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Physical properties of superheated water at one bar : a base to define the « normal » components of expansivity and compressibility of stable water

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Résumé. — Nous présentons et analysons les propriétés physiques de l'eau surchauffée à 1 bar jusqu'à 220 °C; ces données sont obtenues soit directement à partir de mesures (densité et vitesse du son), soit par extrapolation des mesures (C_p). La précision et la cohérence de ces données sont examinées.

A partir de ces données, nous proposons une estimation des composantes « normales » des propriétés physiques de l'eau. Ces composantes seraient celles d'une eau hypothétique sans liaisons; elles peuvent être considérées comme un niveau de référence dans l'analyse des contributions des liaisons et des effets structuraux dans l'eau.

Abstract. — We present and discuss the physical properties of superheated water at one bar up to 220 °C; these data are obtained directly from measurements (density and sound velocity) or from extrapolation of measurements (C_p). Their accuracy and coherence are examined.

Starting from these data, we propose estimates of the « normal » components of the physical properties of water. These components are those of a hypothetical unbonded water. They can be considered as a useful background in the analysis of bonding and structural contributions in water.

Introduction.

Some of the more unusual physical properties displayed by liquid water are the following [1, 2]: the negative volume change after melting, the density maximum at 4 °C, the minimum of the isothermal compressibility at 46 °C, the minimum of the isobaric heat capacity, C_p , the decrease of the isochore specific heat, C_v , with increasing temperature... So far, no physical mechanism has been found to describe satisfactorily these unusual liquid phenomena and there still exists a lack of unanimity on the subject. However, many authors agree with the hypothesis that « liquid water consists of a random hydrogen-bond network, with frequent strained and broken bonds, that is continually subject to spontaneous restructuring » [3]. The key to understanding liquid water lies in the concept of the « hydrogen-bond » [3-5]. Starting with this concept many models have been proposed which can be roughly classified into two categories: (a) distorted hydrogen bond or « continuum » models, (b) mixture/interstitial models. In mixture models, one assumes the existence of two

apparently stable states of association of water molecules. These models are used to predict the abnormal contribution to the physical properties of water, i.e. the deviation from normal behaviour. Most thermodynamic properties are supposed to be separable into « normal » and « abnormal » components, the « abnormal » ones being directly connected with the existence of the hydrogen bonds affecting the liquid structure. Of course, this decomposition cannot be applied to all the physical properties. In the case of the mixture model with the hypothesis of an ideal mixing, this decomposition can be applied to the specific volume v , the enthalpy H , and consequently to the expansivity α , the isothermal compressibility β_T and the isobaric heat capacity C_p . This decomposition simplifies the theoretical approach, but implies the knowledge of the « normal » contributions.

Until now the « normal » components in water have been deduced from studies of thermodynamic properties of aqueous solutions [9-14]. The physical properties have been measured *versus* the concentration and the results obtained in these binary X-H₂O mixtures analysed making two basic assump-

tions : (1) the « abnormal » components vanish at high enough concentrations of X (around fifty per cent); (2) the mixture X-« normal » H_2O is an ideal mixture (here « normal » H_2O is a hypothetical liquid, the properties of which are the « normal » components of liquid water). In fact, on close examination of the results, one realizes that the « normal » contributions so deduced depend on the aqueous solutions; thus one must conclude that the assumptions are not fully satisfied. However, this analysis is the first and unique attempt at defining the normal components of liquid water.

The aim of this paper is to provide a new approach to the problem, starting with the analysis of the thermal properties of water in highly superheated states ($160^\circ < T < 250^\circ C$). In this case, the structural contributions can be neglected and the « normal » contributions to compressibility and to expansivity can be identified with the measured values.

We first recall the main results known for superheated water from density, sound velocity and isobaric specific heat measurements. The accuracy of the data is closely examined. In the second part, we define the physical properties of the « normal » or hypothetically unbonded and unstructured water over a large range of temperature : the expansivity and compressibility are deduced from values measured in superheated water by extrapolation using empirical laws which apply to unassociated liquids. The isochore heat capacity is identified with the vibrational specific heat and calculated using the Debye model with vibration frequencies deduced from the infra-red [15] and Raman [16] measurements. Finally, some other physical properties can be derived using classical thermodynamic relations.

1. Physical properties of superheated water at one bar.

1.1 DENSITY ρ . — One can find in the literature a great deal of data on the density of water in the stable range, particularly at one bar with a relatively high precision (typically 10^{-5}) [17, 18]. In the metastable range the only measurements are due to Chukanov and Skripov [19] between $140^\circ C$ and $230^\circ C$ with a precision of 7×10^{-4} . Many simple state equations have been proposed to fit the thermal evolution of the density in the stable state. We have selected the ones which are also adequate to fit the density in the superheating range. Two simple equations seem particularly convenient; the first was proposed by Wasserman [20] for stable water in the range : $0-350^\circ C$, $0-10$ kbar; the second is used by Kell [17] to fit accurately the temperature dependence of the density at one bar.

