MEASUREMENT OF THE SPEED OF SOUND IN THE VAPOR OF FREON 113 AND DIETHYL ETHER

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The speed of sound is a thermophysical characteristic widely used directly in calculations on thermodynamic processes. If the speed has been measured, one can deduce the specific heats at constant volume and pressure, etc. The speed can also be used to calculate or revise the individual constants in the equation of state.

Here we report measurements of the speed of sound as a function of temperature and pressure from normal conditions up to the critical points for freon 113 ($C_2Cl_3F_3$) and diethyl ether ($C_4H_{10}O$).

The measurements were made at 500 kHz with an acoustic interferometer modified from [1-3] to suit operation at boiling points exceeding room temperature. The vessel for preparing the vapor, the pressure gauge, and all the handling valves were mounted in a single unit.

The high sensitivity of the interferometer was retained throughout the temperature and pressure ranges by mounting the quartz plate in the neutral plane in a holder of chuck type.

The interferometer unit was placed in a TS-24 liquid thermostat controlled to ±0.05°. The actual temperature fluctuations in the working medium were much less because a massive block was used. The temperature was monitored to ±0.02°C with a standard platinum thermometer (R_0 = 10 Ohm) and a R-307 potentiometer. A PM-60 piston gauge (grade 0.05) was used above 5 bar, while the range 2-5 bar was covered by a mercury U-tube. The bellows-type pressure transducer had a limit of detection of 1 mm Hg.

The calculated total error in the speed was 0.1% in the superheating region and 0.2% on the saturation line. The spread of the observed points fell within these limits.

The following substances were examined:

Freon 113

Boiling point 47.4°C at 760 mm Hg
Final distillation temperature 48°C at 760 mm Hg
Nonvolatile residue 0.003%
No free chlorine
No acids

Diethyl Ether

Boiling point 35°C at 760 mm Hg
No acid, SO_2, H_2O_2, or aldehydes
Nonvolatile residue 0.007%

The substances before use were additionally dried by passage through silica gel. The autoclave was evacuated to 10^{-3} mm Hg with a VN-1MG pump.

In measuring the speed of sound on the saturation line, we obtained incidentally values for p_s and t_s (saturation pressure and temperature) between 20 and 212°C. The results agreed well with those of [4], which provides an indirect confirmation of the accuracy and parity.

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TABLE 1. Speed of Sound as a Function of Pressure for Freon 113

p, bar	c, m/sec
$T = 320.56$° K	
0.25	122.6
0.312	122.2
0.402	121.8
0.453	121.61
0.564	120.88
0.723	120.16
0.807	119.77
0.816	119.77
0.847	119.3
1.00	119.3
$T = 342.56$° K	
0.063	127.6
0.095	127.5
0.163	126.93
0.205	126.5
0.208	126.87
0.292	126.6
0.397	126.0
0.385	126.1
0.518	125.89
0.707	124.4
1.14	123.4
1.596	121.75
1.841	121.5
1.935	121.23
$T = 362.46$° K	
0.094	130.9
0.165	130.56
0.227	130.34
0.308	130.17
0.360	129.8
0.418	129·9
0.584	129.3
0.775	128.85
1.054	127.9
1.316	127.13
1.343	126.83
1.705	125.69
1.966	124.9
2.4	123.4
2.74	122.2
3.00	120.8
3.4	120.2
$T = 382.16$° K	
0.245	133.8
0.513	133.0
0.756	132.35
1.145	131.4
1.546	130.16
2.08	128.6
2.465	127.4
2.905	126.23
3.305	124.8
3.745	123.34
4.205	121.74
4.565	120.98
5.0	119.5
5.325	118.03
$T = 403.56$° K $f = 500$ kHz	
0.237	137.4
0.525	136.58
0.836	136.11
1.155	135.33
1.513	134.38
1.936	133.41
2.577	131.65
3.08	130.45
3.54	129.23
4.08	127.86
4.54	126.65
5.25	124.5
5.83	123.1
6.216	122.34
6.7	120.75
7.1	119.49
7.436	118.4
7.72	117.6
$T = 403.56$° K $f = 900$ kHz	
0.0435	143.97
0.056	140.56
0.058	140.26
0.069	138.95
0.0725	139.6
0.087	138.4
0.193	138.3
0.215	137.9
0.415	137.3
1.046	135.75
1.63	134.25
2.31	132.56
3.33	129.67
4.51	126.8
5.58	123.8
6.55	120.7
7.49	118.4
$T = 422.96$° K	
0.504	140.1
1.1	138.7
2.027	136.8
3.107	134.56
3.9	132.5
4.97	130.38
6.067	127.77
7.027	125.35
8.01	122.58
8.99	119.9
10.267	115.85
11.067	113.05
11.457	118.83
11.98	110.22
12.13	110.12
12.207	109.81
$T = 443.26$° K	
1.17	142.9
2.16	140.7
3.49	138.1
4.92	135.56
6.57	132.2
8.14	128.5
8.42	125.6
10.95	121.8
12.37	117.96
13.93	113.4
15.25	109.1
16.13	105.7
16.67	103.8
17.13	102.9
$T = 463.76$°K	
1.075	146.99
2.136	145.0
3.536	142.8
5.066	140.1
7.046	136.1
8.84	132.8
11.23	128.35
13.45	123.35
15.27	118.86
16.61	115.8
19.23	108.27
20.77	103.1
22.03	97.55
23.07	94.1
23.45	91.97
23.89	90.3

