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Pressure Coefficients of Acoustic Velocity for Nine Organic Liquids

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With a pressure supersonic interferometer especially devised for this purpose, nine organic liquids are examined at frequencies a little less than 200 kc and at temperatures varying from 22.7°C to 25.5°C for the various liquids. The acoustic velocity is measured at intervals from atmospheric pressure to a pressure of 300 kg/cm². The values of the acoustic velocity (in meters per second) in the liquids at the pressures indicated are given below:

Liquid	C ₂ H ₅ Br	C Cl ₄	CHCl ₃	C ₂ H ₅ OC ₂ H ₅	C ₆ H ₁₂	CS ₂	C ₆ H ₆	C ₇ H ₈	C ₆ H ₅ NH ₂
Atmospheric Pressure	885.	912.	986.	993.	1005.	1136.	1290.	1313.	1640.
300 kg/cm ² Pressure	1000.	1048.	1097.	1255.	1281.	1268.	1416.	1447.	1745.

This method is being used for the determination of the value of the specific heats at other than atmospheric pressure.

TEMPERATURE and pressure coefficients of acoustic velocity in liquids serve a useful purpose in the evaluation of thermodynamic coefficients. Temperature coefficients of acoustic velocity at atmospheric pressure are already available for a number of liquids but thus far no attempt appears to have been made to measure the effect of change of pressure on the acoustic velocity in liquids.

An instrument has been devised for this purpose¹ following closely the design of the sonic interferometer for liquids of Hubbard and Loomis,² modifications being made so as to permit measurements at different pressures. The instrument consists essentially of a cylindrical liquid chamber, about 6.1 cm in diameter (crystal and reflector slightly smaller) and approximately the same in length, of about 250 cc capacity, in a block of special cast steel of dimensions 8×5×5 inches. Within the chamber is placed the acoustic system which consists essentially of a piezo-electric quartz disk, a moving reflector parallel to the surface of the disk and the liquid to be studied. The quartz disk is sputtered with gold on its two faces and rests upon a disk of Bakelite in the bottom of the chamber. Four external outlets from this chamber are provided: one for the lead wire to the lower electrode surface of the quartz, the upper electrode being grounded to

the body of the instrument; a second outlet permits the screwing of a piston in it to serve as a means of adjusting the pressure in the liquid; through the third outlet passes the shank of a shaft accurately threaded on the part inside the chamber, so as to control and measure the to-and-fro movement of the reflector without disturbing the pressure in the liquid; and a fourth outlet provides connection to a Bourdon gauge of $\frac{1}{2}$ of one percent accuracy. The quartz disk in the interferometer chamber, when excited at a frequency in the neighborhood of 200 kc, is set into vibration and constitutes the source of the acoustical waves. The maximum wave-length in the liquids used was of the order of 0.8 cm while the diameter of the liquid chamber was of the order of 6.1 cm. Thus the ratio of the diameter of the liquid chamber to the wave-length is of such magnitude that no tube corrections are necessary.

Resonance positions of the reflector, one-half acoustic wave-length apart, were determined by the electro-acoustic method of Hubbard and Loomis.² A Hartley oscillator was used to drive the crystal and its frequency was measured by a General Radio precision wave meter calibrated at the Bureau of Standards, two other such wave-meters being used as a check upon its constancy of calibration. The experiments were carried out in a room below ground level so that special temperature regulation was not considered necessary, the temperature changing only a fraction of a degree during a run upon a given

¹ J. Chester Swanson, R. S. I. 4, 603-605 (1933).

² J. C. Hubbard and A. L. Loomis, Phil. Mag. 5, 1178 (1928).

TABLE I. Measured values of the acoustic velocity.