The experimental data and the values given by the two equations are compared in figure 1; one observes a good agreement between them, the differences being less than 5×10^{-4} in the temperature range $-20^\circ C$ to $200^\circ C$; however in the superheated state

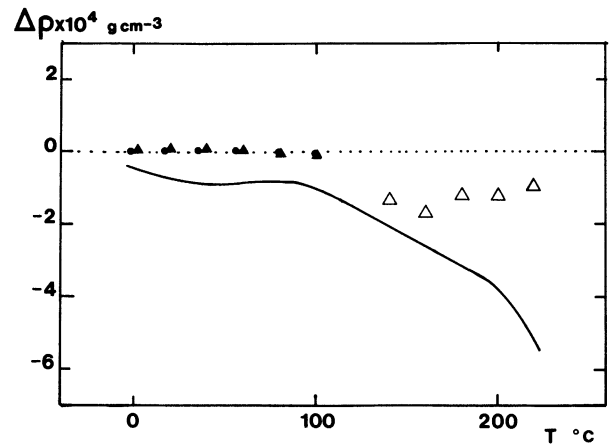


Fig. 1. — Differences between density of water from Kell equation and other sources $\rho = \rho(\text{other source}) - \rho(\text{Kell})$, — ref. 20, ● ref. 21, △ ref. 19, ▲ ref. 18.

the Kell equation seems to be more suitable to fit the experimental data given by Chukanov [19].

1.2 THERMAL EXPANSIVITY : α_p . — The thermal expansivity has been calculated by differentiating the Kell equation. The results are in agreement up to $210^\circ C$ with those obtained from Wasserman equation and with those proposed by Bukalovich *et al.* [22] (Fig. 2).

1.3 SOUND VELOCITY : v_s . — The sound velocities v_s measured by Brillouin light scattering [23] are in agreement with the results obtained by classical ultrasonic techniques up to $220^\circ C$ [24, 25]. Conse-

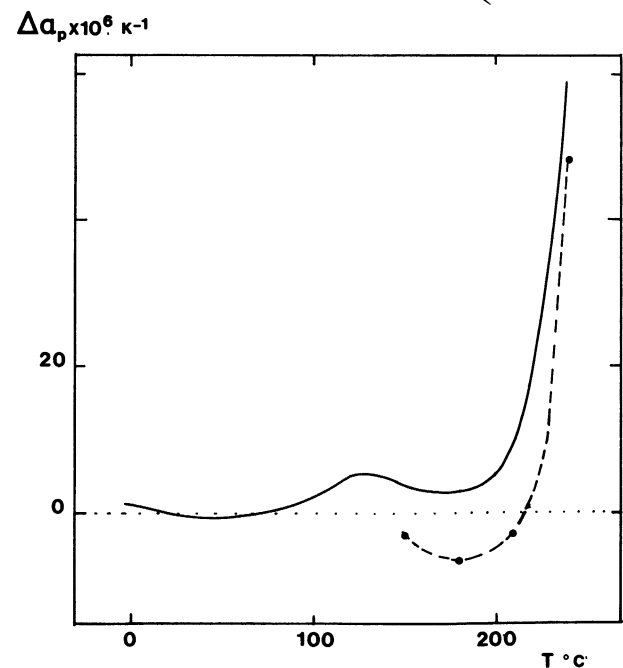


Fig. 2. — Differences between expansivity of water from Kell equation and other sources; $\Delta\alpha_p = \alpha_p(\text{other source}) - \alpha_p(\text{Kell})$, — ref. 20, ---- ref. 22.

quently it is not possible to show up any significant velocity dispersion. An attempt to fit the thermal dependence of sound velocity by means of a polynomial gives the following fourth degree polynomial :

$$v_s = 1\,418.8 + 4.076\,5\,t - 3.605\,2 \times 10^2\,t^2 + 8.684\,4 \times 10^{-5}\,t^3 - 1.033\,4 \times 10^{-7}\,t^4 \text{ for } 100\text{ }^\circ\text{C} < t < 220\text{ }^\circ\text{C} \quad (1)$$

with a standard error of 3 m/s.

1.4 SPECIFIC HEAT AT CONSTANT PRESSURE : C_p . — The most accurate values of C_p in the temperature range 0-100 °C are due to de Haas [26]. His work takes into account the results obtained by Osborne *et al.* [27]. Above 100 °C, there are no experimental results for C_p at one bar (in the superheated range). Then, we can only evaluate C_p by extrapolating the experimental values known for pressures higher than the saturation pressure. The accuracy of C_p is about 0.05 % up to 150 °C [28, 29], but only 0.5 % at higher temperatures [30, 31]. Figure 3 gives some examples of extrapolation. The values of C_p extrapolated at one bar are presented in figure 4.

1.5 SPECIFIC HEAT AT CONSTANT VOLUME : C_v . — The values have been derived by extrapolating the data given by Amirklanov [32] from 50 °C to 300 °C and between 50 and 1 000 bar; this extrapolation was facilitated by the fact that $(\partial C_v / \partial P)_T$ is almost constant. The results are represented in figure 6.

