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Determination of the Thermodynamic Properties of Water from Measurements of the Speed of Sound in the Temperature Range 251.15–293.15 K and the Pressure Range 0.1–350 MPa

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The speed of sound in water has been measured in a broad region around the liquid-solid transition, that is, in the temperature range from 251.15 K to 293.15 K and in the pressure range from 0.1 to 350 MPa. An iterative method of calculation was used to determine the thermodynamic properties in the same *P-T* diagram. Anomalies observed for the isothermal compressibility and the specific heat at constant pressure are discussed in terms of statistical mechanical considerations.

KEY WORDS: high pressure; liquid-solid transition; speed of sound; supercooled region; thermodynamic properties; water.

1. INTRODUCTION

Up to now very few experiments have been carried out on the thermodynamic properties of water in the region of the phase diagram extending from 0.1 to 350 MPa in pressure and from 251.15 K to 293.15 K in temperature. For various reasons it was interesting to undertake such measurements. During the last 10 years, some detailed work has been published on the so-called abnormal behavior of supercooled water [1–9]. It was interesting to compare the thermodynamic data calculated both from this work and our measurements and to show how the behavior of water under pressure between 251.15 K and 293.15 K can be extrapolated to the supercooled region.

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We also show that the knowledge of the speed of sound under pressure associated with the specific heat at constant pressure and the density at atmospheric pressure was adequate to determine all thermodynamic properties of water in the region of this study. Moreover, the possibility of maintaining biological substances at very low temperatures in liquid aqueous media might have important scientific and economic applications. The above-given various reasons justified a study of the thermodynamic properties of water at low temperatures.

2. DETERMINATION OF THERMODYNAMIC PROPERTIES

Knowledge of the following three quantities, the specific heat at constant pressure, C_p, the density, ρ, and the speed of sound, u, allows the determination of a set of thermodynamic properties which characterizes the liquid state of a substance. Generally, it is difficult to measure these three quantities with the same accuracy. Particularly at high pressures, there is no simple way to measure directly, with high accuracy, the specific heat (at constant pressure) of a fluid. So it seems appropriate to use an indirect method of determination.

From an experimental point of view, of the three quantities C_p, ρ, and u, the speed of sound is the easiest to measure at high pressures with a good accuracy. Thus the speed of sound and the density can be measured with an accuracy better than 0.5%, but the specific heat is rarely determined with an accuracy better than 1%, even in the most careful experiments.

From speed of sound data, in the entire pressure range, and from the knowledge of ρ and C_p along one isobar (which is generally taken at atmospheric pressure), an iterative method is used to calculate ρ, C_p, α, the isothermal and isobaric compressibilities, and the ratio $\gamma = C_p/C_v$ in the P-T diagram. The starting relations are

$$d\rho = \left(\frac{1}{u^2} + \frac{M\alpha^2 T}{C_p}\right) dP \qquad (1)$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad (2)$$

where α, M, and ρ are, respectively, the expansion coefficient, the molar mass, and the density. This method has been used to calculate thermodynamic properties of different fluids [10–13]. Previously, we applied this method to the determination of thermodynamic properties of a molten salt under pressure [14]. At atmospheric pressure there are a large number of data between 251.15 K and 288.25 K which can be used in the calculations.

Values of the specific heat at constant pressure were taken from ref. [6] and values of the density from ref. [3]. Calculations were performed in the range from 251.15 K to 228.15 K and from 0.1 to 380 MPa.

3. EXPERIMENTAL METHOD OF SPEED OF SOUND MEASUREMENTS

To measure the speed of sound, we used the method of echo overlapping which was developed by Papadakis [15]. The frequency used was 10 MHz. The tight cell was made of stainless steel. Measurements were performed by reflection from a polished surface made of tungsten, which is known for its good reflective properties. The piezoelectric element, which is an x-cut quartz, was connected to the buffer rod by a liquid of very low vapor pressure. It was centered and held on this buffer rod with a screw. Mechanical motions due to pressure change were compensated by springs (Fig. 1). The thickness of the sample was defined by a calibrated ring made of stainless steel. In the final results, corrections were made to take into account the compressibility and the thermal expansion of the calibrated ring.

