

SPEED OF SOUND IN FREONS ON THE SATURATION LINE

S. G. Komarov, A. N. Solov'ev, and E. P. Sheludyakov

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The speed of sound propagation in the liquid and vapor phases of freons has hardly been investigated at all so far. Yet data on the speed of sound on the saturation line are of interest both from the practical viewpoint and from the viewpoint of corroborating theoretical ideas, particularly the verification of the formula obtained in [1] for calculation of the speed of sound in saturated vapors. With this aim we carried out investigations for three of the most commonly used freons: F-11, F-12, and F-142.

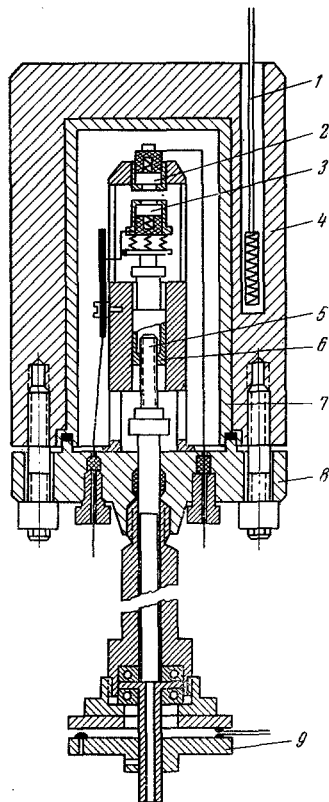


Fig. 1

The most suitable method for the experimental investigation of the speed of sound in a liquid and its saturated vapor in a wide range of temperature, including the critical region, is the ultrasonic interferometer. The method is accurate enough to allow investigations with small amounts of substance and has already been used for similar measurements [2, 3].

In this investigation we used a modification of this method in which the distance was varied and the frequency kept constant.

Figure 1 shows a diagram of the working part of the interferometer. Ultrasonic emitter 3 and receiver 2 (lead titanate zirconate crystals) are mounted on stages with Teflon rings. The lower stage of the emitter is provided with adjusting screws. The receiver is fixed in position, while the emitter can be moved up and down by means of micrometer screw 5 and nut 6. The screw is mounted in two supporting bearings and turned by a PR reversing motor. The insertion of the micrometer screw from below allows considerable reduction in the height of the column of liquid over the investigated volume (from 130 mm in [2] to 12 mm) and this greatly reduces the gravitational effect in measurements in the near-critical region. The time required to move the emitter through the entire height of 19 mm is 19 min. After each half-turn a short pulse from disk contactor 9 is delivered to the measuring circuit. The interferometer is placed in a 900-ml copper autoclave 4

which can withstand a pressure of up to 100 atm abs. The autoclave has stainless steel lining 7 to prevent contact of the investigated substance with the copper. Cover 8 of the autoclave, the connecting lines, and all the fittings are also made of stainless steel. All the gaskets and seals are made of Teflon. Hole 1 is drilled into the autoclave wall, for the temperature sensor. The autoclave in turn is placed in a 80-l oil thermostat, in which the temperature is controlled by a mercury contact thermometer.

A complete block diagram of the apparatus is shown in Fig. 2. An electric signal from G-4-1A generator 1 of frequency 220 kHz, amplified by tuned amplifier 2, is transmitted to ultrasonic emitter 3, where it is converted to an acoustic signal, passes through the investigated medium, and is received by ultrasound receiver 4. The received acoustic signal is again converted to an electrical one, is amplified by tuned amplifier 5, and delivered through detector 6 to an EPP-09 recording potentiometer.

The frequency of the signal is measured by Ch4-1 wavemeter 8. The other numbers on the diagram are: 9) PR motor drive; 10) micrometer screw; 11) resistance thermometer; 12) reversing switch; 13) M 193 milliammeter; 14) R32 resistance box; 15) PMS-48 potentiometer; 16) 100-ohm standard resistance coil; a) to freon cylinder; b) to pump.

The ultrasound emitter moves steadily relative to the receiver. During its motion there is periodically a whole number of half-waves between the emitter and receiver and the voltage on the receiver varies. This variation is recorded by the potentiometer.

An analysis of traces of voltage on the receiver against time showed that the use of the EPP-09 recording potentiometer, despite the large permissible transit time of the recording device, did not introduce any error into the determination of the position of the peak and, hence, was quite justified.

Figure 3 shows a typical trace of receiver voltage against time, obtained in one of the experiments with saturated F-12 vapor ($t = 51.6^\circ \text{C}$, $p = 23.7 \text{ kg/cm}^2$, $f = 222.4 \text{ kHz}$). Each peak (from 1 to 16) on this curve corresponds to a whole number of half-waves. The curve also shows marks (from 1' to 10') of the contactor indicating emitter position, from which the distance between the receiver and emitter for each peak can be found, i.e., the wavelength can be determined.

