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Speed of Sound in Liquid CCl_3F under Saturated Vapor

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The speed of sound in saturated liquid trichlorofluoromethane has been measured from its triple point temperature (162.7 K) to 458 K by using the pulse echo overlap method. Our data were combined with available density data to obtain the isentropic compressibilities.

Introduction

The experimental data of the speed of sound for CCl_3F under saturated liquid have been represented by a quadratic function of temperature T by Aziz (*1*) and by Chávez et al. (*2*). These equations show a positive curvature and decrease continuously with increasing temperature, and extrapolated for higher temperatures predict a zero sound speed at 570.76 and 539.78 K. However, from the relation of speed of sound W with isentropic compressibility β_s and saturated density ρ_σ

$$W^2 = (\beta_s \rho_\sigma)^{-1} \tag{1}$$

a value of zero is expected for W at the critical temperature T_c = 471.15 K (*3*).

In this paper new measurements of the speed of sound from triple point temperature up to near-critical temperature (T/T_c = 0.97) are presented. Typical experimental results are depicted in Figure 1. These data show a positive curvature at low temperatures as found previously, an inflection point around 343.5 K, and a negative curvature at higher temperatures with a general trend toward $W = 0$ at T_c. An empirical equation having seven parameters was required to mathematically represent our data within the expected uncertainty and gives a zero speed of sound at T_c.

Experimental Procedure

The speed of sound was measured by using the pulse echo overlap (PEO) method as developed by Papadakis (*4*). This technique and the apparatus are described in an earlier paper (*5*). Measurements were made by using two plane parallel 10-MHz X-cut quartz crystals (2.54 cm in diameter) pressed to the end of a tubular stainless-steel spacer by two electrode springs. The spacer has a length of $d = 9918 \pm 1$ μm. The emitter crystal was forced to vibrate between 3 and 12 MHz by an electrical pulse. The excitation frequency of the crystal was 1/100 or 1/1000 of the triggering repetition frequency of the x axis of the scope. The repetition frequency f is the reciprocal of the round trip travel time of the acoustic pulse through the fluid and it is used to calculate the speed of sound by

$$W = 2df \tag{2}$$

For measurements of speed of sound below room temperatures, it was found that keeping the sample cell in a bath at 162 K for more than an hour did not decrease the temperature of the liquid in the cell below 162.683 K. This constant temperature in the liquid probably arrises because the triple point temperature T_t was attained and some liquid had been solidified. The only datum of the T_t for CCl_3F seems to be that of Osborne et al. (*6*) published in 1941. They define 0 °C = 273.16 K; therefore T_t has to be diminished by 0.01 K according to the actual definition of 0 °C. Taking the correction of the IPTS-48 to IPTS-68 the values of T_{t-48} have to be increased by approximately 0.01 to give T_{t-68} = 162.68 ± 0.05 K which is in good agreement with our measurement.

On the other hand, in the initial run, after measurements above room temperatures to about 434 K, the cell was opened and white solid deposits (probably chlorine) were found on the quartz crsytals and internal walls of the cell. Also the liquid had a light brown color. We believe this was an electrolytic effect at high temperatures. Trying to avoid the former effect we conducted four additional runs as follows. The voltage applied to the emitting crystal was decreased from 130 to 70 V. The excitation frequency was reduced from 1/100 to 1/1000 of the triggering repetition frequency. Then, although the temperature of the liquid was increased to 460 K, no changes in the liquid were observed, and only a very small amount of the white deposits was found in the cell.

The uncertainty in the speed of sound measured with the PEO method is estimated to be less than 0.05%. However, near the critical temperature the signal on the oscilloscope is very small. The right overlapping criteria of the pulse and the remaining echo become difficult to distinguish, and the uncertainty is several times bigger.

In each run, each datum was measured at two or more frequencies, using in total five frequencies between 3 and 12 MHz. From a preliminary analysis, no dispersion of the data was observed in all the vapor pressure curve. Therefore only two measurements made at essentially the same temperature measured at two different frequencies, where the signal on the oscilloscope was clear, are reported.