The cell was filled under vacuum with distilled water. A metallic bellows made of stainless steel was used as the pressure transmitter and compensator for the fluid compressibility and expansion. The tightness of the cell was secured by a needle. The cell was set up in a high pressure vessel immersed in a thermostated bath. In these conditions temperature gradients were nonexistent at the level of the sample under study. The temperature was measured inside the cell with a type E thermocouple well adapted to the temperature range of these experiments. The pressure was generated by a pneumatic compressor associated with a dry-piston intensifier. The compressing gas was dry argon.

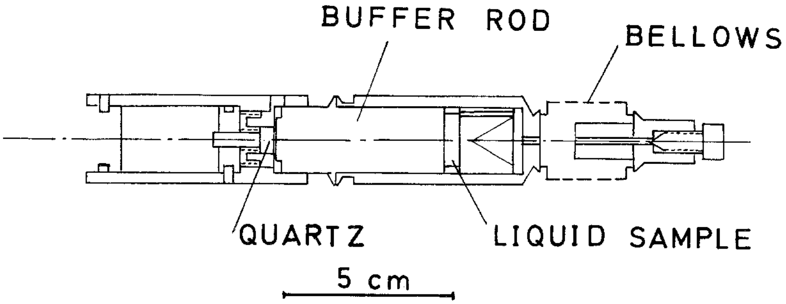

Fig. 1. Tight cell used to measure the speed of sound.

4. RESULTS

Experimental results are reported in Table I. They were fitted by a least squares method to a polynomial function of T and P. To avoid uncertainties related to the extrapolation of the polynomial below 273.15 K, we have used, for the fit, experimental measurements of the speed of sound at atmospheric pressure reported in ref. [7]. The polynomial form which was used is

$$u(T,P) = \sum_i \sum_j A_{i,j} T^i P^j \tag{3}$$

where u is given in $\mathrm{m \cdot s^{-1}}$, T in °C, and P in 10^5 Pa (bar). Coefficients of the polynomial are given in Table II. The standard deviation is defined by $[\sum(u_{\mathrm{exp}} - u_{\mathrm{cal}})^2/n]^{1/2} = 2.1\ \mathrm{m \cdot s^{-1}}$, where n is the number of experiments. The estimation of the empirical standard deviation of fitted values is defined by $[\sum(u_{\mathrm{exp}} - u_{\mathrm{cal}})^2/n(n-m)]^{1/2} = 0.2^{-1}\ \mathrm{m \cdot s^{-1}}$, where $(n-m)$ is the number of degrees of freedom.

In Fig. 2 we report the standard deviation of the experimental values with regard to fitted ones along three isotherms. In Fig. 3, isobars of the speed of sound are shown. The limiting value of the speed of sound at the lower temperature in the liquid phase, i.e., at −22°C and 204.5 MPa is 1690 $\mathrm{m \cdot s^{-1}}$. If we compare our results with those of Vedam and Holton [10] along the 0°C isotherm, our values deviate by 0.1% at 100 MPa, 0.2% at 200 MPa, and 0.4% at 300 MPa.

Table I. Experimental Results of the Speed of Sound of Water in the Temperature Region Below 20°C, Including the Supercooled Region

P (MPa)	T (°C)	u_{exp} $(\mathrm{m \cdot s^{-1}})$	u_{calc} $(\mathrm{m \cdot s^{-1}})$
0.1	22.4	1488.7	1487.2
0.1	16.9	1473.0	1472.9
0.1	14.2	1463.5	1463.3
0.1	13.8	1462.1	1461.8
0.1	9.3	1443.5	1443.7
0.1	7.8	1437.9	1437.1
0.1	2.7	1414.0	1412.9
11.0	2.9	1434.5	1434.0
11.0	2.0	1428.9	1429.4
10.8	0.7	1422.6	1422.2
0.1	0	1402.0	1399.3
0.1	− 5.0	1374.0	1372.9
0.1	− 15.0	1322.0	1319.4

Table I. Continued.

