{-6}$
$T_c^a = 386.41$ K	$p_c^a = 4.517$ MPa	$u_0^b = 646.6$ m·s $^{-1}$	$\delta_{\max}^c = -0.16\%$ ,	$\delta_{\text{mean}}^c = 0.046\%$	$n = 145$	

<sup>a</sup>  $T_c$  and  $p_c$  are the critical temperature and pressure, respectively. <sup>b</sup>  $u_0$  is the speed of sound in a saturated liquid at 298.15 K. <sup>c</sup>  $\delta_{\text{mean}} = \Sigma|100(u_{\text{exptl}} - u_{\text{calcd}})/u_{\text{calcd}}|/n$ , where  $n$  is the number of data points.

**Figure 2.** Deviations  $\delta_r(u) = 100(u_{\text{exptl}} - u_{\text{calcd}})/u_{\text{calcd}}$  of experimental speeds of sound in liquid 1,1-difluoroethane from eq 1.  $\Delta$ , 243.15 K;  $\nabla$ , 263.15 K;  $\diamond$ , 283.15 K;  $\circ$ , 298.15 K;  $\diamond$ , 313.15 K;  $\times$ , 333.15 K.**Figure 3.** Deviations  $\delta_r(u) = 100(u_{\text{ref}} - u_{\text{calcd}})/u_{\text{calcd}}$  of speeds of sound reported in literature sources,  $u_{\text{ref}}$ , from values reported in this work,  $u_{\text{calcd}}$ . Deviations from eq 1 for 1,1-difluoroethane:  $\square$ , Beliajeva et al.;<sup>9</sup>  $\circ$ , Outcalt and McLinden.<sup>10</sup> Deviations for tetrachloromethane:  $\diamond$ , CCl $_4$  at 298.15 K and 0.1 MPa;<sup>7</sup>  $\Delta$ , CCl $_4$  Lainez et al.<sup>13</sup>

Outcalt and McLinden<sup>10</sup> have formulated the modified Benedict–Webb–Rubin (MBWR) equation of state for 1,1-difluoroethane on the basis of the experimental data for the density ( $PVT$ ), speed of sound, heat capacity, and second virial coefficient. Several thermodynamic quantities calculated in the wide ranges including the saturation line and compressed liquid are tabulated in their paper. The authors have compared the speeds of sound derived from the dense liquid from the equation of state with experimental values of Ahn et al.<sup>11</sup> and found agreement within  $\pm 0.2$ – $0.3\%$  in the range of (235 to 375) K and for pressures up to 30 MPa. But the original paper of Ahn et al.<sup>11</sup> on the speeds of sound in liquid 1,1-difluoroethane, which is listed by Outcalt and McLinden,<sup>10</sup> was not found in the journal. Therefore, a direct comparison of our experimental data with those reported by Ahn et al.<sup>11</sup> is unfortunately impossible. Deviations of values tabulated in ref 10 from those calculated using eq 1 are also plotted in Figure 3. As can be seen in the Figure, the values<sup>10</sup> show small negative deviations (about 0.2%) in the lower-temperature range and then become positive (up to 0.5%) in the higher-temperature range.

In this work, the acoustic fixed path,  $L$ , was obtained by measuring the period in liquid tetrachloromethane, and the

speed of sound value reported in ref 7 was adopted. (See text above.) This value corresponds to the point of a diamond shape in the deviation plot in Figure 3, and the deviation is naturally zero. To investigate the authenticity of deviations plotted in the Figure, speeds of sound in liquid tetrachloromethane were also measured at (283.15, 298.15, 313.15, and 333.15) K and at pressures up to 30 MPa.<sup>12</sup> Obtained values were compared with data reported by Lainez et al.<sup>13</sup> that were measured in the same laboratory as those by Ahn et al.<sup>11</sup> The deviations (triangle data points in Figure 3) from our data are negative with a maximum deviation of less than 0.2%. The deviations originate from the difference in the speed of sound for tetrachloromethane used for the determination of the acoustic path  $L$  of our instrument ( $921.11$  m·s $^{-1}$ )<sup>7</sup> and the value reported by Lainez et al.<sup>13</sup> ( $920.12$  m·s $^{-1}$ ).<sup>14</sup> From these facts, it seems reasonable to estimate that the speeds in liquid 1,1-difluoroethane measured by Ahn et al.<sup>11</sup> are a little higher in the higher-temperature region than our data, although our data show a maximum deviation of  $\pm 0.2$ – $0.3\%$  at 333.15 K from eq 1 as illustrated in Figure 2.

