ULTRASONIC VELOCITY IN AND THERMODYNAMIC PROPERTIES OF BENZENE AND CARBON TETRACHLORIDE UNDER PRESSURES

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A new experimental apparatus for the accurate measurement of ultrasonic velocity in compressed liquids has been developed, employing the pulse technique and an electronic digital counter circuit. The sound velocity measurements are carried out in liquid benzene in the temperature range between 10 and 70°C under pressures up to 2,100 atm, and in liquid carbon tetrachloride in the temperature range between 5 and 70°C under pressures up to 2,500 atm, with an estimated accuracy better than 0.2 per cent. The freezing pressures of both liquids are also determined at several experimental temperatures. The adiabatic compressibility and the specific heat ratio are derived over the whole range of temperature and pressure.

Introduction

The velocity of sound in a fluid is one of the important thermodynamic properties which can be determined experimentally with a considerable accuracy. Under the condition of low frequencies and small amplitudes, the velocity of sound U is related to the specific volume v and the adiabatic compressibility β_S as follows:

$$U = (v/\beta_S)^{1/2}. \tag{1}$$

Furthermore, provided the P–V–T data are available, some thermodynamic properties, such as the specific heat ratio γ and the specific heats, C_P and C_V, could be derived from the well-known relations:

$$\gamma = \frac{C_P}{C_V} = \frac{\beta_T}{\beta_S} = -\frac{U^2}{v^2}\left(\frac{\partial v}{\partial P}\right)_T. \tag{2}$$

and

$$C_P = \frac{-T(\partial P/\partial T)^2 P}{1 + v^2/U^2}, \tag{3}$$

where the isothermal and adiabatic compressibilities are defined as follows:

$$\beta_T = -\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial P}\right)_T, \tag{4}$$

$$\beta_S = -\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial P}\right)_S. \tag{5}$$

Although the velocity of sound in various liquids under the ordinary pressure has been reported by many investigators, the works on the pressure dependence are scarce, and the accuracy in the measurements was often unsatisfactory to calculate other thermodynamic properties. The ranges of temperature and pressure covered in those works were rather narrow, because of the difficulty arisen from the experimental techniques employed. Recently, the pulse technique has been applied to the

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measurements of sound velocity in compressed fluids. Van Itterbeek and coworkers[1] in Belgium reported the results on several liquefied gases at low temperatures by means of a pulse superposition apparatus. Boelhouwer[2] in Netherland published the values of liquid alkanes under pressures up to 1,400 bars using a pulse technique.

   The present report describes a new apparatus developed for the precise measurement of ultrasonic velocity in compressed liquids, and deals with the experimental results in liquid benzene and carbon tetrachloride.

Instrumentation

   Although the pulse technique may be the most suitable method for the measurement of the sound absorption, it has long been considered to be less accurate in the sound velocity measurement than the interferometer method, because of the difficulty in the accurate determination of the time interval between an original pulse and the echo signal. In our present instrumentation, a precise digital counter circuit is applied to the measurement of the time interval. The block diagram of the present fixed-path, two-crystal apparatus is given in Fig. 1.
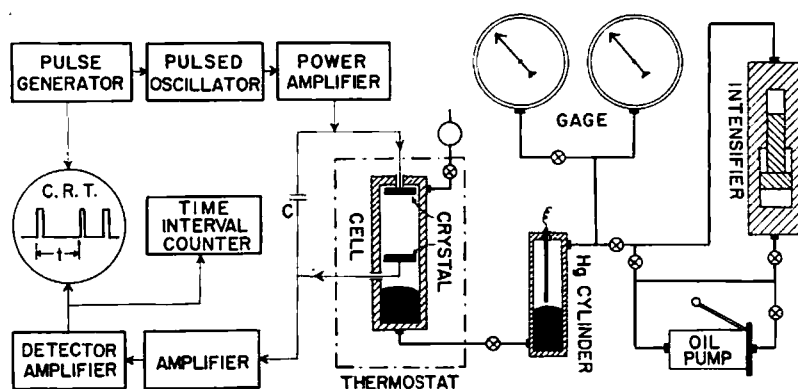

Fig. 1   Block diagram of ultrasonic velocity apparatus

   An electronic pulse signal, whose repetition frequency can be adjusted between 4 and 10 kc and whose duration is approximately 15 μsec, is generated in a trigger oscillator. The pulse is modulated in a pulsed oscillator, whose frequency is matched with the characteristic frequency in the thickness of x-cut quartz crystals (1 Mc). The amplified signal excites the upper quartz plate (transmitter) to produce the ultrasonic pulse in the liquid contacting it. The pulsed ultrasonic waves travel down through the liquid column and reach the lower quartz plate (receiver) after time lag. The ultrasonic waves excite the quartz to resonance and are converted again into the electronic signal. Both the original pulse and received signal, amplified and detected in the electronic circuits, are displayed on