The apparatus was also first checked on nitrogen and helium, and checks during the measurements were made with argon.

Tables 1 and 2 give the results, which were recorded at 500 kHz.

A transmitter-receiver system was also used at 900 kHz with freon 113 at 130°C with pressure variation in order to establish the limits to the equilibrium thermodynamic speed of sound. The output signal from the receiving quartz crystal was recorded by an ÉPPV-60 potentiometer recorder.

The range in f/p was 1-85 MHz/bar.

Figure 1 shows the results. The solid line has been calculated from

$$\left(\frac{c}{c_0}\right)^2 = 1 + R\,\frac{C_{v_0} + (\omega\tau)^2 C_{v\infty}}{C_{v_0}^2 + (\omega\tau)^2 C_{v\infty}^2} \qquad (1)$$

TABLE 2. Speed of Sound in Diethyl Ether

p, bar	c, m/sec
$T = 320.56^\circ$ K	
0.25	196
0.4313	194.5
0.637	192.5
1.1015	190.1
1.462	188.2
1.71	187.2
$T = 342.78^\circ$ K	
0.2091	202.6
0.591	200.2
1.055	197.9
1.636	194.8
2.225	190.5
2.585	189.0
2.985	187.6
$T = 362.5^\circ$ K	
0.215	208.3
0.6260	206.1
1.22	203.5
1.94	200.1
2.48	197.6
2.895	196.0
3.5	193.17
4.195	189.7
4.605	187.7
5.07	186.2
$T = 382.86^\circ$ K	
0.257	213.4
1.025	210.6
2.025	206.4
3.155	201.8
4.04	199.0
4.825	195.5
6.125	189.3
6.95	185.3
7.595	182.6
8.03	179.8
$T = 403.96^\circ$ K	
0.363	218.4
1.0821	216.73
1.967	213.62
3.48	209.1
5.017	203.1
6.06	200.5
7.05	196.0
7.76	192.66
8.57	190.4
9.55	185.3
10.15	184.0
10.65	181.8
11.9	173.9
12.01	172.26
$T = 423.56^\circ$ K	
0.385	223.47
1.43	220.24
3.43	215.67
5.41	208.4
5.9	208.0
8.03	199.86
9.9	195.0
10.4	195.87
11.9	189.6
13.3	181.99
14.9	175.28
16.42	166.0
17.48	161.99
17.8	160.28
180.2	156.9
$T = 444.36^\circ$ K	
0.32	229.8
1.335	227.46
2.29	225.3
4.85	220.1
5.5	215.3
8.25	210.59
10.7	202.32
13.53	193.67
15.1	189.63
16.57	184.8
19.2	174.0
20.1	171.5
21.25	165.19
22.54	157.1
23.03	153.9
24.0	145.4
25.0	136.0

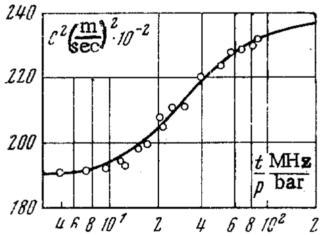

Fig. 1

Here c_0 is the speed of sound at zero frequency, ω is the working frequency, τ is relaxation time, C_{V0} is the specific heat at constant volume at low frequencies, $C_{V\infty}$ is the same at high frequencies, and R is the gas constant.