Liquid	Pressure kg/cm ²	Velocity m/sec.	Liquid	Pressure kg/cm ²	Velocity m/sec.
C_2H_5Br	Atmos.	886.	CS_2	Atmos.	1137.
	179.	948.		25.	1154.
(24.7°C)	153.	941.	(23.5°C)	34.	1151.
	197.	962.		63.	1171.
(197.7 kc)	216.	971.	(193.9 kc)	88.	1174.
				111.	1178.
CCl_4	Atmos.	912.		118.	1189.
	35.	928.		152.	1185.
	49.	936.		178.	1215.
(23.0°C)	77.	959.		218.	1214.
	118.	966.			
(197.8 kc)	162.	986.	C_6H_6	Atmos.	1285.
	216.	998.		35.	1306.
			(25.5°C)	74.	1325.
$CHCl_3$	Atmos.	986.		94.	1337.
	38.	1001.	(193.7 kc)	155.	1363.
(22.7°C)	49.	1007.		184.	1377.
	72.	1019.		210.	1383.
(196.5 kc)	98.	1024.		229.	1388.
	120.	1029.		250.	1394.
	141.	1036.		281.	1403.
	170.	1050.		301.	1410.
	181.	1053.		350.	1438.
	211.	1062.			
$C_2H_5OC_2H_5$	Atmos.	994.	C_7H_8	Atmos.	1311.
	30.	1025.		35.	1330.
(23.6°C)	42.	1029.	(25.0°C)	56.	1346.
	63.	1050.		71.	1353.
(196.6 kc)	77.	1061.	(172.0 kc)	83.	1353.
	79.	1063.		130.	1368.
	96.	1076.		155.	1385.
				177.	1392.
C_8H_{12}	Atmos.	1006.		194.	1399.
	43.	1051.		270.	1434.
(23.9°C)	70.	1071.		310.	1460.
	98.	1093.			
(197.7 kc)	113.	1104.	$C_6H_5NH_2$	Atmos.	1647.
	114.	1108.		60.	1659.
			(23.7°C)	99.	1677.
				136.	1687.
			(197.7 kc)	183.	1707.
				288.	1737.

liquid; the mean temperature of all the measurements was 24°C and the maximum departure from the mean for any one liquid was 1.5°C. Time was allowed for temperature equilibrium to be reached after the adiabatic heating or cooling of the liquid caused by adjustments of pressure. Equilibrium was hastened by the reflector being moved up and down for that purpose. Moreover, the large mass of metal in the instrument (100 lbs.) reduced net departures of equilibrium temperature within the instrument from the temperature of the room to a fraction of a degree.

The liquids used were Baker's analyzed C.P. chemicals and were chosen so as to provide a wide range of densities, compressibilities, viscosities and sound velocities.

Table I gives the experimental data consisting of the temperature and frequency for each liquid, and the run of pressures and corresponding velocities in meters per second for each liquid. Fig. 1 shows the relationship between velocity and pressure. In the relatively small pressure range of these experiments a nearly linear relationship between pressure and velocity is to be expected and such a relationship is found to represent best the experimental results, in most cases within the errors of measurement. It should be noted that the velocities at atmospheric pressure are in exceedingly good agreement with those before obtained.³ As the pressure increases, pentane and ether show approximately twice the

³ E. B. Freyer with J. C. Hubbard and D. H. Andrews, J. Am. Chem. Soc. 51, 759 (1929).

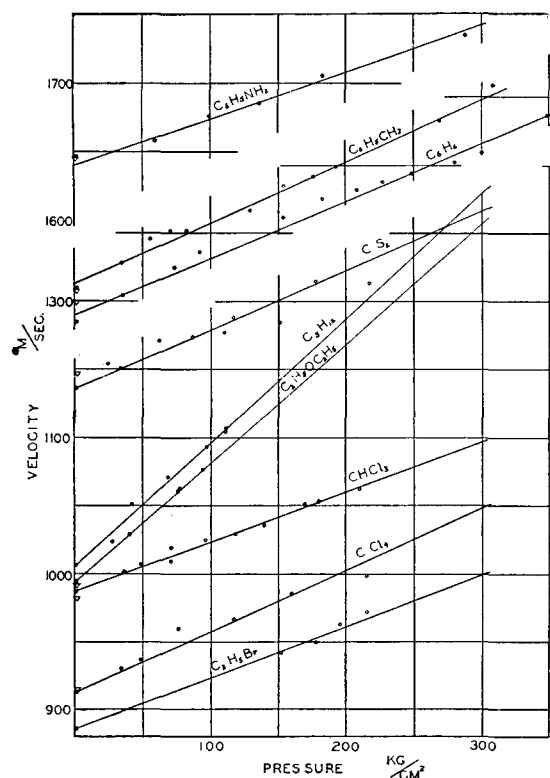


FIG. 1. Experimentally determined values of the acoustic velocity in liquids under pressure. The triangular marks at atmospheric pressure show the values obtained by Freyer³ of the acoustic velocity for these liquids.

variation of velocity with pressure shown by the remaining seven liquids in the same pressure range. Table II gives the value of the velocity at atmospheric pressure and a pressure of 300 kg/sq. cm and summarizes the average change of velocity within this range in pressure units of 100 kg/sq. cm and 1000 lbs./sq. in.

