International Journal of Thermophysics, Vol. 7, No. 5, 1986

Velocity of Sound in Supercritical Water up to 700°C and 300 MPa

J. P. Petitet,[1] L. Denielou,[1] R. Tufeu,[1] and B. Le Neindre[1]

Received October 24, 1985

The velocity of sound in water was measured up to 700°C and 300 MPa. A classical pulse method has been used. The frequency was typically 5 MHz. The mean accuracy of the data is 0.5% of the velocity. The greatest error in velocity is due to the uncertainty in the temperature measurements at high pressures.

KEY WORDS: high pressure; high temperature; velocity of sound; water.

1. INTRODUCTION

The investigation of acoustical properties of substances is useful for the calculation of various thermodynamic quantities. Such data can be used to check or obtain accurate equations of state. In the temperature range 200–700°C and for pressures up to 300 MPa, a number of equations of state for water are available [1–5], and in this range the various schematic representations of thermodynamic-state surfaces exist which correspond to these different equations of state. However, accurate data for the ultrasonic velocity as a function of pressure and temperature are necessary in order to improve the quality of the equation of state, especially when extrapolated.

There are only a few measurements of ultrasonic velocity in the range of interest, and mainly for the temperature and pressure range below 400°C and 100 MPa [6, 7]. A preliminary set of measurements was presented by the authors in a previous communication [8]. The aim of this work is to present a new set of measurements in the same range of pressure and temperature, taking into account modifications, suggested by the previous measurements, in order to improve the accuracy of the data.

[1] Laboratoire des Interactions Moléculaires et des Hautes Pressions, Centre Universitaire Paris-Nord, Avenue Jean-Baptiste Clément, 93430 Villetaneuse, France.

0195-928X/86/0900-1065$05.00/0

2. EXPERIMENTAL METHOD

The method for ultrasonic velocity measurements is an extended pulse-echo technique originally developed for measurements as a function of the temperature at atmospheric pressure in different liquids [9]. This method is actually well adapted for experiments needing buffer rods between the

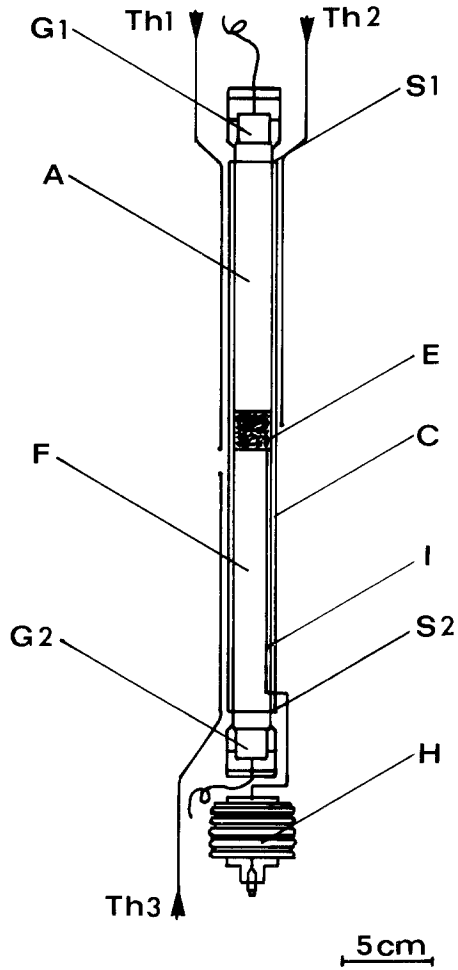

Fig. 1. High pressure cell. A, upper buffer rod; F, lower buffer rod; C, cartridge of the acoustical cell; E, water sample; G1 and G2, piezoelements; H, bellows; I, filling tube; S1 and S2, welding between the cartridge and the buffer rods: Th1 and Th2, thermocouples; Th3, regulation.

sample and the piezoelements. The cell displayed in Fig. 1, made of stainless steel (X18BC; known for its resistance against steam), is closed at both ends by stainless-steel buffer rods. The main tube is 300 mm long; the inside and outside diameters are 19 and 23 mm, respectively. The space between the inner faces of the buffers defines the sample length. In order to improve the quality of the signals, the buffer rods are manufactured by HIP from powdered 316 stainless steel. Also, in order to avoid most parasitic reflections, the longitudinal sides of the buffers are beveled and the parallelism of the ends is particularly elaborate. The cell is closed off from the pressure-transmitting fluid (here argon gas) by a bellows at the lower end. This bellows transmits pressure from the pressure chamber to the sample.