In the case of heat pump working fluids and/or refrigerants, the thermophysical properties at the vapor–liquid coexistence condition are important. In this work, the measurements in the lower-pressure region were carried out at narrow pressure intervals. Therefore, the speed of sound in the saturated liquid,  $u_s$ , was determined by extrapolation to the saturated vapor pressure,  $p_s$ , from speeds of sound in compressed liquid using about 10 experimental data points measured in the low-pressure range of each isotherm. The vapor pressure,  $p_s$ , required in the extrapolation process was also measured by an acoustic absorption technique.<sup>8</sup> The measured values are presented in Table 4 and were correlated using the Wagner-type equation

$$\ln\left(\frac{p_s}{p_c}\right) = \left(\frac{1}{T_r}\right) [-7.7664(1 - T_r) + 2.5850(1 - T_r)^{1.5} - 5.8545(1 - T_r)^3] \quad (2)$$

where  $p_s$  and  $p_c = 4.517$  MPa are the saturated vapor and critical pressures, respectively, and  $T_r = T/T_c$  ( $T_c = 386.41$  K) is the reduced temperature. Experimental values of vapor pressure are reproduced by eq 2 within  $\pm 10$  kPa (Table 4). A large number of the experimental studies on the vapor pressure of 1,1-difluoroethane are reported in the literature. Outcalt and McLinden<sup>10</sup> critically evaluated available experimental data and correlated them as a function of temperature. A comparison is presented in Table 4 that shows very good agreement between our values and those calculated from the Outcalt and McLinden correlation.

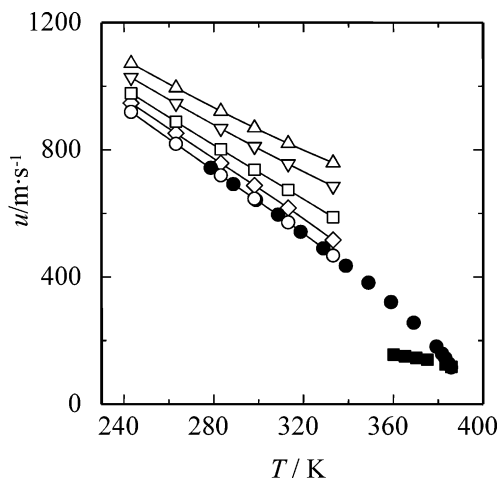
Speeds of sound  $u_s$  in the saturated liquid 1,1-difluoroethane obtained by the extrapolation are recorded in Table 4. The values are fit by the equation

$$u_s/(\text{m}\cdot\text{s}^{-1}) = 2.2281 \times 10^3 - 3.4042 \times 10^1(T_r^{-1}) - 1.9932 \times 10^3 T_r \quad (3)$$

**Table 4. Vapor Pressure,  $p_s$ /MPa, and Speeds of Sound in the Saturated Liquid,  $u_s$ /(m·s<sup>-1</sup>), for 1,1-Difluoroethane**

T/K	this work				Outcalt, McLinden <sup>a</sup>		Kraft, Leipertz <sup>b</sup>
	$p_s$ /MPa	$p_s$ /MPa	$u_s$ /(m·s <sup>-1</sup> )	$u_s$ /(m·s <sup>-1</sup> )	$p_s$ /MPa	$u_s$ /(m·s <sup>-1</sup> )	$u_s$ /(m·s <sup>-1</sup> )
	(exptl)	(calcd, eq 2)	(exptl)	(calcd, eq 3)			
243.15	0.073	0.073	920.1	919.8	0.077	918.6	
263.15	0.179	0.178	820.1	820.7	0.181	821.0	
283.15	0.372	0.372	721.0	721.1	0.373	722.7	720.5
298.15	0.595	0.597	646.6	646.1	0.596	646.1	646.2
313.15	0.907	0.909	570.9	570.8	0.909	571.7	571.2
333.15	1.499	1.495	469.9	470.1	1.500	466.9	467.4

<sup>a</sup> Reference 10. <sup>b</sup> Reference 15.

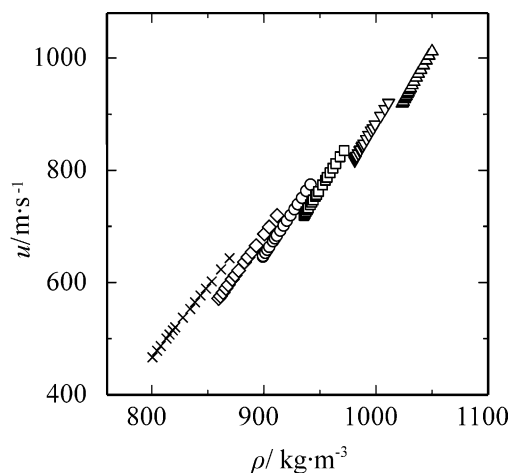


**Figure 4.** Temperature dependence of speeds of sound  $u$  in liquid 1,1-difluoroethane. Open symbols, this work;  $\Delta$ , 30 MPa;  $\nabla$ , 20 MPa;  $\square$ , 10 MPa;  $\diamond$ , 4.517 MPa ( $p_c$ );  $\circ$ ,  $\bullet$ , saturated liquid;  $\blacksquare$ , saturated vapor;  $\bullet$ ,  $\blacksquare$ , Kraft and Leipertz.<sup>15</sup>

