MEASUREMENT OF THE SPEED OF SOUND AND CALCULATION OF ENTROPY IN FREON-11

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As shown in [1, 2], a very promising method of constructing the entropy diagrams for unfamiliar substances, such as most freons, is that based on the speed of sound and density.

However, there are no data on the speed of sound in freons. The existing data on the speed of sound in the superheated vapors of other substances usually embrace regions located either to the right-hand side or to the left-hand side of the maximum in the saturated vapor (in speed of sound-temperature coordinates). However, to get a clear picture of the dependence of the speed of sound on the parameters of state we need data in both these regions at the same time. Accordingly, we have measured the speed of sound in saturated and superheated freon-11 (CF_3Cl) vapor over a broad range of the parameters of state.

An apparatus for measuring the speed of sound in water and mercury vapor using standing waves in a resonator was described in [3, 4]. On the basis of this apparatus we designed a special system for investigating the speed of sound in saturated and superheated freon vapor. The temperature range was considerably expanded, the control of the temperature field improved, and the accuracy of the temperature, pressure, and frequency measurements refined. The transducers, the resonator, the autoclave and the general block diagram remained essentially as before. In order to cover a broad temperature range (from −40 to +400° C) the apparatus was divided into three sections: the first for operating at temperatures from −40 to +20° C, the second for 20–200° C, and the third for 200–400° C. In the first and third sections, the autoclave containing the resonator was placed in a horizontal copper block 770 mm long, with inside and outside diameters of 100 and 150 mm, respectively. Five differential thermocouples were positioned along the length of the copper block to monitor the uniformity of the temperature field.

In the first section, the autoclave and the surrounding copper sleeve were surrounded by thermal insulation. By means of a special funnel, liquid nitrogen is introduced into the space between the insulation and the copper block to obtain negative temperatures. The temperature was regulated and equalized by varying the amount of nitrogen introduced, and also by means of a series of electric heaters distributed along the length of the block. In the third section, one main and several auxiliary electric heaters, intended for equalizing the temperature field, were wound along the length of the copper block. A layer of asbestos served to insulate the apparatus from the ambient medium.

In working with the first and third sections, the maximum temperature difference between different points on the copper block did not exceed 0.1–0.2° C. In the second section, the autoclave and resonator were arranged vertically and placed in an oil bath. The autoclave temperature was equalized by stirring the oil. Each section was monitored by the filling and pressure-measuring system.

The temperature in the autoclave was measured with a platinum resistance thermometer or a set of mercury thermometers graduated in 0.1° C. Pressures below atmospheric were measured with a class 0.5 reference vacuum gauge with a correction for barometric pressure.

Pressures above atmospheric were measured with a class 0.05 MP-60 plunger manometer combined with a reference manometer. The latter served to cover the interval between adjacent pressure values corresponding to two neighboring values of the standard weights of the plunger manometer. Structurally, the differential manometer consisted of a chamber with a viewing window connected with the plunger manometer and, inside the chamber, a class 0.35 reference manometer connected with the autoclave. Before the test substance was introduced, the entire system was carefully flushed and evacuated to a pressure of 10^{-2} mm Hg.

The speed of sound was measured as follows. By varying the frequency of the af oscillator, we obtained 10–15 maxima on the oscillograph, each of which corresponded to a standing wave. In our case, the measurements were made principally at frequencies from 1000 to 2000 Hz. The frequency was measured with a ChZ-4 frequency meter. The speed of sound was determined from the formula

$$c = \frac{2Lf}{n} \quad (1)$$

Table 1

Speed of Sound c (m/sec) in Saturated Freon-11 Vapor as a Function of Temperature t (°C)

t	c	t	c	t	c
−40.0	126.0	40.0	138.6	145.0	127.0
−35.0	127.1	50.0	139.2	150.0	125.0
−30.0	128.2	60.0	139.5	155.0	122.6
−25.0	129.1	70.0	139.5	160.0	120.2
−20.0	130.0	80.0	139.2	165.0	117.6
−15.0	130.9	90.0	138.5	170.0	114.7
−10.0	131.8	100.0	137.4	175.0	113.1
−5.0	132.7	110.0	136.2	180.0	107.7
0.0	133.6	120.0	134.3	185.0	103.5
5.0	134.4	125.0	133.2	190.0	98.8
10.0	135.2	130.0	132.0	195.0	93.5
20.0	136.7	136.0	130.5	196.0	92.1
30.0	137.8	140.0	128.8	197.0	90.2
				193.0	87.0