The clamping of the piezoelements to the end of the buffer rods is performed by a mechanical device. The tight cell is placed in a classical pressure chamber made of 819B steel. The available volume is a cylinder

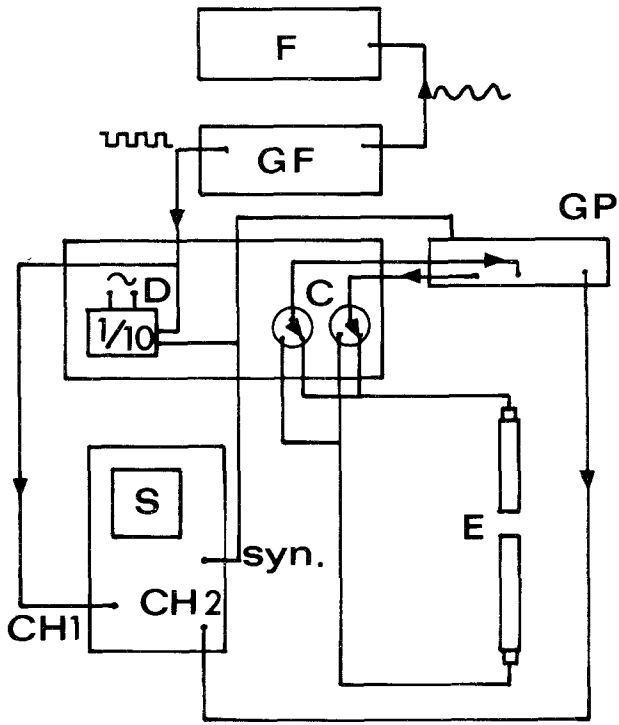

Fig. 2. Experimental arrangement. F, Frequency meter; GF, frequency generator; GP, pulse generator; D, divisor; C, connectors; S, scope; E, experiment cell.

600 mm long and 58 mm in inside diameter. The electric furnace is built to work up to 800°C; it is set up inside the pressure vessel. Two resistances are wound around the ultrasonic cell and the power delivered can be adjusted to control the longitudinal gradient. The pressure is measured with a precision pressure gauge (HEISE). The temperature is controlled by two thermocouples set in the front of the liquid sample. A block diagram of the entire apparatus is shown in Fig. 2. The piezoelectric element is excited by pulses with a period of 30 ms obtained from a generator (Type 5052 UA, Panametric). After transmission through the sample under test, the signal is displayed in the first channel of an oscilloscope. This signal is compared with that from a frequency generator (Krohn-Hite Corp., 4100 A) displayed in the second channel of the oscilloscope. Both pulse and frequency generators are simultaneously triggered by the frequency generator. The velocity measurements are typically carried out at a frequency of 5 MHz.

In a typical run, the cell is filled with water double-distilled at room temperature under vacuum. The liquid is degassed, although this seems not to be necessary since all available work indicates that the effect of dissolved gas on sound velocity is below the accuracy of the measurements. However, this is prefered to prevent any additional corrosion hazard by the dissolved gas.

The initial rise of the first echo in the water sample is positioned in front of the reference signal and the time may be determined to better than 0.005 s with a precision frequencymeter. Then, the initial rise of the second echo in the sample is positioned in front of the reference signal and the time determined. The process is repeated until three or four intervals have been determined. The sound velocity is calculated from the average time per echo and the known cell length (here it is 22.6 mm at room temperature).

3. ACCURACY OF MEASUREMENT

3.1. Temperature

Two thermocouples are positioned along the cell in a groove (see Fig. 1) in both the top and the bottom of the cell. In addition, an experiment was performed in order to measure the temperature difference between the middle and the ends of the sample as a function of the pressure. Below 450°C, the longitudinal gradient is not important (~ 1 K). Above 450°C, because of the vertical position of the furnace, the longitudinal gradient becomes more important as the temperature and pressure increase (up to 40 K at 600°C and 300 MPa). However, in the

high-pressure–temperature range, the acoustical signals are very reproducible and hence the time measured refers to the average temperature between the two extreme values.

