SPEED OF SOUND, ISOCHORIC HEAT CAPACITY, AND COEFFICIENTS OF ADIABATIC AND ISOTHERMAL EXPANSION IN METHYL ALCOHOL AT ATMOSPHERIC PRESSURE

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The frequency-pulse method is used to measure the speed of sound in ethyl and methyl alcohols at atmospheric pressure over the temperature range 293-351°K. Values of isochoric heat capacity and coefficients of adiabatic and isothermal expansion of methyl alcohol at atmospheric pressure are calculated for the pressure range 175.47-337.85°K.

The speed of sound in methyl alcohol at atmospheric pressure has been studied in a number of studies, either over a narrow temperature range [1-6], basically from 273 to 323°K, or in a single point at room temperatures [7-10].

In comparing the literature's data on the speed of sound, a large amount of contradiction can be noted. Divergence in values of the speed of sound reaches 5-10 m/sec and higher. Such divergence is produced not only by inaccuracy of the methods used, but also by varying water content in the alcohol used. Thus, estimates using the results of [4], which studied the speed of sound in water—methanol solutions, show that at low water concentrations the speed increases by an average of 9 m/sec for each percent of dissolved water. This fact shows the necessity of observing purity requirements in the alcohols studied.

Analysis of available experimental data shows that above 323°K and below 273°K information on the speed of sound in methanol is practically completely absent, at both atmospheric and elevated pressures.

To study the propagation rate of ultrasound in alcohols, the frequency pulse method with a fixed distance was chosen. A diagram of the experimental apparatus is shown in Fig. 1. The experimental equipment and method permit realization of speed of sound measurements in the liquid phase over a wide range of temperature and pressure.

The basic element of the experimental equipment is the acoustical cell, consisting of two plates of X-cut piezoquartz, 20 mm in diameter, with a resonant frequency of 3 MHz, separated by a tube of calibrated length. The separator tube is made of 1Kh18N10T stainless steel with internal diameter of 18 mm and wall thickness of 1 mm. The tube material was thermally processed to stabilize it. The end faces of the tube are well machined, being parallel to within ±1 μm. To decrease the contact area between the separator tube and the piezoelements, the tube face had three recesses spaced 120° apart. The tube length at 293°K was 67.434 mm.

The acoustical cell was filled with pressure removed. The cell was then placed in autoclave 3, which is sealed by Teflon washers, a pressure flange, and threaded rods. Electrical connections were made to the piezoelements in the "cold" zone.

Autoclave temperature was maintained by a VTI liquid thermostat. Thermostat temperature was maintained by a VRT-2 temperature regulator to within ±0.005°K and measured by a PTS-10 platinum resistance thermometer with accuracy of 0.01°K. Atmospheric pressure was measured by a reference cistern barometer with scale divisions of 0.1 Pa.

The autoclave was filled with the liquid to be studied through the deairator, observing all measures to eliminate lengthy contact of the liquid with the air. Before filling, the autoclave and deaerator were carefully placed under a vacuum. The liquid to be studied was isolated from the atmosphere by a U-shaped mercury manometer.

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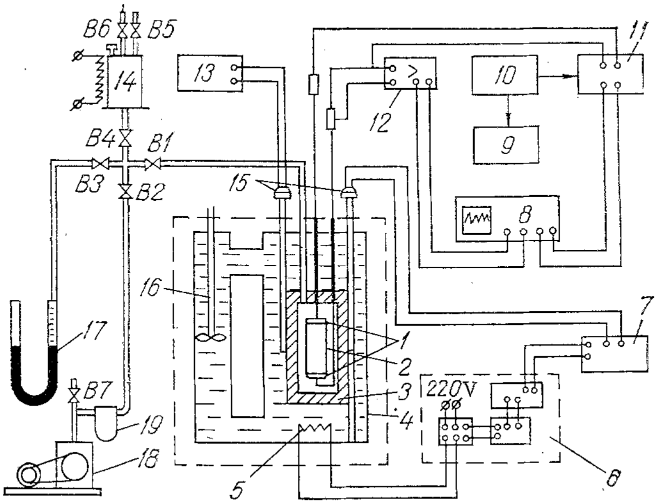

Fig. 1. Diagram of experimental apparatus: 1) piezoelements; 2) separator tube; 3) autoclave; 4) liquid thermostat; 5) regulating heater; 6) VRT-2 regulator; 7) R-348 potentiometer; 8) S1-70 oscilloscope; 9) ChZ-34 frequency meter; 10) GZ-34 pulse generator; 11) G5-4B pulse generator; 12) wideband amplifier; 13) R-363 potentiometer; 14) deaerator; 15) platinum resistance thermometer; 16) propeller mixer; 17) mercury manometer; 18) vacuum pump; 19) nitrogen trap.