The result for the relaxation time for the vibrational degrees of freedom was

$$\tau^* = 3 \cdot 10^{-8} \text{ sec}$$

Figure 1 shows that the dispersion in the speed lies within the limits of error of measurement even at p = 0.05 bar.

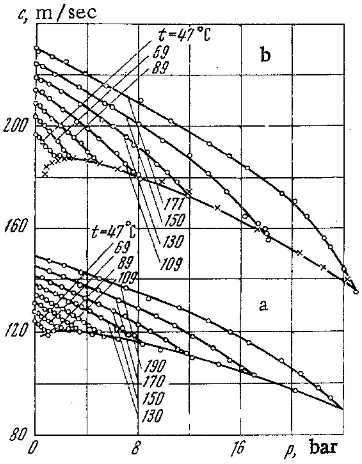

Fig. 2

The relaxation time for diethyl ether is given [5] as

$$\tau^* = 6.6 \cdot 10^{-8} \text{ sec}$$

which corresponds to the onset of appreciable dispersion for $p \leq 0.1$ bar.

The following are results for k_0 (the adiabatic constant at low pressures) and k_{0p} (the value deduced from the C_p^0 from [4]):

t° C =	47	69	89	109	130	150	170
k_{0p} =	1.085	1.072	1.068	1.065	1.061	1.058	1.054
k_0 =	1.086	1.073	1.068	1.067	1.061	1.058	1.055
k_{0p} =	1.0715	1.071	1.069	—	—	—	—
k_0 =	1.072	1.069	1.067	1.063	1.061	1.059	1.057

The first two lines relate to $C_4H_{10}O$ and the second two to $C_2Cl_3F_3$. The discrepancies do not exceed 0.2%, which corresponds to 0.1% difference in the speed of sound. This all indicates that there is no dispersion for either substance for $p > 0.1$ bar and that the thermodynamic speed of sound applies.

The results were processed by computer to find the speed of sound as a function of the density and the virial coefficients in the equation of state:

$$\left(\frac{c}{c_0}\right)_T^2 = 1 + 2\rho\left[B + T(k_0-1)\frac{dB}{dT} + \frac{T^2(k_0-1)^2}{2k_0}\frac{d^2B}{dT^2}\right] + \rho^2\left[\frac{(2k_0+1)}{k_0}C + \frac{T(k_0^2-1)}{k_0}\frac{dC}{dT} + \frac{T^2(k_0-1)^2}{2k_0}\frac{d^2C}{dT^2}\right] \tag{2}$$

Here c_{0T} is the speed of sound at constant temperature for zero pressure, c_T is the actual speed at constant temperature, ρ is density, k_0 is as above, B is the second virial coefficient, and C is the third one.

The virial coefficients were calculated from the Lennard-Jones potential [6], which was chosen on the basis that the molecules of $C_2Cl_3F_3$ and $C_4H_{10}O$ are nearly spherical. This assumption is reasonable because the calculated and observed speeds agree closely.

The coefficients in the polynomials

$$B = A_{11} + \frac{A_{21}}{T} + \frac{A_{31}}{T^2}\left(\frac{\mathrm{m}^3}{\mathrm{kg}}\right),\quad C = A_{12} + \frac{A_{22}}{T} + \frac{A_{32}}{T^2}\left(\frac{\mathrm{m}^3}{\mathrm{kg}}\right)^2$$

were calculated as

$A_{11}\cdot 10^6$	$A_{21}\cdot 10^4$	$A_{31}\cdot 10^2$	$A_{12}\cdot 10^8$	$A_{22}\cdot 10^6$	$A_{32}\cdot 10^4$
—0.133868	1.40925	—4.1762	—0.4454	4.07464	—9.56721
3361.08	—29335.4	10260.8	—1702.68	22813.1	—79773.3

The first line is for $C_4H_{10}O$ while the second is for $C_2Cl_3F_3$.

Figure 2a shows eight isotherms used in comparing the calculated and observed speeds as functions of p and T for freon 113, while Fig. 2b shows seven for diethyl ether. Each isotherm has 11 points.

The circles in Figs. 1 and 2 denote the observed values, while the solid lines are calculated values and the crosses are results from [3].

The discrepancies are largest near the saturation line and increase as the critical point is approached, but they do not exceed 0.9% in the region covered by the calculations.

The larger discrepancies near the saturation line may be ascribed to molecular association [7], which is not taken into account in the Lennard-Jones potential.

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