Temperature was measured by using a platinum resistance thermometer calibrated on the IPTS-68. This thermometer was located in a thermowell inside the sample cell in contact with the liquid. The temperature could be maintained within ±0.005 K during the measurements. The fluid sample was obtained by successively degassing and freezing commercially available

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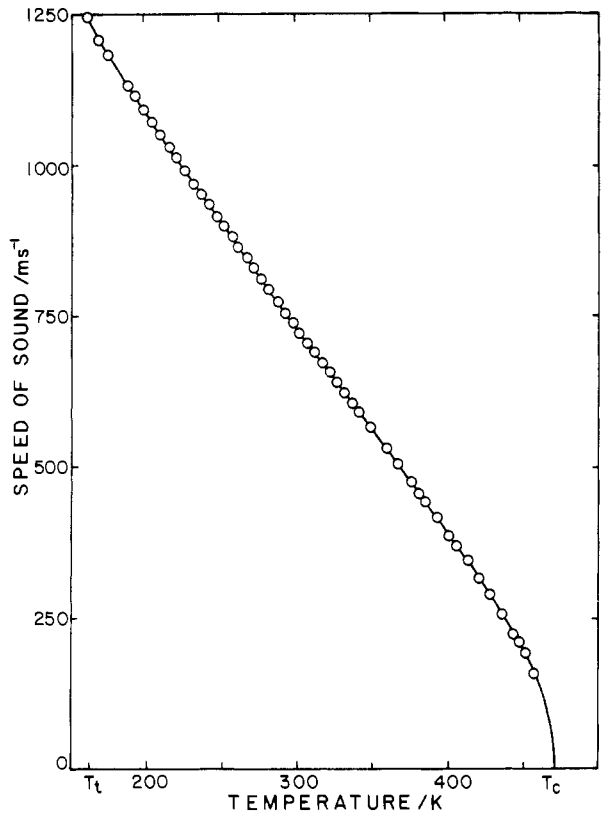

Figure 1. Speed of sound in saturated liquid CCl_3F as a function of temperature: O, experimental data; —, eq 3.

industrial trichlorofluoromethane. A minimum purity of about 99.5% is expected from the agreement of the present data and the previous data set (*2*) where the purity of the sample used was better than 99.5% according to chromatographic analysis.

Results and Discussion

The sound speeds data were fitted to an equation of the form

$$W_{calcd} = (1 - T/T_c)^{\alpha} \sum_{i=0}^{5} b_i T^i \qquad (3)$$

where T is the absolute temperature and the critical temperature T_c has been taken as 471.15 K (*3*). The expression $(1 - T/T_c)$ forces W_{calcd} to attain the value zero at $T = T_c$. The exponent α was first chosen by trial and error and the coefficients b_i were found by an unweighted least-squares method. The coefficients obtained are $b_0 = 2088.061\,192$, $b_1 = -4.812\,220\,910$, $b_2 = 9.193\,607\,744 \times 10^{-3}$, $b_3 = -2.371\,428\,315 \times 10^{-5}$, $b_4 = 4.471\,461\,46 \times 10^{-8}$, $b_5 = -4.242\,877\,489 \times 10^{-11}$, and $\alpha = 0.39$. The number of digits in these coefficients are given in order to reproduce the tables and are not all necessarily significant. Increasing the number of parameters showed no signifcant improvement in the fit. Measured values are tabulated together with the percent differences in Table I. Deviations of the data from eq 3 appear to be random, and except near the critical point, they are less than the estimated experimental uncertainty of 0.05% as indicated in Figure 2.

Equation 3 was compared with the equation fitted to the data measured previously in this laboratory (*2*) with the pulse echo superposition (PES) technique. From 248 to 339 K the agreement is within the expected experimental error of 0.05%. However, in the last 10 K (340–350 K) the differences increases up to 0.2% as shown in Figure 3. We have shown previously (*7*) an agreement between the PES and PEO methods, used in the two data sets, within about 0.04% and therefore do not account for the differences. In the first data set by the PES method, the high sound attenuation prevented us from making measurements above 350 K. The PEO method permits measurements at higher temperatures because of the high energy input (about 100 times bigger) to the emitting crystal

Table I. Speed of Sound W_{exptl} in Saturated Liquid CCl_3F and Percent Deviation[a]