The autoclave temperature is measured with a resistance thermometer or a set of mercury thermometers with 0.1°C scale divisions. The pressure is measured by an MP-60 piston manometer 19 of accuracy class 0.05 in conjunction with standard manometer 18. The latter is used to cover the interval between the nearest pressure values corresponding to two neighboring values of standard weights of the piston manometer and also to separate the investigated substance and the oil of the piston manometer. The differential manometer is built in the form of a chamber which has an inspection window and is connected

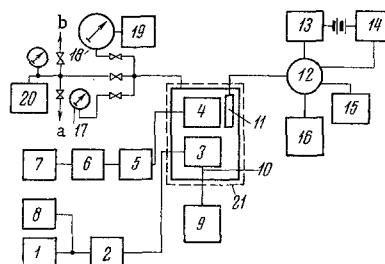


Fig. 2

to the piston manometer. This chamber is contained in the chamber of a standard 6-atm abs. manometer of accuracy class 0.35, which is connected to the volume of the autoclave.

Table 1

Speed of Sound (m/sec) in Vapor (c'') and Liquid (c') in Freons on Saturation Line

t, °C	c'	t, °C	c''	t, °C	c'	t, °C	c''	t, °C	c'	t, °C	c''
F-11				F-12				F-142			
-10	883	20	142.3	-4	636.0	5	137.5	-3.8	822.0	-10	160.7
0	844	30	142.5	0	618.8	10	137.6	0	784.0	0	159.9
10	804	40	142.5	10	577.0	20	137.0	10	710.0	10	158.8
20	768	50	142.4	20	534.2	30	135.6	20	662.0	20	157.5
30	733	60	142.2	30	492.4	40	133.5	30	619.0	30	155.6
40	699	70	141.8	40	450.5	50	130.4	40	577.0	40	153.6
50	665	80	141.1	50	408.6	60	126.4	50	534.0	50	151.3
60	632	90	140.0	60	367.0	70	121.5	60	492.0	60	148.7
70	599	100	138.5	70	324.5	80	116.5	70	449.0	70	145.8
80	566	110	136.7	80	278.8	90	111.2	80	405.0	80	142.0
90	531	120	134.5	90	229.0	100	105.3	90	360.0	90	137.5
100	500	130	131.8	100	173.0	108.8	97.0	100	311.0	100	132.2
110	464	140	128.6					110	260.0	110	125.3
120	427	150	124.2					120	204.0	120	115.6
130	390	160	119.2					130	140.0	130	102.6
140	353							133	116.3	134.9	94.6
150	314										
160	273										

The p-v-t data for the calculation were taken from [4-6].

Table 2

Speed of Sound c'' (m/sec) in Saturated Freon Vapors

t, °C	c''	t, °C	c''	t, °C	c''	t, °C	c''
F-13		F-21		F-40		F-113	
-135	108.6	-37.5	146.2	0	216.5	50	123.7
-130	111.1	-30	148.3	10	217.6	60	124.6
-120	115.2	-20	150.8	20	218.0	70	125.7
-110	118.3	-10	153.6	30	218.0	75	126.0
-100	122.6	0	156.0	40	218.1		
-90	125.4	10	158.2	50	217.5		
-80	127.8	20	160.1	57.5	216.0		
-70	130.0	30	161.3				
-60	130.6	37.5	162.0				
-50	130.4			F-113			
-40	129.6			-25	109.9	-35	113.0
-30	127.0			-20	111.4	-30	114.0
-20	123.7			-10	113.5	-20	115.5
-10	119.6			0	115.7	-10	117.5
0	113.9			10	117.5	0	118.8
10	103.1			20	119.2	10	120.2
20	82.2			30	121.0	20	121.0
				40	122.4	30	121.4
						40	121.6
						50	122.0
						55	121.4

Before being filled with the investigated liquid the whole system is thoroughly washed and evacuated to a pressure of 10^{-2} mm Hg. The

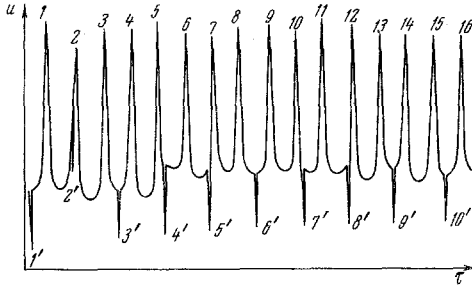


Fig. 3

system is first filled with freon through the main line a directly from the cylinder. Ballast vessel 20 with a heater can be filled simultaneously; this vessel can be used later to alter the amount of substance in the autoclave. In measurements of the speed of sound in vapor the liquid level must be below the emitter and with measurement in a liquid the liquid must be above the receiver. In both cases the vapor phase is essential and its presence is determined from the agreement between the saturation pressure and the tabulated values. When the liquid level lies between the receiver and emitter, there is no signal on the receiver. The phase in the space between the emitter and receiver is determined from the magnitude of the signal on the receiver.