Table 2

Speed of Sound c (m/sec) in Superheated Freon-11 Vapor on Isotherms t (°C) as a Function of the Pressure p (kgf/cm^2)

p	c
$t = 193.0$	
0	177.1
4.0	172.4
8.0	167.3
12.0	161.9
16.0	156.5
20.0	150.5
24.0	143.7
28.0	136.7
32.0	128.8
36.0	120.1
40.0	109.8
42.0	102.6
43.0	97.5
44.0	89.5
44.15	87.0
$t = 195.0$	
0	176.6
4.0	171.8
8.0	166.6
12.0	161.2
16.0	155.7
20.0	149.8
24.0	143.0
28.0	135.8
32.0	127.7
36.0	120.1
38.0	115.2
40.0	109.8
41.0	101.0
42.0	96.3
42.6	93.6
$t = 190.0$	
0	175.6
4.0	170.6
8.0	167.3
12.0	159.8
16.0	154.1
20.0	147.8
24.0	140.7
28.0	133.1
32.0	124.1
36.0	112.8
38.0	106.2
39.0	101.8
39.45	99.2
$t = 180.0$	
0	173.8
4.0	168.3
8.0	162.5
12.0	156.7
16.0	150.4
20.0	143.3
24.0	135.1
28.0	125.4
32.0	114.2
33.0	111.2
34.0	108.1
$t = 168.0$	
0	171.4
4.0	165.6
8.0	159.5
12.0	152.9
16.0	145.5
20.0	137.2
24.0	127.7
26.0	132.4
28.15	116.3

p	c
$t = 153.8$	
0	168.8
4.0	162.6
8.0	155.8
12.0	148.3
16.0	140.0
20.0	130.3
21.0	127.5
22.15	124.2
$t = 139.3$	
0	166.0
4.0	159.3
8.0	151.8
12.0	143.3
16.0	133.7
17.65	129.4
$t = 124.3$	
0.0	163.1
4.0	155.8
8.0	147.2
10.0	142.5
12.0	137.3
13.4	133.6
$t = 109.5$	
0	160.1
1.0	158.5
3.0	154.6
5.0	150.0
7.0	145.0
9.0	139.5
10.2	136.2
$t = 99.1$	
0.0	158.0
2.0	153.9
4.0	149.2
6.0	143.8
7.0	141.0
8.2	137.5
$t = 84.8$	
0.0	155.0
1.0	153.0
2.0	150.7
3.0	148.2
4.0	145.5
5.0	142.4
6.0	138.9
$t = 69.6$	
0.0	157.9
1.0	149.7
2.0	147.1
3.0	143.7
4.0	139.8
4.1	139.5
$t = 61.6$	
0.0	150.2
1.0	147.6
2.0	144.5
3.0	140.8
3.3	139.5

p	c
$t = 50.9$	
0.0	147.9
1.0	144.7
2.0	140.9
2.3	139.2
$t = 35.6$	
0.0	144.6
0.5	143.9
1.0	141.5
1.2	140.2
1.5	138.3
$t = 20.0$	
0.0	140.8
0.15	140.6
0.30	140.4
0.45	140.0
0.60	139.3
0.75	138.4
0.85	137.4
0.90	136.9
$t = 10.0$	
0.0	138.7
0.10	138.6
0.20	138.4
0.30	138.2
0.40	137.8
0.50	137.1
0.60	135.7
0.62	135.1
$t = 0.0$	
0.0	136.3
0.10	136.2
0.20	135.9
0.30	135.4
0.40	133.9
0.41	133.4
$t = -10.0$	
0.0	134.0
0.10	133.8
0.15	133.6
0.20	133.2
0.25	132.3
0.26	131.8
$t = -20.0$	
0.0	131.5
0.05	131.4
0.10	131.2
0.15	130.6
0.16	130.0
$t = -30.0$	
0.0	129.1
0.025	129.1
0.05	129.0
0.075	128.8
0.094	127.9

where c is the speed of sound in m/sec, L is the distance between the speaker and the microphone diaphragms in m, f the frequency of the sound waves in Hz, and n the number of half-waves in the resonator.

The distance L was determined from the speed of sound in air. The air was first passed through silica gel to remove traces of moisture. The distance L was then found to be 553 mm. This value was also used in the calculations. The speed of sound in air was calculated from the formula $c = 20.0067\ T^{1/2}$. The distance L was also measured directly and found to be 551.5 mm. The values of f/n obtained at different frequencies were averaged. The maximum deviation may be 1% and sometimes slightly more. However, as a rule the mean deviation does not exceed 0.3–0.5%. In order to obtain thermodynamic equilibrium, before the measurements were made the temperature in the autoclave was kept constant to within 0.1° C for 20–30 min. The freon-11 was subjected to a chromatographic analysis. No impurities were found. The speed of sound was measured on the apparatus for the temperature interval from −40 to +200° C and on the pressure interval from 0.05 to 43 kg/cm^2. Altogether 200 experimental points were recorded. Measurements of the speed of sound only in the superheated vapor were made along the isotherms. Graphic interpolation was used in analyzing the data. The mean deviation was 0.4%. From a previously obtained theoretical formula [5], we calculated values of the speed of sound in the saturated vapor which coincided with the measured values correct to 1%. The results for saturated vapor are presented in Table 1, those for superheated vapor in Table 2.