T/K	W_{exptl}/(m·s^{-1})	$100\Delta W/W$	T/K	W_{exptl}/(m·s^{-1})	$100\Delta W/W$
162.683	1248.6	−0.000	328.112	639.6	0.001
162.686	1248.5	−0.012	333.175	622.5	−0.013
162.691	1248.5	−0.004	333.176	622.5	−0.003
162.692	1248.3	−0.022	338.165	605.8	0.000
171.024	1213.8	−0.014	338.165	605.8	0.000
171.051	1213.7	−0.013	342.846	590.0	−0.008
176.857	1190.2	0.012	342.846	590.0	−0.008
176.861	1190.3	0.022	347.950	572.9	−0.011
189.168	1140.6	0.016	347.951	572.9	−0.010
189.346	1140.2	0.043	349.790	566.9	0.013
194.485	1119.4	0.005	349.804	566.8	0.004
194.485	1119.4	0.005	352.867	556.4	−0.006
200.160	1097.1	0.003	352.873	556.4	−0.002
200.170	1097.0	0.003	359.865	532.9	−0.012
205.851	1075.0	0.003	359.879	532.9	−0.003
205.853	1075.0	0.004	363.549	520.4	−0.016
211.109	1054.6	−0.004	363.554	520.4	−0.023
211.112	1054.6	−0.004	368.301	504.5	0.004
216.599	1033.4	−0.027	368.311	504.4	−0.009
216.618	1033.5	−0.020	370.713	496.3	−0.003
221.515	1015.1	−0.001	370.714	496.2	−0.017
221.696	1014.6	0.013	373.016	488.5	−0.008
226.896	994.9	−0.004	373.028	488.4	−0.010
226.906	994.9	−0.004	377.274	474.2	0.028
232.506	973.9	−0.015	377.276	474.2	0.029
232.510	974.0	−0.007	382.327	456.8	0.014
237.647	954.9	−0.022	382.328	456.8	0.015
237.648	955.0	−0.010	386.232	443.4	−0.001
242.749	936.2	−0.018	386.234	443.4	0.001
243.029	935.2	−0.024	388.675	434.9	−0.022
247.944	917.4	−0.017	388.680	434.8	−0.034
247.948	917.2	−0.027	391.952	423.7	0.013
252.873	899.5	−0.019	391.953	423.7	0.014
252.883	899.4	−0.031	392.686	421.2	0.031
253.506	897.4	−0.002	393.308	418.8	−0.033
253.512	897.4	−0.004	396.851	406.4	−0.035
257.829	881.8	−0.015	396.852	406.4	−0.035
257.836	881.9	−0.004	402.514	386.5	−0.033
262.749	864.4	−0.007	402.517	386.5	−0.030
262.754	864.3	−0.008	407.131	370.2	0.004
263.628	861.3	−0.004	407.136	370.2	0.008
263.633	861.2	−0.008	408.611	364.7	−0.045
267.620	847.1	−0.002	408.614	364.8	−0.017
267.626	847.1	−0.001	412.790	349.9	0.036
271.260	834.6	0.026	412.799	349.9	0.039
272.454	830.3	0.014	417.626	332.3	0.044
273.031	828.4	0.030	417.630	332.2	0.037
277.333	813.0	−0.005	420.958	319.9	0.040
277.347	813.0	0.003	420.959	319.8	0.022
282.193	796.1	0.001	421.608	317.2	−0.028
282.196	796.1	−0.000	421.608	317.2	−0.028
288.253	775.4	0.038	425.280	303.5	0.024
288.257	775.4	0.039	425.267	303.5	0.005
293.530	756.8	−0.015	429.103	288.6	−0.052
293.532	756.8	−0.014	429.104	288.6	−0.050
298.366	740.6	0.031	430.048	285.0	−0.033
298.367	740.6	0.033	430.070	284.9	−0.024
303.116	724.2	0.012	434.142	269.0	0.043
303.121	724.3	0.021	434.145	269.0	0.048
308.254	706.8	0.019	437.439	255.5	−0.031
308.258	706.8	0.025	444.636	224.9	−0.108
313.356	689.3	−0.009	444.637	224.9	−0.106
313.357	689.3	−0.010	447.862	211.1	0.125
318.230	673.0	0.014	447.870	211.1	0.143
318.234	673.0	0.017	452.104	191.3	0.253
323.014	656.7	−0.006	452.104	191.3	0.253
323.015	656.7	−0.005	457.719	161.0	−0.484

[a] $100(W_{exptl} - W_{calcd})/W_{calcd}$; W_{calcd} from eq 3.

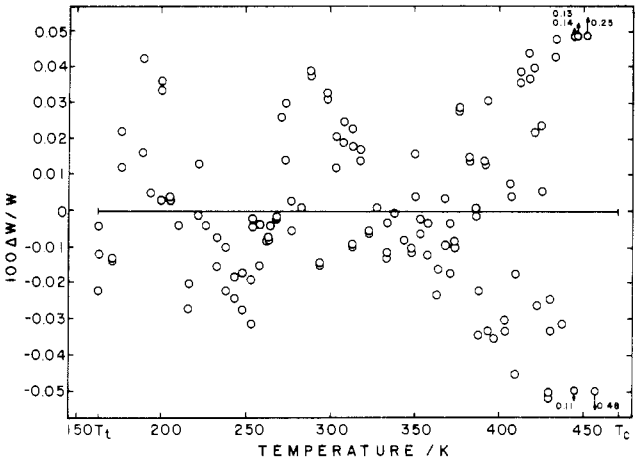

Figure 2. Plot of the deviation of sound speeds in saturated liquid CCl_3F compared with values calculated from eq 3.