P (MPa)	T (°C)	u_{exp} ($\mathrm{m \cdot s^{-1}}$)	u_{calc} ($\mathrm{m \cdot s^{-1}}$)
0.1	− 10.0	1346.0	1346.0
0.1	− 20.0	1293.0	1293.9
20.3	− 0.17	1433.4	1434.4
39.0	− 0.73	1462.1	1465.2
75.6	− 0.60	1530.1	1531.9
116.5	− 0.41	1608.7	1606.9
169.8	− 0.12	1705.9	1703.4
226.7	− 0.14	1805.5	1804.6
288.3	− 0.31	1904.7	1905.9
328.3	− 0.44	1965.0	1967.0
376.1	− 0.49	2035.0	2032.3
239.0	− 5.9	1805.7	1807.4
309.8	− 6.0	1921.3	1925.5
338.1	− 6.2	1964.8	1967.0
196.2	− 6.1	1731.5	1729.1
196.2	− 5.9	1732.4	1729.9
161.9	− 5.7	1669.0	1667.0
136.7	− 5.7	1620.1	1620.0
99.4	− 5.7	1549.4	1550.3
99.6	− 5.6	1550.3	1551.2
87.8	− 5.6	1526.9	1529.3
79.0	− 5.6	1509.0	1512.9
114.1	− 8.7	1563.6	1564.4
114.1	− 10.0	1555.0	1558.8
149.3	− 10.1	1625.1	1625.3
197.1	− 10.2	1718.2	1715.3
243.9	− 10.2	1802.6	1801.5
291.9	− 10.2	1884.4	1884.6
281.9	− 10.1	1869.4	1868.4
339.0	− 10.2	1959.5	1959.1
332.3	− 10.2	1949.4	1949.2
325.6	− 10.2	1938.0	1939.0
319.7	− 10.1	1928.5	1930.1
359.4	− 10.2	1989.3	1988.0
351.7	− 10.2	1978.4	1977.4
342.0	− 10.2	1964.2	1963.5
308.9	− 9.9	1913.8	1913.6
173.7	− 11.0	1667.3	1668.0
195.2	− 11.4	1708.8	1707.2
155.2	− 13.2	1623.4	1623.7
193.2	− 13.3	1698.0	1696.1
250.4	− 13.4	1803.4	1802.5
245.9	− 13.4	1794.7	1794.3
240.1	− 13.4	1784.9	1783.7
297.1	− 13.4	1881.4	1884.3
283.8	− 13.8	1860.9	1860.5

Table I. Continued.

P (MPa)	T (°C)	u_{exp} ($m \cdot s^{-1}$)	u_{calc} ($m \cdot s^{-1}$)
277.4	− 13.8	1850.2	1849.3
334.6	− 13.8	1942.8	1943.4
325.4	− 14.1	1927.7	1928.3
315.8	− 14.1	1911.6	1913.1
364.3	− 14.0	1989.0	1985.8
354.1	− 14.2	1970.9	1971.0
344.9	− 14.2	1957.9	1957.7
336.2	− 14.2	1943.6	1944.7
187.9	− 15.7	1677.3	1676.8
181.5	− 16.4	1660.7	1661.6
247.9	− 16.4	1789.7	1788.8
244.9	− 16.5	1783.8	1782.9
300.1	− 16.7	1879.2	1880.2
287.3	− 16.9	1858.0	1858.0
276.4	− 16.9	1838.6	1839.1
184.9	− 17.7	1662.0	1663.2
245.9	− 17.9	1781.2	1781.1
229.4	− 18.0	1749.6	1749.5
288.3	− 18.0	1856.5	1857.1
281.4	− 18.2	1843.7	1844.8
266.6	− 18.1	1817.2	1818.8
241.5	− 18.2	1772.1	1772.1
219.6	− 18.2	1729.8	1730.0
207.9	− 19.4	1704.8	1703.4
249.3	− 19.7	1784.4	1783.7
247.7	− 19.7	1780.6	1780.7
239.1	− 20.0	1765.2	1763.6
236.6	− 20.0	1760.1	1758.8
253.9	− 20.5	1790.5	1791.1
234.2	− 20.0	1754.8	1754.1
243.9	− 20.5	1772.3	1772.0
215.7	− 20.3	1717.7	1716.6
214.7	− 20.2	1714.9	1714.8
197.0	− 20.2	1679.9	1678.7
198.1	− 19.8	1677.1	1682.3
39.2	19.4	1544.4	1547.5
70.7	19.4	1599.2	1600.9
118.1	19.4	1680.2	1679.6
141.6	19.3	1717.4	1717.9
198.1	19.4	1809.4	1807.7
255.8	19.4	1897.4	1896.1
323.9	19.4	1995.6	1995.6
389.9	19.4	2084.8	2086.4
444.5	19.4	2155.2	2156.7
456.3	19.4	2169.8	2171.2
461.6	19.5	2175.8	2172.5