   1)   A. van Itterbeek et al., *Physica*, **28**, 861 (1962); **29**, 965 (1963); **31**, 1643 (1965); **35**, 162 (1967);
        Cryogenics, **1**, 226 (1961)
   2)   J. W. M. Boelhouwer, *Physica*. **34**, 484 (1967)

the screen of an oscilloscope, as shown in Fig. 1. The time interval between the original and received pulses is measured by means of a digital electronic counter (Takeda Riken: TR-5178). When the electric level of the original pulse attains to a pre-set value, the gate of the counter circuit is opened. The circuit starts to count the numbers of signals of 10 Mc standard frequency, and therefore the counting unit is 0.1 μsec. The gate is closed when the level of the received pulse comes to another pre-set value. The counting results are given digitally within an error of 0.1 μsec. As the time delay in the rise of each pulse becomes less than 0.1 μsec provided the levels of the counting circuit are properly set, no correlation is made for the measurement of the time interval.

Since the time interval, t, should be the traveling time of ultrasonic waves in the distance l of the liquid column between the transmitter and the receiver plates, the velocity of sound U can be determined by

$$U = l/t. \qquad \cdot \qquad (6)$$

In this experiment, the average value of time intervals is taken of at least twenty readings, in which the fluctuation does not exceed ± 0.1 μsec. As the distance l between the two quartz plates is 172.74 mm at 25°C, the reproducibility of the sound velocity is always better than 0.2 per cent.

Fig. 2 shows the acoustical system, in which the two quartz plates are kept parallel by means of springs at both ends. The distance between the quartz plates is fixed by two rings connected with three rods of stainless steel (SUS-27). The change in the distance due to variation in temperature is corrected at each experimental temperature. The change with pressure is negligibly small in the present experimental range. This acoustical system is enclosed in a high pressure cylinder. The pressure of the sample liquid is transmitted through mercury by means of an oil pump and an intensifier, as illustrated in Fig. 1.
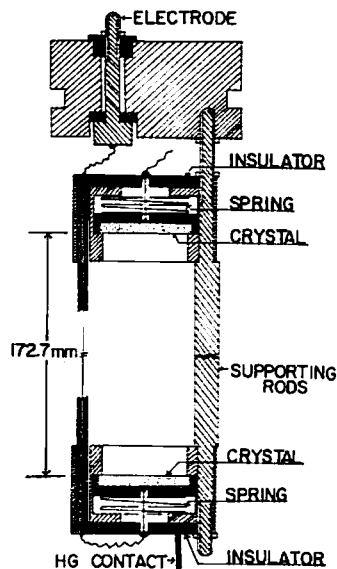

Fig. 2   Acoustical system in high
pressure cylinder

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Experimentals

The high pressure cylinder containing the acoustical system is kept in a liquid thermostat, whose temperature is regulated within ±0.01°C. The experimental temperatures are measured by means of a set of standard thermometers calibrated officially.

At each experimental point, the pressure is read on the Heise Bourdon Gages of three pressure ranges, which are calibrated by a dead weight tester. Therefore, the accuracy in the measurement of pressure is better than 0.1 per cent over the whole range.

The sample liquids used are obtained from the commercial source (Spectroscopy Grade of Merck's Reagenzien). Benzene is purified by fractional crystallizations and carbon tetrachloride by fractional distillations. in order to remove mainly the trace of water. The physical properties, such as density, refractive index, freezing point and boiling point, of purified liquids are found to agree very well with the reliable values in literatures.