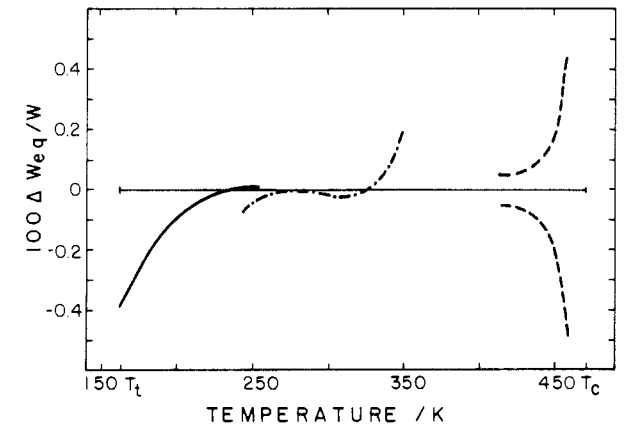

Figure 3. Comparison of sound speeds in saturated liquid CCl_3F against eq 3: —, Aziz; -·-·, Chávez et al.; – – –, this work near critical temperature. $\Delta W_{eq} = W - W_{calcd}$.

which sends the vibrations through the liquid to the receiving crystal. We believe the differences in the sound speed measurements are the reusits of the inherent difficulties associated with measurements under large sound attenuation. As the sound attenuation increases, the right superposition of the pulse and the remaining echo becomes increasingly more difficult to distinguish on the oscilloscope and the uncertainty increases, and this affected our previous data around 350 K.

Aziz (*1*) reported a least-squares regression of his experimental data for the speed of sound for CCl_3F measured from near triple point to 257 K by a resonance technique. The reported uncertainty in his data is ±0.1%. The percent differences of his equation from eq 3 are shown in Figure 3. Above about 200 K the agreement is within 0.1%. However for lower temperatures the differences increase as the temperature decreases. His sound speed values are lower than those from eq 3 with a maximum difference of about 0.4% near the triple point temperature. We cannot give an explanation for the differences.

Also in Figure 3 we have drawn with dashed lines the envelopes for the deviation of our data from eq 3. These give a measure of the uncertainty of the data and of the problems found in fitting data near critical temperatures.

Equation 3 has been combined with the orthobaric densities reported by Spencer and Adler (*3*) to calculate adiabatic compressibilities. Adiabatic compressibilities are reported in Table II at 10 K intervals.

Table II. Speed of Sound W_{calcd} Calculated from Eq 3, Saturated Density, and Derived Values of the Isentropic Compressibility β_s in Saturated Liquid CCl_3F

T/K	W_{calcd}/(m·s^{-1})	ρ/(g·cm^{-3})	β_s/GPa^{-1}
162.68	1248.6	1.757	0.3651
170	1218.2	1.7432	0.3866
180	1177.3	1.7243	0.4184
190	1137.1	1.7052	0.4536
200	1097.7	1.6858	0.4923
210	1058.9	1.6661	0.5353
220	1020.8	1.6461	0.5830
230	983.4	1.6258	0.6361
240	946.4	1.6051	0.6955
250	910.1	1.5840	0.7622
260	874.2	1.5626	0.8374
270	838.8	1.5407	0.9226
280	803.8	1.5183	1.0195
290	769.1	1.4955	1.1305
300	734.8	1.4720	1.2582
310	700.7	1.4480	1.4065
320	666.9	1.4233	1.5798
330	633.2	1.3979	1.7842
340	599.6	1.3716	2.0277
350	566.1	1.3444	2.3213
360	532.5	1.3161	2.6800
370	498.7	1.2866	3.1250
380	464.7	1.2557	3.6876
390	430.4	1.2231	4.4145
400	395.5	1.1884	5.3797
410	359.9	1.1512	6.7061
420	323.3	1.1107	8.6127
430	285.3	1.0659	11.5282
440	245.0	1.0148	16.4164
450	200.9	0.9537	25.9801
460	148.6	0.8727	51.9142

Registry No. CCl_3F, 75-69-4.

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