The electronic-acoustical circuit, a block diagram of which is shown in Fig. 1, operates in the following manner. The type GZ-34 sine-wave generator 10 triggers the G5-4B pulse generator 11, producing rectangular pulses 0.1 μsec long with a regulated amplitude of not more than 10 V. This pulse excites the radiating piezoelement. The acoustical pulse resulting is converted by the receiver piezoelement into an electrical pulse which is then amplified by wideband amplifier 12 and observed on the screen of the S1-70 oscilloscope 8. The oscilloscope display is synchronized with the G5-4B generator through a delay circuit. By varying the repetition rate of the pulses, one can cause coincidence of a pulse which passes through the material a single time with a pulse which has been reflected from the receiver and transmitter piezoelements twice.

Production of test pulses with an amplitude less than 10 V eliminates the phenomenon of contact coating removal from the transmitter element and improves experimental conditions by decreasing the energy dissipated by the quartz. To maintain the purity of the liquid under study the piezoelement contact surfaces were vacuum-deposited gold. To improve the directionality of the transmitter quartz, the gold was deposited on the surface directed toward the separator tube in the pattern recommended in [11].

To increase the accuracy of the speed of sound measurements, the pulse repetition frequency was measured by a ChZ-34 electronic frequency counter 9, operating in the mode of measuring the ratio of a generator reference frequency and the measured signal frequency. A crystal-controlled 10-MHz oscillator was used to produce the reference frequency F_{ref}.

The speed of sound was calculated with the expression

$$W = \frac{2l_t \cdot 10^4}{\bar{n}} - \Delta W_{\text{dif}} , \qquad (1)$$

where l_t is the length of the separator tube at the experimental temperature; $\bar{n}$, arithmetic mean of a series of measurements (10-15) of the ratio of reference to measured frequencies; ΔW_{diff}, a correction for diffraction.

The correction for change in tube length with temperature was calculated. Maximum error in tube length determination did not exceed ±1 μm. The diffraction correction was calculated with the expression [12]

$$\Delta W_{\text{dif}} = \frac{W\lambda^{3/2}}{2\pi^2 d l_t^{1/2}}, \qquad (2)$$

TABLE 1. Experimental Values of Speed of Sound in Alcohols

T., °K	W, m/sec	T, K	W, m/sec
		Ethanol	
293,15	1159,86	333,15	1024,78
293,15	1159,80	343,15	991,17
293,55	1158,23	348,15	974,30
303,15	1125,53	350,15	967,46
313,15	1091,69	351,15	964,05
323,15	1058,30		
		Methanol	
293,15	1118,91	336,15	979,07
303,15	1085,57	337,15	975,93
313,15	1052,94	337,45	974,97
323,15	1020,64	337,65	974,32
327,15	1007,83	338,05	973,14
328,15	1004,61	338,45	971,84
333,15	988,65		

where λ is the wavelength and d is the inner diameter of the tube.

The diffraction correction calculated with Eq. (2) comprises 0.01% of the speed of sound. As was shown in [12, 13], the accuracy of introducing this correction can be estimated at 10%, which gives an uncertainty in the speed of sound from introduction of the correction of 0.001%. Estimates revealed that the effect of sound dispersion was negligibly small, so it was not considered in the calculations.

Type KhCh alcohols for chromatography with purity not less than 99.95 mass % were used. No further purification of the alcohols was carried out.

The error in the experimental data obtained is estimated at 0.02% without consideration of concentration error.

Before the commencement of the experiments, control measurements were performed using ethyl alcohol. The speed of sound was measured over the range 293-351°K (Table 1). A comparison of the results obtained in the present study with the most reliable data of [14] is shown in Fig. 2.