Results and Discussions

Ultrasonic velocity
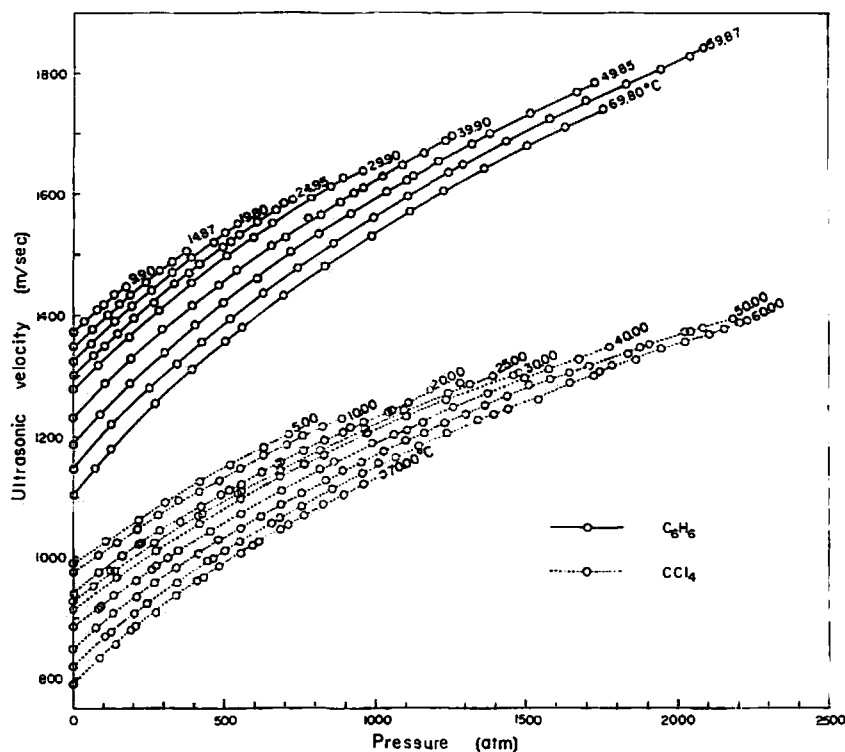
Fig. 3   Ultrasonic velocity isotherms of liquid benzene and carbon tetrachloride

The experimental ultrasonic velocity data in both liquids are drawn as isotherms against the pressure in Fig. 3. The data at the ordinary pressure are found to agree well with the values in literatures of benzene[3][4] and of carbon tetrachloride[4]-[6]. On the pressure dependence, the data in benzene show a good coincidence with the values of Richardson and Tait[4] at 25 and 40°C under pressures up to 600 atm. The data obtained for carbon tetrachloride under pressures agree well with the values of Mifsud and Nolle[5] at 25°C up to 1,000 atm, but show somewhat systematic deviations from the results of Richardson and Tait[4] at 25°C up to 600 atm.

The experimental data of the sound velocity in both liquids are fitted by the least square method to the following formula:

$$U'(\text{m/sec}) = a + bP + cP^2, \tag{7}$$

where pressure P is given in atm. The coefficients of equation (7) and their applicable ranges of pres-

Table 1   The coefficients of equation (7)

Benzene				
Temperature °C	Upper limit of pressure atm	a	b	$-c \times 10^4$
9.90	170.5*	1373.90	0.457497	1.27416
14.87	374.3*	1349.29	0.474071	1.49662
19.80	542.9*	1325.63	0.480080	1.23358
24.95	725.4*	1301.27	0.481741	1.10822
29.90	957.1*	1277.83	0.493075	1.19148
39.90	1254.3	1236.32	0.489900	1.01269
49.85	1212.6	1191.49	0.516798	1.13818
59.87	1245.4	1151.11	0.524059	1.09416
69.80	1226.9	1108.84	0.556229	1.26168

Carbon tetrachloride				
Temperature °C	Upper limit of pressure atm	a	b	$-c \times 10^5$
5.00	712.5	989.525	0.360179	8.48041
10.00	888.7	975.000	0.358231	7.91081
20.00	1182.5*	943.655	0.365754	7.70871
25.00	1390.9*	929.162	0.366241	7.33846
30.00	1460.5	914.347	0.368824	7.13541
40.00	1774.2	887.074	0.365510	6.15177
50.00	2180.1	861.279	0.365064	5.66417
60.00	2443.1	836.704	0.365665	5.34356
70.00	1026.1	796.002	0.441764	1.08075

* These values include the supercooled liquid exceeding normal freezing pressures.

3) A. Weissler, *J. Am. Chem. Soc.*, **71**, 421 (1949)
    F. Danusso and E. Fadigati, *Rendiconti Accad. Naz. Lincei, Cl. Sci. Mat. e Natur.*, **14**, 81 (1953)
    I. Gabrielli and L. Verdini. *Recerca Scientifica*, **25**, 1125 (1955)
4) E. G. Richardson and R. I. Tait, *Phil. Mag.*, **2**, 441 (1957)
5) J. F. Mifsud and A. W. Nolle, *J. Acous. Soc. Am.*. **28**, 469 (1956)
6) H. J. McSkimin. *ibid.*, **29**, 1185 (1957)

sure at each temperature are given in Table 1. These equations are found to reproduce the experimental data under pressures with a maximum deviation of 0.3 per cent.