Table II. Coefficients of Eq. (3) for $-22°C < T < 15°C$

	i				
j	0	1	2	3	4
0	0.139925×10^{4}	0.515237×10^{1}	-0.288879×10^{-1}	-0.115415×10^{-2}	-0.938893×10^{-7}
1	0.178644	0.106602×10^{-2}	0.152637×10^{-3}	-0.280402×10^{-5}	-0.438551×10^{-6}
2	0.146866×10^{-5}	$-0.1220313 \times 10^{-5}$	-0.980294×10^{-7}	0.195967×10^{-8}	0.286168×10^{-9}
4	$-0.288305 \times 10^{-12}$	0.601807×10^{-13}	0.507289×10^{-14}	$-0.988517 \times 10^{-16}$	$-0.148316 \times 10^{-16}$

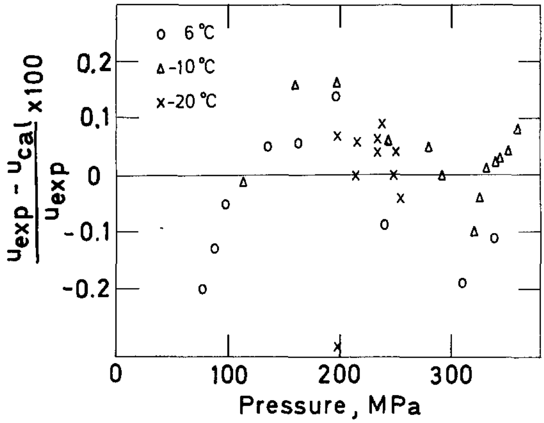

Fig. 2. Values of the standard deviation of experimental data of speed of sound in water with respect to calculated ones.

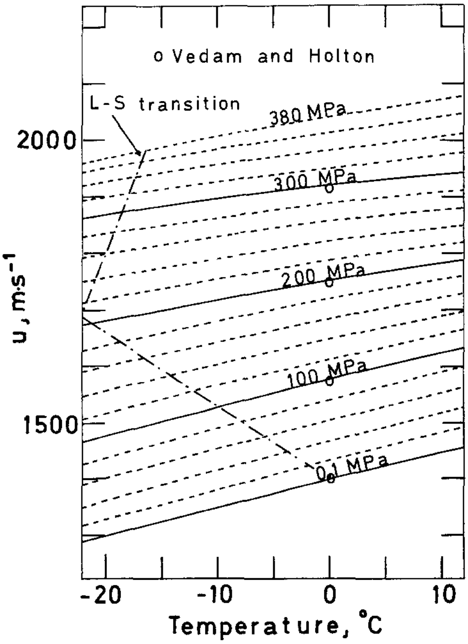

Fig. 3. Isobars of speed of sound in water as a function of temperature.