The sound speed measurements were made only in the steady state, which was established in 2-3 hr. In these series of experiments the temperature was measured with a set of mercury thermometers and the pressure by a set of standard manometers graduated on a piston manometer. The temperature, pressure, and signal frequency were determined before and after the voltage on the receiver was recorded. During the recording the temperature and pressure usually varied by not more than 0.1% and the frequency by not more than 0.01%.

For each freon we carried out several series of measurements with different amounts of substance and found no systematic discrepancies. The wavelength was determined from the trace of the voltage on the receiver by the method used in [2]. Using the scale marks we determined the coordinates of several peaks at the beginning and end of the trace. We then calculated the distance between corresponding pairs of peaks and divided it by the number of half-waves. In the calculation we used the arithmetic mean of these measurements. The mean deviation in the wavelength was 0.2 to 0.3%.

We investigated the speed of sound in the liquid and vapor phase on the saturation line in freons F-11, F-12, and F-142 at $t = -10$ to $+160^\circ$ C and from $p = 1$ to $p = 43$ atm abs.

The F-11, prepared in the State Institute of Applied Chemistry, was subjected to chromatographic analysis. Within the limits of error of the method the analysis did not reveal any impurities. Technical F-12 and F-142 were subjected to multiple distillation and the central fraction was taken. They were then dried with silica gel and freed from noncondensing impurities by evacuation at -190° C. In all cases the p - t relationship on the saturation line agreed within the limits of accuracy of the instruments used with the tabled relationship [4, 5]. This provided indirect evidence of the adequate degree of purity of the investigated freons.

The results of measurements of the speed of sound from the smoothed curves are given in Table 1 and in Fig. 4, where curve 1" relates to liquid F-11, 2' to liquid F-12, 3' to liquid F-142, 1" to saturated F-11 vapor, 2" to saturated F-12 vapor, and 3" to saturated F-142 vapor. The mean deviation from the interpolating curves is 0.4%. The points in Fig. 4 are the results of calculation of the speed of sound c " (m/sec) in saturated vapor from the formula which we previously obtained [1]

$$c = \left[-g (v'')^2 \frac{dp''}{dv} \left(\frac{c_p''}{c_v} \right)^{1/2} \right]^{1/2} \quad (1)$$

After analysis of numerous c_p/c_v data for various freons we took the value of c_p/c_v on the saturation line as constant and equal to 1.1 for each of the freons. As Fig. 4 shows, the difference between the calculated and experimental values of the speed of sound in the temperature range from 0.6 T to 0.9 T (as fractions of critical) for all the freons does not exceed 1%. This indicates the high accuracy of formula (1) and its applicability for calculation of the speed of sound in saturated Freon vapor.

Calculations at temperatures above $0.9 T_c$ were not made owing to the absence of c_p/c_v data for these temperatures, nor below $0.6 T_c$, owing to the absence of experimental data on the speed of sound. We think that the difference between the experimental and calculated values of the speed of sound in the case of saturated F-11 vapor and in the case of saturated F-142 vapor at low pressures is due to the effect of dispersion on the results of the measurements. This is confirmed by the fact that at frequencies and pressures close to actual values dispersion has already been discovered in F-40 vapor [8]. In addition, calculation of the speed of sound for Freon-11 at 20° C from the formula for an ideal gas gives a result which is lower than the experimental result. From formula (1) we calculated the speeds of sound in saturated vapors of five freons: F-40, F-13, F-21, F-113, and F-114. The results of this calculation are given in Table 2. The p - v - t data for the calculation were taken from [6, 7]; c_p/c_v was taken as constant and equal to 1.1.

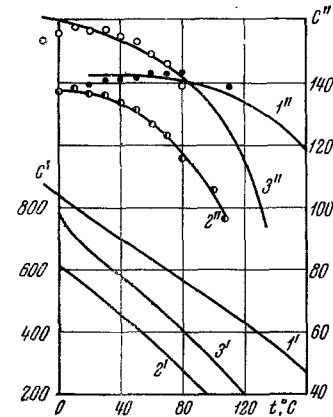


Fig. 4

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