On the other hand, it is noticeable that the ultrasonic velocity is in linear relation to the density at a constant temperature, as graphically drawn in Fig. 4. The slope of each isotherm resembles each other in a liquid, and the sections of each isotherm are nearly a linear function of temperature. From this point of view, a simple representation could be possible for the ultrasonic velocity as a function of density and temperature. The most probable equations for the present two liquids are determined as follows:

Benzene: $U \text{ (m/sec)} = 5885.68\,\rho + 1.4035\,T - 3874.60,$

Carbon tetrachloride: $U \text{ (m/sec)} = 2418.78\,\rho + 1.28235\,T - 2939.12,$

where density ρ is in g/cm^3 and T in °C. The above equations are found to represent the experimental data within the deviation less than 0.3 per cent for benzene at temperatures from 10 to 60°C and densities above $0.86\,g/cm^3$, and for carbon tetrachloride at temperatures from 5 to 70°C and densities above $1.57\,g/cm^3$. Below the densities described above, the deviation would increase.
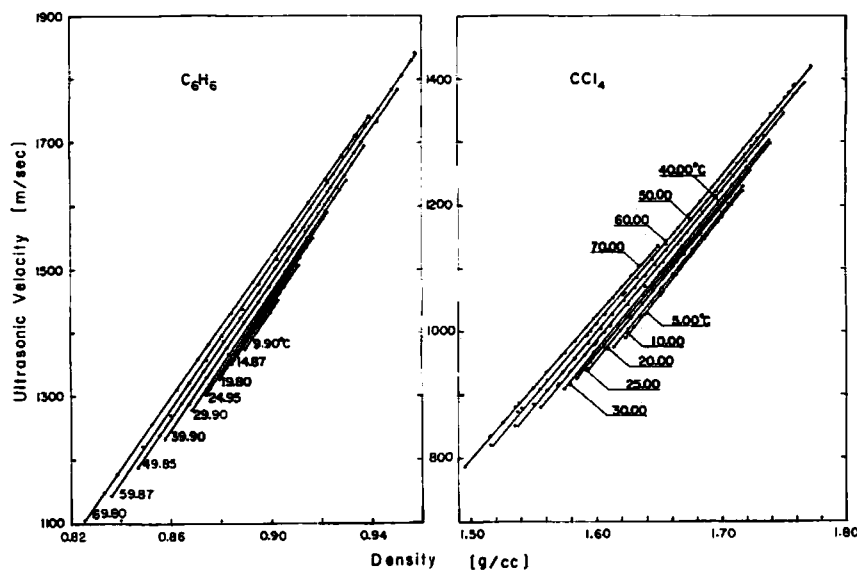

Fig. 4   Ultrasonic velocity *versus* density diagrams of liquid benzene and carbon tetrachloride

The values of density used in the above correlation are calculated from Tait's equation[7], which has long been considered to be the best empirical equation of state for liquids, because the direct experimental data of P–V–T relations for both liquids failed to cover the present detailed ranges of temperature and pressure. Tait's equation is written by

$$v = v_0[1 - C \log(B+P)/(B+1)] \qquad (8)$$

7)   J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids", John Wiley and Sons, New York (1954)

at a temperature, where v and v_0 are the specific volumes in cm^3/g at a high pressure and the atmospheric pressure, respectively, and P is in atm, B and C being empirical constants. In the present calculation, the following values are taken from literatures:

Benzene[8]: $C=0.21591$

$$B\,(atm)=957.32-7.2736(T-25)+0.015791(T-25)^2$$

$$v_0\,(cm^3/g)=1.14464+139.1\times10^{-5}(T-25)+2.5\times10^{-6}(T-25)^2$$

Carbon tetrachloride[9]: $C=0.21290$

$$B\,(atm)=855.66-6.7190(T-25)+0.016906(T-25)^2$$

$$v_0\,(cm^3/g)=0.647109+8.2822\times10^{-4}(T-45)+14.776\times10^{-7}(T-45)^2+4.50\times10^{-9}(T-45)^3,$$

where T is in $°C$. -

Agreement between the calculated density values and the reported values in literatures[10] is found to be satisfactory. Therefore the accuracy in the density values used would be better than 0.5 per cent at pressures up to 1,500 atm. Uncertainty would increase under higher pressures.

From the present results of ultrasonic velocity measurements, it is concluded that the variation of the velocity with temperature and pressure is smooth over the whole experimental conditions up to the freezing point. The coefficient $(\partial U/\partial P)_T$ is always positive, $(\partial U/\partial T)_P$ being negative. Furthermore, no evidence of the anomalous absorption or dispersion of the ultrasonic waves is found at the present frequency (1 Mc).