Speed-of-sound measurements were carried out for methyl alcohol over the temperature range 293-338.47°K (Table 1). In all, 13 experimental values were obtained, nine of which were in a region previously unstudied. A number of experimental values were obtained in the superheated liquid range, since the normal boiling point of methyl alcohol is 337.85°K [15]. Figure 3 shows a comparison of the results obtained with data of other authors. As is evident from the figure, the divergence between the present data and that of [3, 5, 7-10] is less than the total experimental error, not exceeding 0.1%. The divergence from the data of [1, 2] comprises 0.25% on the average, with the present data being systematically lower. It should be considered that in [1] the purity of the methyl alcohol was not indicated, while in [2] alcohol 99.90% pure by volume was used. It follows from comparison of the present data for ethanol and methanol with that of [2] that the divergence for both alcohols is of the same character. Since in [2] the ethanol was 99.80% pure by volume, then based on the character of the divergence, it can be assumed that the methanol was of the same order of purity. If the speed of sound values are recalculated for the concentrations used in the present study, agreement improves to within 0.1%.

Since the speed of sound in methyl alcohol at low temperatures has been studied little (we have only the three experimental points of [6] at 181, 193, and 213°K and the smoothed data of [5] for the interval 243-293°K), an attempt was made to approximate these data together with the data of the present study from the solidification temperature (175.47°K) to the normal boiling point (337.85°K) by an equation. The solidification and boiling points are taken from [15].

Using the least-squares method on a BÉSM-4 computer, the following equation was obtained:

$$W = \sum_{i=0}^{5} a_i \left(\frac{T}{100}\right)^i , \tag{3}$$

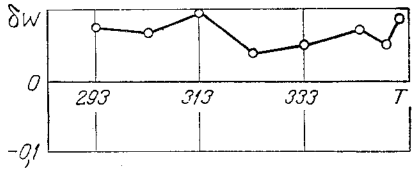

Fig. 2

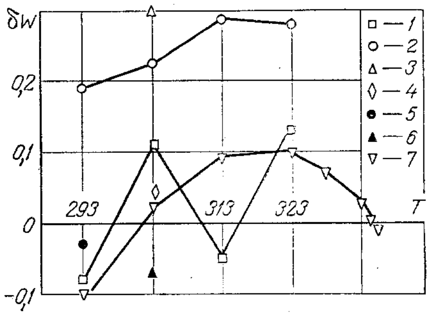

Fig. 3

Fig. 2. Comparison of experimental speed of sound values in ethyl alcohol with data of [14]: δW = (W[14] — W/W)· 100%.

Fig. 3. Comparison of experimental speed-of-sound values in methyl alcohol with data of other authors: δW = (W[i] — W/W)·100% (1, [3]; 2, [1, 2]; 3, [8];, 4, [9, 10]; 5, [5]; 6, [7]; 7, calculation with Eq. (3)).

TABLE 2. Calculated Values of Thermodynamic Properties of Methyl Alcohol

T, K	c_V, kJ/kg·deg	$\beta_T \cdot 10^5$, 1/MPa	$\beta_S \cdot 10^5$, 1/MPa	W, m/sec
175,47	1,676	55,02	42,34	1615,2
178,15	1,680	55,50	42,76	1609,8
183,15	1,688	56,60	43,75	1596,2
188,15	1,698	57,97	44,99	1578,8
193,15	1,710	59,58	46,45	1558,3
198,15	1,722	61,42	48,11	1535,5
203,15	1,736	63,47	49,96	1511,1
208,15	1,750	65,71	51,99	1485,6
213,15	1,764	68,14	54,17	1459,4
218,15	1,779	70,73	56,50	1433,0
223,15	1,795	73,48	58,95	1406,8
228,15	1,810	76,36	61,53	1380,9
233,15	1,826	79,37	64,20	1355,6
238,15	1,842	82,49	66,96	1331,1
243,15	1,859	85,71	69,79	1307,5
248,15	1,876	89,02	72,68	1284,8
253,15	1,893	92,41	75,63	1263,1
258,15	1,911	95,87	78,63	1242,3
263,15	1,929	99,39	81,66	1222,4
268,15	1,948	102,99	84,75	1203,4
273,15	1,968	106,67	87,88	1185,2
278,15	1,988	110,42	91,07	1167,6
283,15	2,010	114,28	94,33	1150,6
288,15	2,033	118,24	97,68	1134,0
293,15	2,057	122,34	101,14	1117,7
298,15	2,083	126,59	104,74	1101,7
303,15	2,110	131,02	108,49	1085,8
308,15	2,139	135,67	112,42	1069,9
313,15	2,170	140,54	116,57	1053,9
318,15	2,203	145,68	120,96	1037,8
323,15	2,238	151,10	125,62	1021,6
328,15	2,275	156,82	130,57	1005,3
333,15	2,315	162,86	135,81	988,9
337,85	2,354	168,81	141,00	973,50

where $a_0 = -17{,}452.20$; $a_1 = 37{,}303.07$; $a_2 = -28{,}072.94$; $a_3 = 10{,}220.21$; $a_4 = -1825.468$; $a_5 = 128.4465$.