Table III. Coefficients of Eq. (3) for 0°C < T < 30°C

			i		
j	0	1	2	3	4
0	$0.139798 \times 10^{+4}$	$0.521827 \times 10^{+1}$	-0.453385×10^{-1}	-0.141974×10^{-2}	0.412602×10^{-4}
1	0.181690	-0.103841×10^{-2}	0.499023×10^{-4}	0.184564×10^{-5}	-0.879570×10^{-7}
2	-0.180147×10^{-5}	-0.299188×10^{-7}	-0.142270×10^{-7}	-0.585304×10^{-9}	0.312137×10^{-10}
4	$-0.966763 \times 10^{-13}$	0.525605×10^{-14}	0.155797×10^{-15}	0.983139×10^{-17}	$-0.567790 \times 10^{-18}$

We have also fitted our results between 0 and 20°C and from 0.1 to 350 MPa, those of Vedam and Holton [10] between 0 and 30°C and from 0.1 to 700 MPa, and those of Alexandrov and Parkin [16] between 0 and 10 K and 0.1 and 100 MPa. We used a polynomial of the fourth degree in temperature and pressure. The estimation of the standard deviation of fitted values for this second polynomial is also 0.2 $\mathrm{m \cdot s^{-1}}$. The coefficients are reported in Table III.

Calculations of thermodynamic properties were made only by using the first polynomial. With the iterative method described previously and based on Eqs. (1) and (2), we calculated densities in the entire region of this study. Values of density obtained by this calculation are compared to those of Kell and Whalley [11] up to 100 MPa above 0°C (Fig. 4). The deviation is smaller than 0.1%. The comparison was also made with the values calculated by the H.G.K. equation of state (derived by Haar et al. [17]) along the 15°C isotherm. The deviation is less than 0.04% up to 220 MPa, but increases to 0.43% at 380 MPa. However, we must remark that this isotherm is just at the boundary of these two series of determinations. The good quality of this result arises from the term $(\alpha^2/C_p)TM\Delta P$, which is

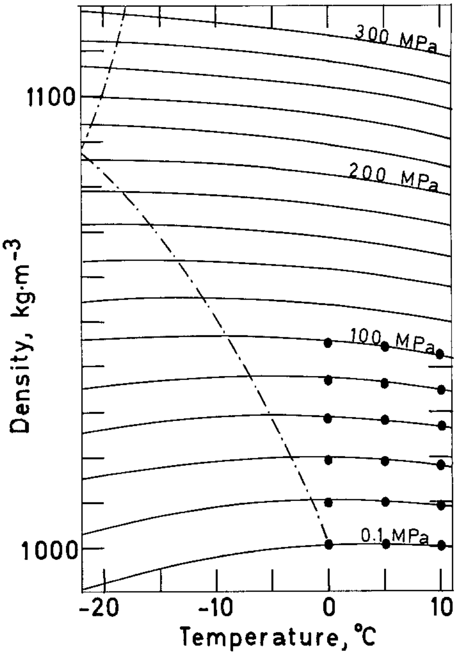

Fig. 4. Density of water calculated from speed of sound measurements as a function of temperature. ●, Data of Kell and Whalley.

Table IV. Values of Adiabatic Compressibility of Water

T (°C)	P (MPa) 0.1	60	100	200	300
− 20	0.6021	0.4984	0.4390	0.3257	0.2560
− 10	0.5530	0.4604	0.4090	0.3122	0.2491
0	0.5105	0.4300	0.3852	0.3001	0.2432
+ 10	0.4778	0.4023	0.3630	0.2913	0.2397

always of an order of magnitude lower than $(1/u^2)\Delta P$, which is measured in the experiment. The value of the density at the lower temperature in the liquid state, i.e., $-22°\mathrm{C}$ at 204.5 MPa, is $1088\ \mathrm{kg \cdot m^{-3}}$.