The results were used to calculate the entropy of freon-11 by the method described in [1]. It was found that the starting points of the isentropes for freons cannot be taken on the saturation line, as recommended in [1], since, in t-s coordinates, the saturation line is too steep. Therefore, as starting points, it was necessary to take values of the entropy on one of the isobars. It is simplest to do this for the isobar corresponding to the lowest pressure; in this case, the gas is close to perfect and the entropy calculation presents no difficulties. As starting values we took the entropy values on the 0.0703 kg/cm^2 isobar [6]. From the data on the speed of sound and density data taken from [6] we calculated values of the entropy for pressures up to 14 kg/cm^2. The results are presented in Tables 3 and 4. The calculated values of the entropy differ from the known values [6] by not more than 0.5% over the entire region of the parameters of state.

Table 3

Values of the Entropy S (kJ/kgf·deg) for Freon-11 on Isobars p (kgf/cm^2) as a Function of the Temperature t (°C)

t	S
p = 0.0703	
−35.0	0.8657
−30.0	0.8762
−20.0	0.8972
−10.0	0.9181
−0	0.9388
10.0	0.9585
20.0	0.9780
30.0	0.9975
40.0	1.0160
50.0	1.0346
60.0	1.0531
70.0	1.0707
p = 0.1406	
−22.56	0.8498
−20.0	0.8558
−10.0	0.8776
0	0.8980
10.0	0.9172
20.0	0.9366
30.0	0.9554
40.0	0.9732
50.0	0.9912
60.0	1.0091
70.0	1.0270
80.0	1.0450
85.0	1.0538
p = 0.2812	
−8.44	0.8368
0	0.8504
10.0	0.8738
20.0	0.8940
30.0	0.9134
40.0	0.9325
50.0	0.9520
60.0	0.9705
70.0	0.9890
80.0	1.0072
90.0	1.0236
100.0	1.0402
105.0	1.0485
p = 0.4218	
0.67	0.8305
10.0	0.8493
20.0	0.8689
30.0	0.8876
40.0	0.9060
50.0	0.9246
60.0	0.9420
70.0	0.9596
80.0	0.9773
90.0	0.9946
100.0	1.0113
110.0	1.0271
120.0	1.0419
130.0	1.0555
p = 0.6327	
10.56	0.8251
20.0	0.8441
30.0	0.8637
40.0	0.8817
50.0	0.8985
60.0	0.9160
70.0	0.9331
80.0	0.9510
90.0	0.9685
100.0	0.9860
110.0	1.0024
120.0	1.0171
130.0	1.0310
140.0	1.0450
145.0	1.0515
p = 0.9842	
22.33	0.8200
30.0	0.8355
40.0	0.8550
50.0	0.8735
60.0	0.8905
70.0	0.9080
80.0	0.9255
90.0	0.9426
100.0	0.9602
110.0	0.9767
120.0	0.9934
130.0	1.0086
140.0	1.0230
150.0	1.0369
160.0	1.0491
165.0	1.0550
p = 1.546	
35.61	0.8167
40.0	0.8260
50.0	0.8455
60.0	0.8640
70.0	0.8812
80.0	0.8980
90.0	0.9142
100.0	0.9309
110.0	0.9465
120.0	0.9626
130.0	0.9774
140.0	0.9920
145.0	0.9995
p = 2.249	
47.67	0.8146
50.0	0.8190
60.0	0.8380
70.0	0.8562
80.0	0.8735
90.0	0.8902
100.0	0.9066
110.0	0.9220
120.0	0.9375
130.0	0.9530
140.0	0.9680
150.0	0.9830
160.0	0.9974
p = 3.515	
63.50	0.8133
70.0	0.8266
80.0	0.8466
90.0	0.8650
100.0	0.8832
110.0	0.8998
120.0	0.9160
130.0	0.9315
140.0	0.9470
150,0	0.9614
160.0	0.9757
170.0	0.9895
175.0	0.9961
p = 5.624	
82.11	0.8129
90.0	0.8280
100.0	0.8466
110.0	0.8654
120.0	0.8820
130.0	0.8980
140.0	0.9141
150.0	0.9300
160.0	0.9450
170.0	0.9600
180.0	0.9745
190.0	0.9886
195.0	0.9960
p = 7.8	
97.2	0.8130
100.0	0.8186
110.0	0.8386
120.0	0.8576
130.0	0.8750
140.0	0.8922
150.0	0.9080
160.0	0.9235
170.0	0.9384
180.0	0.9528
p = 10.545	
111.0	0.8129
120.0	0.8313
130.0	0.8500
140.0	0.8675
150.0	0.8836
160.0	0.8995
170.0	0.9150
180.0	0.9297
190.0	0.9437
195.0	0.9504
p = 14.060	
125.61	0.8121
130.0	0.8204
140.0	0.8381
150.0	0.8548
160.0	0.8705
170.0	0.8855