Deviations of values calculated with Eq. (3) from the present experimental data do not exceed 0.1% (Fig. 3), 0.8% for the data of [6], and 0.2% for the data of [5], with the exception of the point 243°K, where the deviation is 0.81%. The accuracy of the data in [6] was estimated at 0.5%. Consequently, the accuracy of the speed-of-sound calculations at temperatures below 253°K can be estimated at 0.5-0.8%.

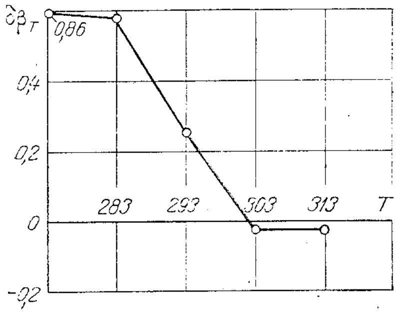

Fig. 4. Comparison of calculated coefficients of isothermal compression with data of [17]: $\delta\beta_T = (\beta_T[17] - \beta_T/\beta_T)\cdot 100\%$.

The isochoric heat capacities and coefficients of adiabatic and isothermal expansion were calculated with the well-known expressions

$$C_V = \frac{C_P}{1 + \frac{W^2 T \alpha^2}{C_P}}, \tag{4}$$

$$\beta_S = \frac{v}{W^2}, \tag{5}$$

$$\beta_T = \frac{v}{W^2}\left(1 + \frac{W^2 T \alpha^2}{C_P}\right), \tag{6}$$

in which v, α, and C_p were calculated with the expressions of [16].

Values of the speed of sound, isochoric heat capacity, and coefficients of isothermal and adiabatic expansion of methyl alcohol, calculated with Eqs. (3)-(6), are shown in Table 2.

In Fig. 4 the calculated β_T values are compared with reference data from [17], obtained by the piezometric method. Divergence does not exceed 0.6% with the exception of 273°K, where it reaches 0.86%.

NOTATION

T, temperature; v, specific volume; W, velocity of sound; C_V, C_P, isochoric and isobaric heat; β_S, β_T, adibatic and isothermal contraction coefficients; α, coefficient of thermal expansion.

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PROBLEM OF MEASURING THE THERMOPHYSICAL CHARACTERISTICS OF THIN RESISTIVE AND DIELECTRIC FILMS

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We consider the theoretical and experimental possibilities of determining a complex of thermophysical characteristics of thin films on a substrate, on the basis of a nonstationary method with boundary conditions of the fourth kind.

In order to calculate the thermal regimes of operation of microcircuits and thermoprinting matrices, and in a number of other cases, it is necessary to know the thermophysical characteristics of individual film components on a substrate. Such investigations are of interest for their own sake as well [1, 2]. In recent years the greatest amount of attention is being devoted to complex investigation methods, when a single experiment serves to determine all the independent thermophysical characteristics [2, 3]. Pugachev, Volkov, and Churakova [2] gave a detailed analysis of the methods applicable to thin (10-10^2 nm) films of metals without substrates. The investigation of films on substrates is discussed in [4-10], and their authors use mainly pulsed heat sources. The present study is based on the solution of a nonstationary heat-conduction equation with boundary conditions of the fourth kind. A system consisting of a semibounded substrate (A) and a film (F) with an initial temperature of T_{00} (Fig. 1) is brought into thermal contact at time $\tau = 0$ with a semibounded body (B) which has an initial temperature of T_{10}. The heat-conduction equation for this case has the form

$$\frac{\partial T_1(x,\tau)}{\partial\tau} = a_1\frac{\partial^2 T_1(x,\tau)}{\partial x^2} \quad (\tau > 0,\ x > 0),$$

$$\frac{\partial T_0(x,\tau)}{\partial\tau} = a_0\frac{\partial^2 T_0(x,\tau)}{\partial x^2} \quad (\tau > 0,\ 0 > x > -x_0), \tag{1}$$

$$\frac{\partial T_2(x,\tau)}{\partial\tau} = a_2\frac{\partial^2 T_2(x,\tau)}{\partial x^2} \quad (\tau > 0,\ x < -x_0).$$

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