We have also calculated isothermal and adiabatic compressibilities and the ratio of specific heats. In fact, in these three cases, the α^2/C_p term is only a corrective term, and all the results can be considered as satisfactory. Some values of K_s, the adiabatic compressibility, and of $\gamma = C_p/C_v$ are reported in Tables IV and V. Some isobars of the isothermal compressibility are shown in Fig. 5. The value of the isothermal compressibility at $-22°\mathrm{C}$ and 204.5 MPa is $0.325 \times 10^{-9}\ \mathrm{Pa^{-1}}$. This figure is interesting because it shows the limitation in the use of the iterative method. In fact, fluctuations appear at about 300 MPa which have no physical meaning. This phenomenon is well known to authors who have used this method previously [10, 11] and is generated mainly from a deficiency in the mathematical model itself. A similar remark was made in our previous study of a molten salt under pressure [14]. However, our results are in good agreement on the one hand with those of Kanno and Angell (18), and on the other hand, with those of Ter Minassian et al. [4] obtained by two different methods.

In the calculation of the specific heat, the lack of accuracy in the determination of the thermal expansion led us to use the experimental

Table V. Values of $\gamma = C_p/C_v$ of Water

T(°C)	P (MPa) 0.1	60	100	200	300
− 20	1.044	1.003	1.000	1.019	1.044
− 10	1.010	1.000	1.003	1.022	1.045
0	1.001	1.002	1.007	1.027	1.047
+ 10	1.001	1.007	1.014	1.032	1.051

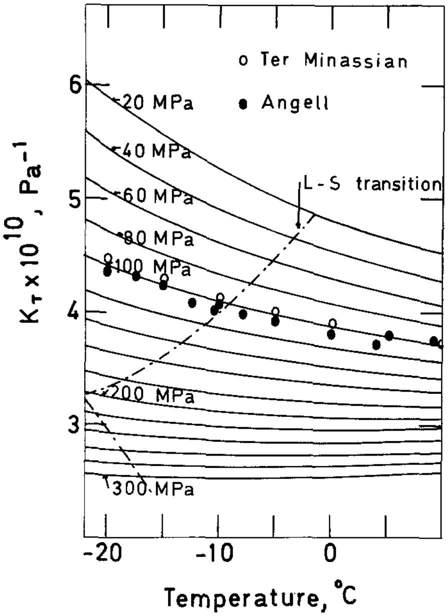

Fig. 5. Isothermal compressibility of water as a function of temperature.

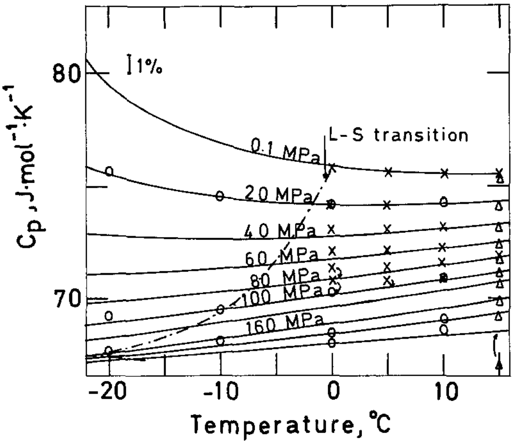

Fig. 6. Specific heat at constant pressure of water (×, Alexandrov et al.; ○, Ter Minassian et al.; △, HGK equation of state).

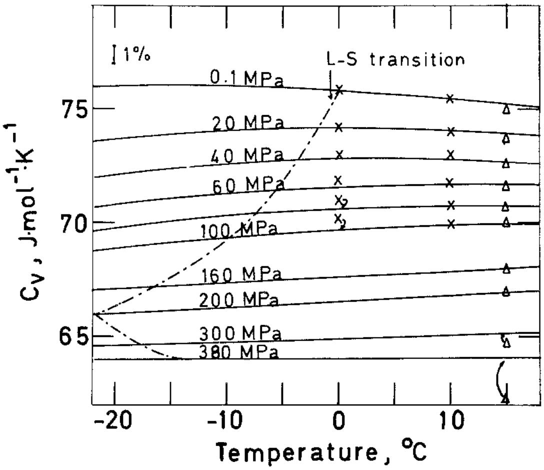

Fig. 7. Specific heat at constant volume of water (×, Alexandrov et al.; △, HGK equation of state).