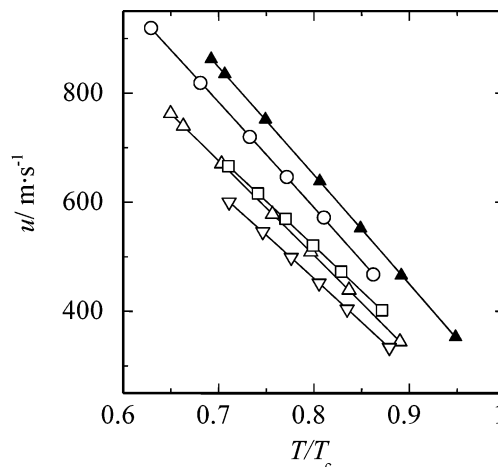
where  $T_r = T/T_c$  is the reduced temperature. Equation 3 reproduces the experimental data within  $\pm 0.1\%$ . Outcalt and McLinden<sup>10</sup> reported speeds of sound along the coexistence line derived from the MBWR equation of state, and Kraft and Leipertz<sup>15</sup> presented the values (including saturated vapor and the critical point region) measured by a dynamic light scattering method. Their values agree well with our smoothed curve as plotted in Figure 4. (See also Table 4.) It is known that the speed of sound in the liquid phase is closely related to the density at the same condition except for the region near the critical point. Figure 5 presents a relation between the speed of sound and density<sup>10</sup> for 1,1-difluoroethane. As can be seen in the Figure, the speed of sound increases linearly with increasing density (i.e., with elevated pressure) at constant temperature.

**Comparison of Speeds of Sound in Liquid Hydrofluorocarbons.** Previously, we have reported speeds of sound in dense liquids for principal hydrofluorocarbons  $\text{CH}_2\text{F}_2$ ,  $\text{CF}_3\text{CH}_2\text{F}$ ,  $\text{CF}_3\text{CHF}_2$ , and  $\text{CF}_3\text{CH}_3$  that are safe (regarding ozone depletion potential) substances to replace hydro- and/or chlorofluorocarbons as  $\text{CCl}_2\text{F}_2$ ,  $\text{CHClF}_2$ , and others. These results show that when the values for ethane-based substances including  $\text{CHF}_2\text{CH}_3$  along coexistence line are compared against reduced temperature,  $T/T_c$ , as shown in Figure 6 the absolute  $u$  values decrease in the order  $\text{CHF}_2\text{CH}_3 > \text{CF}_3\text{CH}_3 > \text{CF}_3\text{CH}_2\text{F} > \text{CF}_3\text{CHF}_2$  corresponding to the increasing number of fluorine atoms in the molecule.

On the basis of the Eyring's liquid theory, we discussed<sup>16,17</sup> the relationship between the speeds of sound and the free volume,  $V_f$ , in the liquid. According to this model, an acoustic wave that is excited in the fluid for measurements of the speed of sound is transmitted mo-



**Figure 5.** Dependences of the speed of sound in liquid 1,1-difluoroethane on density for each of the six isotherms.  $\Delta$ , 243.15 K;  $\nabla$ , 263.15 K;  $\square$ , 283.15 K;  $\circ$ , 298.15 K;  $\diamond$ , 313.15 K;  $\times$ , 333.15 K.



**Figure 6.** Speed of sound in liquid ethane-based hydrofluorocarbons at the saturation line as a function of reduced temperature,  $T/T_c$ .  $\circ$ ,  $\text{CHF}_2\text{CH}_3$ , present work;  $\blacktriangle$ ,  $\text{CH}_2\text{F}_2$ , ref 1;  $\Delta$ ,  $\text{CF}_3\text{CH}_2\text{F}$ , ref 2;  $\nabla$ ,  $\text{CF}_3\text{CHF}_2$ , ref 3;  $\square$ ,  $\text{CF}_3\text{CH}_3$ , ref 4.

mentarily to the intermolecular length. In general, when the value for the free volume in liquid is large (i.e., the intermolecular free length is large), the speed of sound has a low value. For ethane-based hydrofluorocarbons, assuming that the compounds have spherical molecules, the values of  $L_f$  can be estimated for reduced temperature  $T/T_c = 0.8$  and the coexistence line by the same procedure as that described in our previous papers.<sup>16,17</sup> The results are listed in the last column of Table 1. The van der Waals radii adopted for hydrogen and fluorine atoms are (1.20 and 1.35) nm, respectively. As can be seen in the case of HFC compounds investigated (Table 1), the increase of the

number of fluorine atoms causes an increase in  $V_f$ , and the speed of sound decreases. However, it is known that the free volume in a liquid is related to the molecular shape (i.e., the intermolecular free length in compounds with molecules having a spherical and/or symmetrical shape is low, and the low intermolecular free length leads to a high speed of sound). This fact is supported qualitatively by the fact that the  $u$  value in ethane-based fluids considered here increase with decreasing free length,  $L_f$ , as listed in Table 1. According to the Meyer study,<sup>6</sup> the dipole moment of  $\text{CF}_3\text{CH}_3$  is 3.602 D, which is remarkable higher than that of other ethane-based fluids. This large dipole moment would cause a moderate slope of  $u$  with  $T/T_c$  based on strong intra and intermolecular interactions of  $\text{CF}_3\text{CH}_3$  (Figure 6).

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