Apparently no previous attempt has been made to study the effect of pressure on the acoustic velocity of liquids. The only means at hand therefore of checking the present results is by the use of thermodynamic relationships. By this method, however, it is possible to obtain pressure-velocity curves for only three of the liquids studied because of the scarcity of values of isothermal compressibility, dilatation and specific heats at other than atmospheric pressure. Bridgman's⁴ results were obtained for regions of pressure much higher than those here studied, although his work is supplemented in some cases

by that of Amagat and an extrapolation of his own values in this pressure range. It was found impossible to measure the acoustic velocity in several of the liquids studied by Bridgman without extensive alterations in the interferometer, owing to the fact that in the present design the liquid comes into direct contact with the piezoelectric disk and in many samples of liquid available there was sufficient conduction to prevent the production of acoustic waves.

The three liquids for which thermodynamic computations of velocity are possible are carbon disulphide, ether and ethyl bromide. The thermodynamic quantities needed for the computation of acoustic velocity (μ) in liquids are density (ρ), isothermal compressibility (β_T) and ratio of specific heats (k); or density and adiabatic compressibility (β_ϕ). When the isothermal compressibility is used, the relationship is:

$$\mu = (k/\rho\beta_T)^{1/2}$$

This method has the disadvantage of making the specific heats a most significant factor and of all the thermodynamic quantities used they are acknowledged to be the least accurate. For the liquids studied the ratio of specific heats in this pressure range was available in only one case. For these reasons no results from the use of this method are given although we have attempted to use it. When the adiabatic compressibility is used, the relationship is given by the equation:

$$\mu = (1/\rho\beta_\phi)^{1/2}$$

TABLE II. Pressure coefficients of acoustic velocity.*

Liquid	Velocity in meters per sec.		Average change in velocity	
	atmos.	300 kg/cm ²	m/sec. 100 kg/cm ²	m/sec. 1000 lb./in. ²
Ethyl bromide	885.	1000.	38.3	26.9
Carbon tetrachloride	912.	1048.	45.3	31.8
Chloroform	986.	1097.	53.0	23.2
Ethyl ether	993.	1255.	87.3	61.4
Pentane	1005.	1281.	92.0	64.7
Carbon disulphide	1136.	1268.	44.0	30.9
Benzene	1290.	1416.	42.0	29.5
Toluene	1313.	1447.	44.7	31.4
Aniline	1640.	1745.	35.0	24.6

* The values at both atmospheric pressure and 300 kg/cm² are taken from a straight line drawn through the average positions of the experimentally determined values. (Fig. 1.)

⁴ P. W. Bridgman, Proc. Am. Acad. Arts and Sci. **49**, 4-114 (1913).

The disadvantage of this method is that the adiabatic compressibility does not lend itself to ready measurement and therefore, instead of from an experimentally determined value, it must be obtained from the relationship:

$$\beta_\phi = (1/\nu)(\partial\nu/\partial P)_\phi \\ = (1/\nu)[(\partial\nu/\partial P)_T + (T/C_p)(\partial\nu/\partial T)^2_P].$$

Where $(\partial\nu/\partial P)_T$ is the isothermal differential coefficient of compressibility, $(\partial\nu/\partial T)_P$ is the differential coefficient of dilatation at constant pressure, T is the absolute temperature and C_p is the specific heat at constant pressure. These quantities are available for several of the liquids studied. The specific heat at constant pressure also enters in this determination but here it is the divisor of the square of a very small quantity, the whole term merely acting as a correction factor for the isothermal compressibility. This becomes of importance in the computations since the variation of C_p with pressure could be obtained for only one of the liquids. In the case of carbon disulphide Bridgman gives the change of C_p with pressure in this pressure range. The variation between atmospheric pressure and a pressure of 300 kg/cm² was 1.7 percent and for the other liquids for which Bridgman gives values of C_p in this pressure range, the variation is about this value. Such a change of C_p in the above equation would be negligible and so we feel justified in giving these computed values even though we must use a constant value of C_p .