results published by Ter Minassian et al. (4). These authors measured the isothermal heat of compression in a calorimeter. This quantity is given by

$$\Delta q = -\alpha T V \Delta P \tag{4}$$

The advantage of the method is to obtain directly the coefficient of thermal expansion α and to avoid all the inaccurate calculations of the derivative of the volume with respect to temperature. Specific heat at constant pressure C_p and constant volume C_v are shown, respectively, in Figs. 6 and 7. If we take into account the accuracy generally reported for this type of experiment (1% for the best conditions), the agreement is good with values published in the literature [4, 13]. We shall remark that H.G.K. equation of state [17] yields satisfactory results up to 200 MPa, but obviously deviates from our estimation above.

5. DISCUSSION

Experimentally we have shown that the speed of sound decreases when the temperature decreases at constant pressure, but that the effect decreases when the pressure increases. However, if we plot the speed of sound as a function of the density, as shown in Fig. 8, it may be seen that the speed of sound increases smoothly when both the density and the temperature

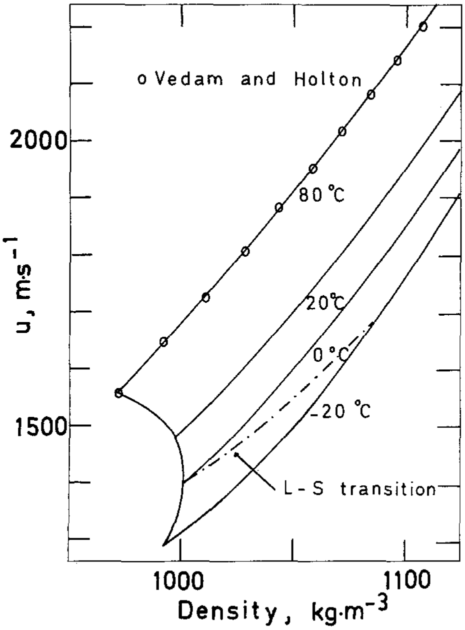

Fig. 8. Speed of sound in water as a function of density.

increase. This figure shows that density effects and temperature effects can be separated.

In water at low temperatures, anomalies were observed in the behaviors of the isothermal compressibility K_T and the specific heat at constant pressure C_p. These anomalies in water are well explained by the presence of molecular ordering described by Stanley et al. [5] and Stanley and Texeira [19].

In Fig. 9, we have plotted TK_T isochores in terms of the temperature. Statistical mechanical considerations relate TK_T to the ensemble average of density fluctuations $\delta\rho = \rho - \bar{\rho}$:

$$k_B T K_T = \left(\overline{\delta\rho}\right)^2 \frac{V}{\bar{\rho}^2} \tag{5}$$

where k_B is the Boltzmann's constant. For most liquids TK_T decreases with decreasing temperature. This is also true for liquid water up to a temperature which depends on the density, but is about 50°C for $\rho = 1005$ $\text{kg} \cdot \text{m}^{-3}$. The enhancement of density fluctuations at low temperatures was explained by Stanley and Texeira as due to the correlations of the spatial

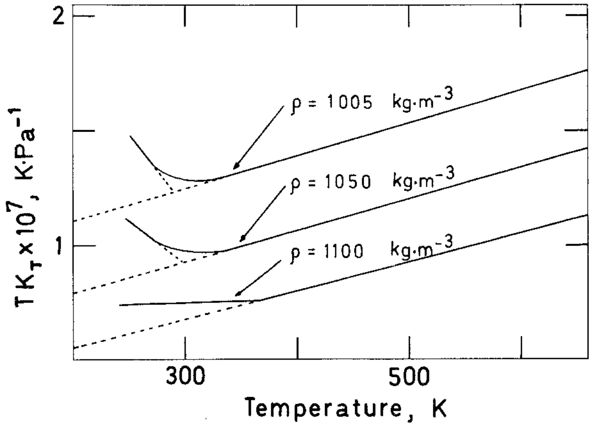

Fig. 9. Isochores of the product of temperature and isothermal compressibility as a function of temperature.

positions of various species. This effect decreases when the density increases, but is almost constant in relative value. We also notice the very high value of the isothermal compressibility (two times larger than for a molten salt under the same pressure condition [14]).