The error in the measured temperature is the most important error in this set of experiments. We report in Fig. 4 the limits of this error for different pressures and temperatures.

3.2. Time

The measured value is the average over three or four echoes. In order to estimate the error in the time, we calculate $(V_i - V_s)/V_m$, where V_i, V_s, and V_m are, respectively, the velocities from the lowest, the highest, and the average time. The effect of this error does not exceed 0.2% of the velocity and is independent of the pressure and temperature.

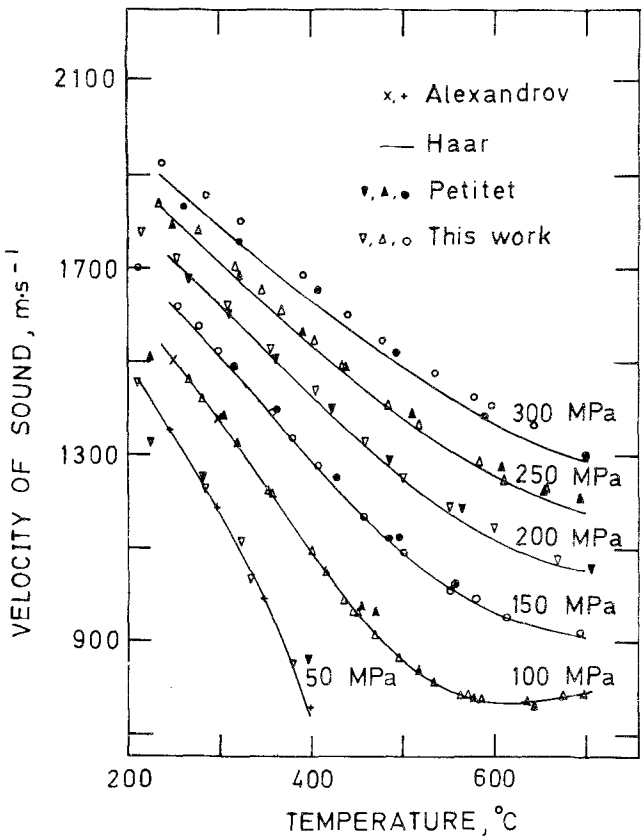

Fig. 3. Isobars of the velocity of sound in water.

Table I. Velocity of Sound of Water for the Pressure and Temperature and Temperature Ranges of 50–300 MPa and 200–700°C

Pressure (MPa)	Temperature (°C)	Velocity ($m \cdot s^{-1}$)
50.0	206.	1467.
	245.	1356.
	286.	1222.
	337.	1031.
	380.	848
100.0	252.	1504.
	269.	1458.
	282.	1424.
	318.	1325.
	361.	1206.
	402.	1088.
	450.	961.
	471.	913.
	537.	807.
	563.	782.
	591.	766.
	356.	1221.
	359.	1210.
	415.	1050.
	495.	862.
	571.	775.
	633.	769.
	674.	777.
	694.	781.
150.0	213.	1700.
	257.	1617.
	278.	1574.
	301.	1521.
	359.	1392.
	407.	1275.
	461.	1163.
	502.	1089.
	578.	988.
	380.	1337.
	457.	1163.
	553.	1005.
	615.	947.
	694.	916.

Table I *(Continued)*

Pressure (MPa)	Temperature (°C)	Velocity ($m \cdot s^{-1}$)
200.0	669.	1075.
	631.	1108.
	599.	1144.
	551.	1190.
	500.	1252.
	459.	1327.
	405.	1438.
	354.	1530.
	307.	1621.
	253.	1720.
	215.	1781.
249.0	346.	1656.
	236.	1837.
	277.	1777.
	318.	1703.
	367.	1616.
	404.	1546.
	434.	1494.
	486.	1411.
	518.	1369.
	562.	1313.
	586.	1285.
	611.	1252.
	654.	1226.
	657.	1226.
300.0	238.	1922.
	286.	1854.
	322.	1799.
	392.	1674.
	440.	1601.
	478.	1546.
	535.	1474.
	578.	1424.
	597.	1406.
	645.	1364.