Table 4

Values of the Entropy S (kJ/kgf·deg) for Freon-11 on Isochores v (m^3/kgf) as a Function of the Temperature t (°C)

t	S
v = 2.0826	
−35.0	0.8657
−30.0	0.8750
−20.0	0.8939
−10.0	0.9127
0	0.9305
10.0	0.9478
20.0	0.9553
30.0	0.9820
40.0	0.9985
50.0	1.0145
60.0	1.0305
70.0	1.0457
75.0	1.0530
v = 1.09249	
−22.56	0.8498
−20.0	0.8549
−10.0	0.8746
0	0.8930
10.0	0.9095
20.0	0.9263
30.0	0.9433
40.0	0.9600
50.0	0.9775
60.0	0.9940
70.0	1.0100
80.0	1.0262
90.0	1.0417
95.0	1.0490
v = 0.57409	
−8.44	0.8368
0	0.8520
10.0	0.8696
20.0	0.8857
30.0	0.9017
40.0	0.9175
50.0	0.9338
60.0	0.9495
70.0	0.9657
80.0	0.9820
90.0	0.9982
100.0	1.0124
110.0	1.0262
120.0	1.0390
130.0	1.0515
v = 0.39405	
0.67	0.8305
10.0	0.8482
20,0	0.8670
30.0	0.8840
40.0	0.9004
50.0	0.9157
60.0	0.9311
70.0	0.9470
80.0	0.9624
90.0	0.9777
100.0	0.9926
110.0	1.0065
120.0	1.0196
130.0	1.0320
140.0	1.0443
145.0	1.0570
v = 0.27056	
10.56	0.8251
20.0	0.8420
30.0	0.8586
40.0	0.8751
50.0	0.8916
60.0	0.9082
70.0	0.9250
80.0	0.9406
90.0	0.9570
100.0	0.9720
110.0	0.9865
120.0	1.0010
130.0	1.0136
140.0	1.0265
150.0	1.0395
160.0	1.0505
v = 0.17942	
22.33	0.8200
30.0	0.8935
40.0	0.8500
50.0	0.8658
60.0	0.8818
70.0	0.8978
80.0	0.9140
90.0	0.9295
100.0	0.9450
110.0	0.9596
120.0	0.9743
130.0	0.9880
140.0	1.0018
v = 0.11774	
35.61	0.8167
40.0	0.8247
50,0	0.8416
60.0	0.8585
70.0	0.8743
80.0	0.8900
90.0	0.9055
100.0	0.9205
110.0	0.9355
120.0	0.9497
130.0	0.9643
140.0	0.9776
150.0	0.9915
160.0	0.9985
v = 0.08278	
47.67	0.8146
50.0	0.8185
60.0	0.8356
70.0	0.8524
80.0	0.8686
90.0	0.8838
100.0	0.8990
110.0	0.9136
120.0	0.9282
130.0	0.9430
140.0	0.9566
150.0	0.9708
160.0	0.9844
170.0	0.9975
v = 0.05426	
63.50	0.8133
70.0	0.8250
80.0	0.8417
90.0	0.8576
100.0	0.8723
110.0	0.8869
120.0	0.9013
130.0	0.9154
140.0	0.9297
150.0	0.9442
160.0	0.9583
170.0	0.9721
180.0	0.9854
190.0	0.9985
v = 0.03449	
82.11	0.8129
90.0	0.8256
100.0	0.8420
110.0	0.8575
120.0	0.8724
130.0	0.8870
140.0	0.9017
150.0	0.9159
160.0	0.9296
170.0	0.9431
180.0	0.9568
v = 0.02490	
97.2	0.8130
100.0	0.8170
110.0	0.8316
120.0	0.8457
130.0	0.8598
140.0	0.8741
150.0	0.8884
160.0	0.9026
170.0	0.9163
180.0	0.9300
190.0	0.9425
195.0	0.9485
v = 0.01840	
111.0	0.8129
120.0	0.8270
130.0	0.8420
140.0	0.8565
150.0	0 8695
160.0	0.8820
165.0	0.8877

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