The ensemble average of the entropy fluctuations $\delta s = s - \bar{s}$ are related to C_p by

$$k_B C_p = (\delta s)^2 \tag{6}$$

In the temperature-pressure diagram shown in Fig. 6, C_p increases at very low temperatures and atmospheric pressure, but at pressures greater than 60 MPa, C_p decreases smoothly.

Finally, let us remark that the specific heat at constant volume C_v (Fig. 7), as shown by the model, is entirely normal whatever the pressure and the temperature. This behavior was explained by the fact that the local density is smaller than the bulk density. All these results are also in good agreement with the model of heterophase fluctuations at low temperatures described by d'Arrigo [20].

6. CONCLUSIONS

With new measurements of the speed of sound between 0.1 and 400 MPa and down to −20°C, we calculated several thermodynamic functions of water. In principle, the method allows us to be free of the second derivative of the density with respect to temperature at constant pressure for the calculation of specific heats. Practically, the density, the compressibilities, and the ratio of specific heats are obtained with a good accuracy. In return, the thermal expansion coefficient and, consequently, specific heats become rapidly inaccurate when the pressure increases. The use of data in the literature [4] to express the thermal expansion coefficient allows us to obtain all the thermodynamic surfaces of water at low temperatures. We have shown that results are well explained by the model suggested by Stanley et al. [5] and Stanley and Texeira [19] to describe the abnormal behavior of water at low temperatures.

REFERENCES

1. C. A. Angell, J. C. Shuppert, and J. C. Tucker, *J. Chem. Phys.* **77**:3092 (1973).
2. G. d'Arrigo, *J. Chem. Phys.* **75**:921 (1981).
3. E. Trinh and P. E. Apfel, *J. Acoust. Am. Soc.* **63**:777 (1978).
4. L. Ter Minassian, P. Pruzan, and A. Soulard, *J. Chem. Phys.* **75**:3064 (1981).
5. E. Stanley, J. Texeira, A. Geiger, and R. L. Blumberg, *Physica* **106A**:260 (1981).
6. C. A. Angell, M. Oguni, and W. J. Sichina, *J. Phys. Chem.* **86**:998 (1982).
7. O. Conde, J. Texeira, and P. Papon, *J. Chem. Phys.* **76**:3747 (1982).
8. J. C. Bacri and R. Rajaonarison, *J. Phys. Lett. (Paris)* **41**:L403 (1979).
9. E. Trinh and R. E. Apfel, *J. Chem. Phys.* **72**:12 (1980).
10. R. Vedam and G. Holton, *J. Acoust. Soc. Am.* **43**:108 (1968).
11. G. S. Kell and E. Whalley, *J. Chem. Phys.* **62**:3496 (1975).
12. K. P. Thakur and L. K. Jha, *Acustica* **43**:77 (1979).
13. A. A. Alexandrov, B. C. Okhotin, and Z. A. Erchova, *Teploenergetika* **4**:74 (1981).
14. L. Denielou, J. P. Petitet, C. Tequi, and G. Syfosse, *Bull. minéral.* (1982), to be published.
15. E. P. Papadakis, *J. Acoust. Soc. Am.* **42**:1045 (1967).
16. A. A. Alexandrov and D. K. Parkin, *Teploenergetika* **28**:74 (1981).
17. L. Haar, J. S. Gallagher, and G. S. Kell, in *Proc. 8th Symp. Thermophys. Properties*, Vol. II, J. V. Sengers, ed. (Am. Soc. Mech. Eng., New York, 1982), p. 298.
18. H. Kanno and C. A. Angell, *J. Chem. Phys.* **70**:9 (1979).
19. H. E. Stanley and J. Texeira, *J. Chem. Phys.* **73**:3404 (1980).
20. G. d'Arrigo, *Nuovo Cimento* **61B**:123 (1981).