3.3. Sample Length

The sample length is known to within 0.01 mm. To estimate the greatest error, we compare the velocities observed for the shortest times with sample lengths differing by 0.01 mm. The shortest times are for low temperatures and high pressures and are about 1.2 s. The maximum error is 0.4% of the velocity.

3.4. Pressure

Experiments were performed at constant pressure (manually adjusted for each temperature). The pressure was measured with a manometric gauge (0–5000 $kg \cdot cm^{-2}$). The maximum error, taking into account the quality of the gauge, is $\sim 10\, kg \cdot cm^{-2}$. The conditions for the greatest

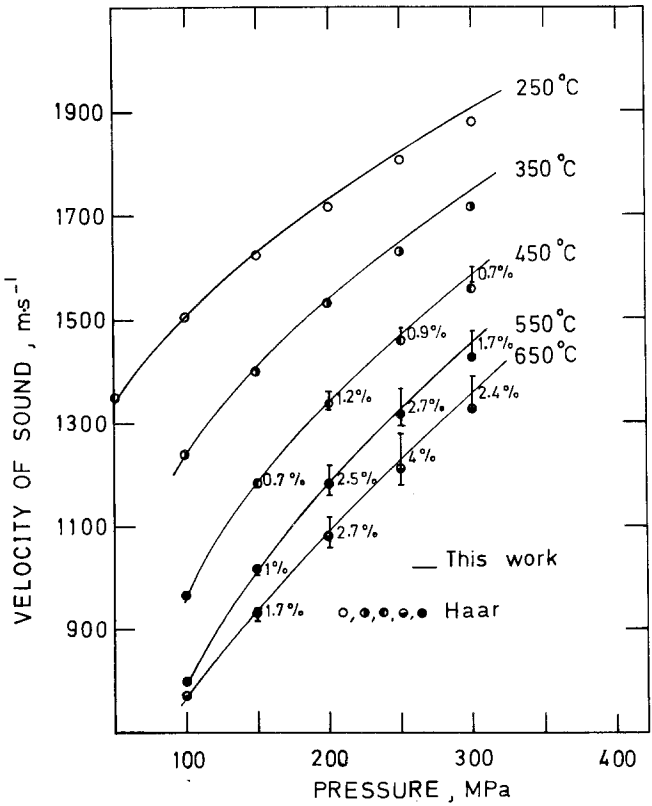

Fig. 4. Isotherms of the velocity of sound in water.

increase in velocity with pressure is about 50 MPa for our experiments. For this range the uncertainty in the pressure measurement induces a 0.4% uncertainty in the velocity.

In conclusion, we can see that the maximum error, without taking into account the effect of the longitudinal temperature gradient, in the worst case will be 1.1% of the measured velocity. However, since we know that different sources of error do not occur with maximum effect under the same conditions of pressure and temperature, we actually assume the error to be within 0.5% of the measured velocity.

4. RESULTS

Our data on the velocity of sound in supercritical water, in the range of 200–700°C and 50–300 MPa within the accuracy cited above, are presented in Table I. We have studied the six isobars presented in Fig. 3. In Fig. 4, we present the data as five isotherms. We prefer not to fit our data for all temperatures and pressures to present there in a more concise form, but to compare the new experimental values with the results from previous authors and with an equation of state. The curves in Figs. 5 and 6 indicate the consistency of our measurements with those of Alexandrov et al. [6, 7], who have made careful experiments up to 100 MPa and 400°C, and those of the equation of state of Haar, Gallagher, and Kell (HGK) [3]. We have