Derived thermodynamic properties

Using the experimental data of sound velocity and the calculated values of the specific volume, the adiabatic compressibility is determined from equation (1), and is graphically drawn in Fig. 5. The isotherms are smooth up to the freezing pressures. The isothermal compressibility is calculated from equation (4) by use of Tait's equation, and is also plotted by dotted curves in Fig. 5, in order to be compared with the adiabatic compressibility. The accuracy of these compressibility values would be better than the order of 1 per cent, taking into consideration the uncertainties of data employed in this derivation.

The specific heat ratio derived from equation (2) is given in Fig. 6. In general the ratio decreases gradually with increasing pressure. However, the scatterings of some experimental points are found at each constant temperature. This would come from the uncertainty in the data of both experimental sound velocity and $P-V-T$ relation. Especially, due to the lack of the accurate experimental $P-V-T$ data at present, the calculated values of specific heat by equation (3) are found to scatter considerably in high pressure region. Therefore, these derived values should be recalculated when the reliable $P-V-T$ data become available in future.

8) R. E. Gibson and J. F. Kincaid, *J. Am. Chem. Soc.*, **60**, 511 (1938)
   R. M. Waxler and C. E. Weir, *J. Res. Natl. Bur. Std.*, **67**(A), 163 (1963)
9) R. E. Gibson and O. H. Loeffler, *J. Am. Chem. Soc.*, **63**, 898 (1941)
10) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **66**, 185 (1931)
   J. W. Glanville and B. H. Sage, *Ind. Eng. Chem.*, **41**, 1272 (1949)

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Freezing pressures

Departing from the thermodynamic derivation. the freezing pressures at several temperatures are also determined during this experimental measurement. The pressure of a pure liquid is always fixed at a constant temperature as far as the solid phase exists together with the liquid phase. Such an

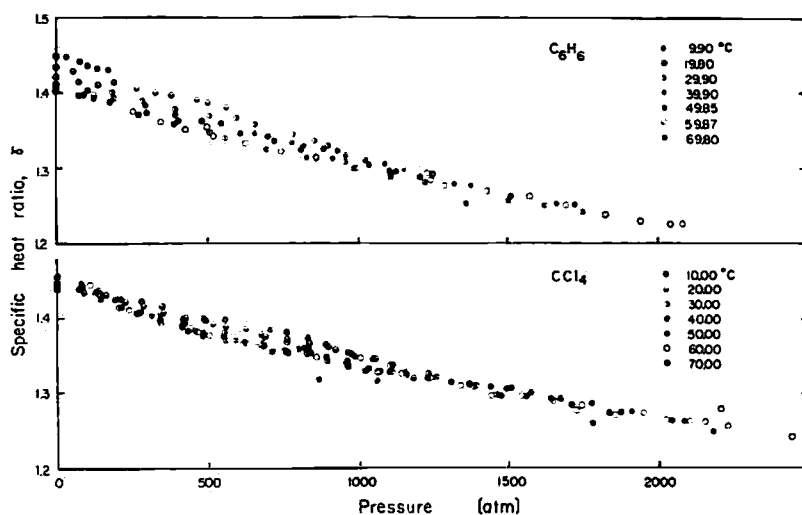Fig. 5   Adiabatic and isothermal compressibilities of liquid benzene and carbon tetrachloride

——— : β_S,   ‥‥‥ : β_T

Fig. 6   Specific heat ratios of liquid benzene and carbon tetrachloride

equilibrium can be easily obtained by the isothermal compression of a sample liquid. In some cases the liquid does not freeze beyond the normal freezing pressure, and the velocity of sound in the super-cooled liquid can be obtained. When the freezing of the liquid occurs, the ultrasonic waves are scattered by the fine crystals and, therefore, the receiving pulse signal disappears on the screen of the oscillo-scope. The equilibrium pressure does not change with further compression or release of pressure as long as the temperature remains constant.

In this investigation, readings of the freezing pressure at a temperature are made several times after compressions or releases of the oil pressure. The experimental results are given in Table 2, where the pressures are accurate within ±0.5 per cent. The more precise determination of the freezing pressure and their discussions in comparison with other investigators will be reported elsewhere.

Table 2   Freezing pressures of benzene and carbon tetrachloride

Benzene		Carbon tetrachloride	
Temperature, °C	Pressure, atm	Temperature, °C	Pressure, atm
10	161	5	736
15	341	10	889
20	516	20	1168
25	703	25	1314
30	896	30	1463
40	1289	40	1779
50	1713	50	2083

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