The results of applying these methods to the only three liquids for which data were available is shown in Fig. 2. The solid lines show the experimental values while the dashed curves show the computed values. The quantities used in the computations are those taken from the work of Bridgman except when otherwise noted. It should be pointed out, however, that had computations been made from some of the data from more recent sources better agreement between calculated and experimental values are attained than with the extrapolations given by Bridgman. We have preferred in this initial study to take all of our thermodynamic data from a single source, namely, that of Bridgman. The value of the specific heat at constant pressure at atmospheric pressure in every case was taken from the *International Critical Tables*. Bridgman gives

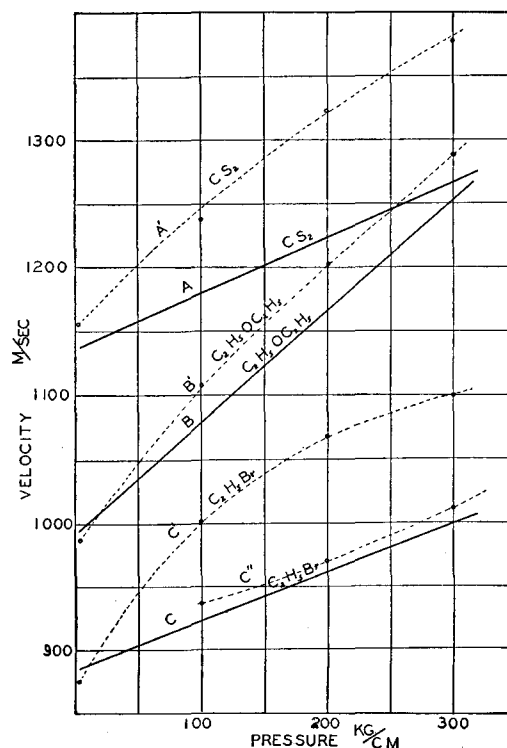


FIG. 2. The relationship between computed and experimentally determined values of the acoustic velocity in liquids under pressure. The solid lines show the experimental values, the dashed lines the computed values.

only the change of specific heats with pressure. The correlation between the calculated and experimental values is not as good as we had expected. However, considering the uncertainty of the values of many of the thermodynamic coefficients used in the computations, they are in very good agreement. In some instances the values given by different observers varied as much as twenty percent.

CARBON DISULPHIDE

For carbon disulphide the computed values increase with increase of pressure more rapidly than the experimental values and have a higher value at atmospheric pressure. It is unfortunate that while the results available for carbon disulphide are the most complete they are less accurate than those for many other liquids. At the same time the experimental values for carbon disulphide are not as reliable as those for the other liquids. Often upon removing the liquid from the instrument, some corrosive action was

noted. This lack of purity of the liquid we feel sure explains the discrepancy between these measurements at atmospheric pressure and those of Freyer³ (shown in Fig. 1). Freyer used a gold plated liquid chamber and the highest degree of purity. This state of purity could not be maintained in this instrument and was not considered necessary in this initial study. The experimental determination was at a temperature of 23.5°C and the computed values are also for this temperature.

ETHYL ETHER

Bridgman states that the thermodynamic properties within this pressure range "are rather more than usually accurate for ether." The computed and the experimental values for ether are in much better agreement than for any other liquid. The experimental values were taken at a temperature of 23.6°C. The data were not available to compute values at this temperature, so the calculated values are for a temperature of 20°C. Since an increase of temperature causes a decrease of velocity in ether, these curves would be in better agreement if it had been possible to obtain the values at the same temperature.

ETHYL BROMIDE

Richards⁵ has done some later work on compressibilities in this pressure range and his values of the isothermal compressibility for ethyl bromide vary by almost twenty percent from

those given by Bridgman. So we give two computed curves for this liquid. Curve *C'* is computed as was the curve for the other liquids, from the values of Bridgman. Curve *C''* uses the same data as curve *C'* except for the values of the isothermal compressibility, which in this case are taken from Richards. Richards gives his values as average compressibilities over rather wide pressure ranges, but by a graphical method it is possible from his results to compute the values at pressures of 100, 200, 300 and 400 kg/cm². He gave no values for atmospheric pressure so we do not draw the curve below a pressure of 100 kg/cm². Here again it was impossible to obtain the calculated values at exactly the same temperature as the experimental determination. The calculated curves are for 20°C and the experimental values were taken at a temperature of 24.7°C. A better agreement between observed and calculated values than that shown here is accordingly to be expected when sufficient data are at hand to make a comparison possible at the same temperatures.

It is the purpose of the author to make a more comprehensive study of these and other liquids, in particular at precisely controlled temperatures, using the method described as a basis for the determination of the ratio of specific heats and other thermodynamic coefficients at other than atmospheric pressure.

It is with a great deal of pleasure that I acknowledge the constant assistance and encouragement of Professor J. C. Hubbard of the Johns Hopkins University. The measurements were taken in his laboratory at the Johns Hopkins University.

⁵ T. W. Richards, J. Am. Chem. Soc. **34**, 988 (1912); **38**, 998 (1916).