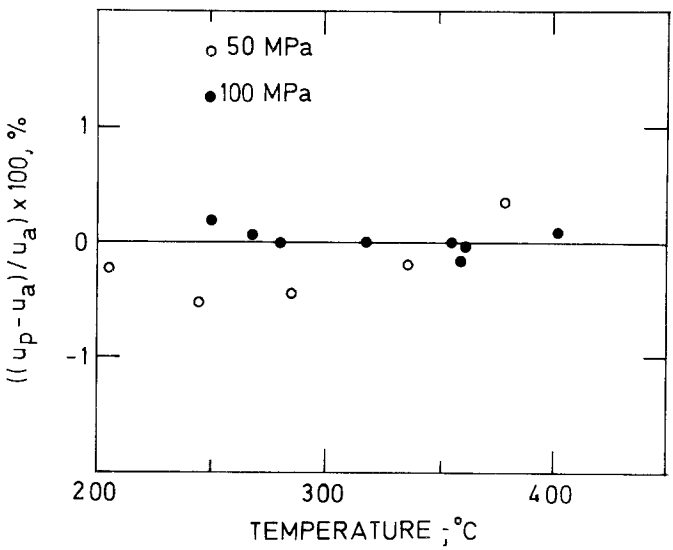

Fig. 5. Comparison between our results and those of Alexandrov et al.

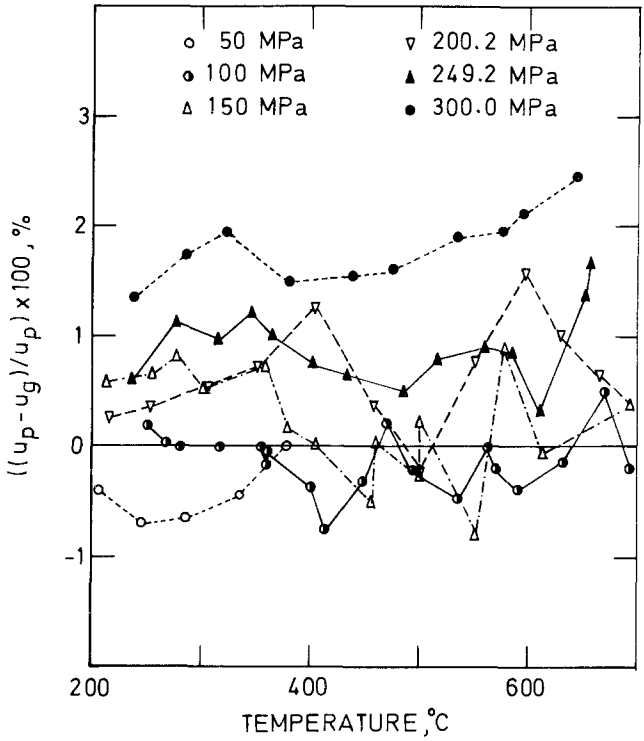

Fig. 6. Comparison between our results and those of the HGK equation.

chosen the HGK equation because they have not used the velocity of sound in the derivation of the thermodynamic surface.

We notice from these figures the following: (i) our measurements agree with those of Alexandrov et al. to within the estimated errors; and (ii) there appears to be a systematic shift at higher pressures between our measurements and those calculated from the HGK equation. This is not important for the calculated thermodynamic parameters for part of the studied range, but our results show that we should substantially alter the behavior of the equation of state at extrapolated pressures and temperatures.

REFERENCES

1. W. Dong-Ping and F. J. Millero, *J. Geophys. Res.* **78**:7122 (1973).
2. C. Chen-Tung, R. A. Fine, and F. J. Millero, *J. Chem. Phys.* **66**:2142 (1977).
3. L. Haar, J. S. Gallagher, and G. S. Kell, WGI IAPS (81) 219 Prague.
4. A. A. Alexandrov, V. S. Okhotin, and Z. A. Ershova, *Teploenergetika* **28**:74 (1981).

5. H. Sato, M. Uematsu, and K. Watanabe, *Proceedings of the 8th Symposium on Thermophysical Properties*, J. V. Sengers, ed. (ASME, New York, 1982), p. 47.
6. A. A. Alexandrov and D. K. Larkin, *Teploenergetika* **2**:75 (1976).
7. A. A. Alexandrov and A. I. Kochetkov, *Teploenergetika* **9**:65 (1979).
8. J. P. Petitet, L. Denielou, E. Azevedo, R. Tufeu, and B. Le Neindre, *Proceedings of the 10th International Conference on the Properties of Steam*, Moscow (Sept. 1984).
9. L. Denielou, J. P. Petitet, and C. Tequi, *Can. J. Chem.* **53**:400 (1974).