1.6 OTHER SPECIFIC PARAMETERS. — In the absence of dispersion, the sound velocity v_s is related to the adiabatic compressibility β_s by :

$$\beta_s = \frac{1}{\rho v_s^2} \quad (2)$$

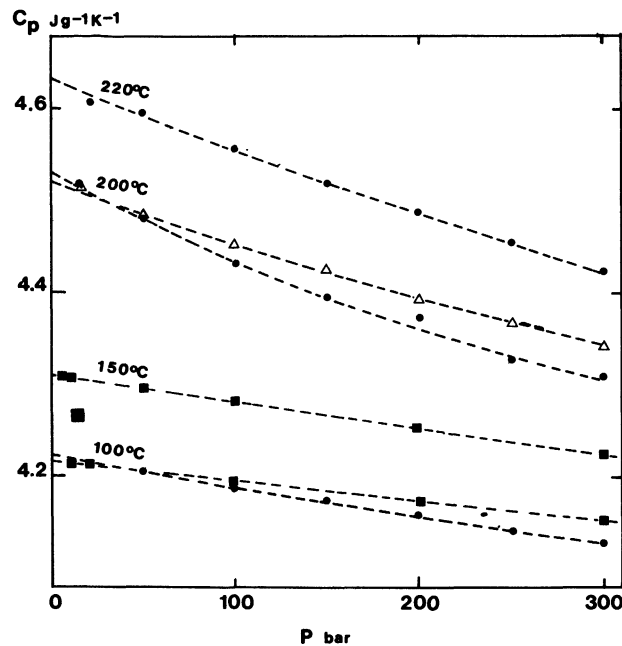


Fig. 3. — C_p versus temperature; examples of extrapolation at one bar, ● ref. 30, △ ref. 31, ■ ref. 28, 29.

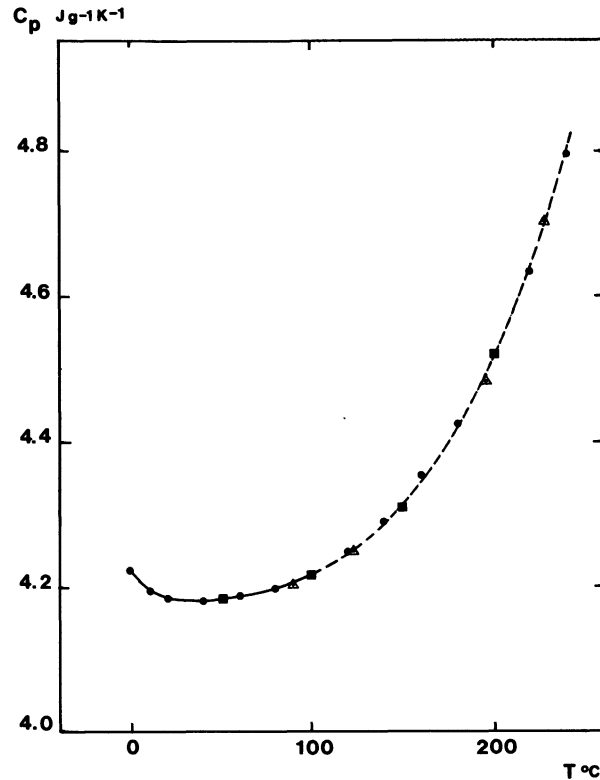


Fig. 4. — C_p at one bar up to 220 °C, deduced from : ● ref. 20, ■ ref. 31, △ ref. 28, 29, — — — ref. 26.

The isothermal compressibility β_T can then be derived by :

$$\beta_T = \frac{1}{\rho v_s^2} + \frac{T \alpha_p^2}{\rho C_p} \quad (3)$$

and the specific heat at constant volume by :

$$C_v = \frac{C_p}{1 + \frac{T \alpha_p^2 v_s^2}{C_p}} \quad (4)$$

The results are presented in table I. Figures 5 and 6 show the variation of β_s , β_T and C_v versus temperature in the stable and superheated range. The values of the isothermal compressibility are in good agreement with those deduced from the equations of Kell and Wasserman. The difference between C_v calculated from equation 4 and C_v obtained by extrapolation of the data given by Amirklanov are typically :

$$\Delta C_v = 0.01 \text{ J/gK at } 100\text{ }^\circ\text{C}$$

$$\Delta C_v = 0.02 \text{ J/gK at } 200\text{ }^\circ\text{C}.$$

These differences are below the experimental error.

2. Physical properties of the « normal water ».

We define the « normal water » as a hypothetical monomeric water.

Table I. — *Physical properties of the superheated water at one bar.*

t (°C)	ρ (°) g/cm ³	α_P (°) K ⁻¹	C_P J/gK	C_V J/gK	β_S bar ⁻¹	β_T bar ⁻¹
100	0.958 4	7.501	4.216	3.769	43.9	49.1
120	0.943 0	8.574	4.246	3.664	46.0	53.3
140	0.925 9	9.689	4.288	3.576	49.2	59.0
160	0.907 0	11.00	4.348	3.495	53.4	66.5
180	0.886 3	12.50	4.421	3.414	59.0	76.4
200	0.863 5	13.37	4.514	3.340	66.3	89.6
220	0.838 4	15.70	4.623	3.267	75.9	107.4

(°) Reference 19.

(°) Reference 17.

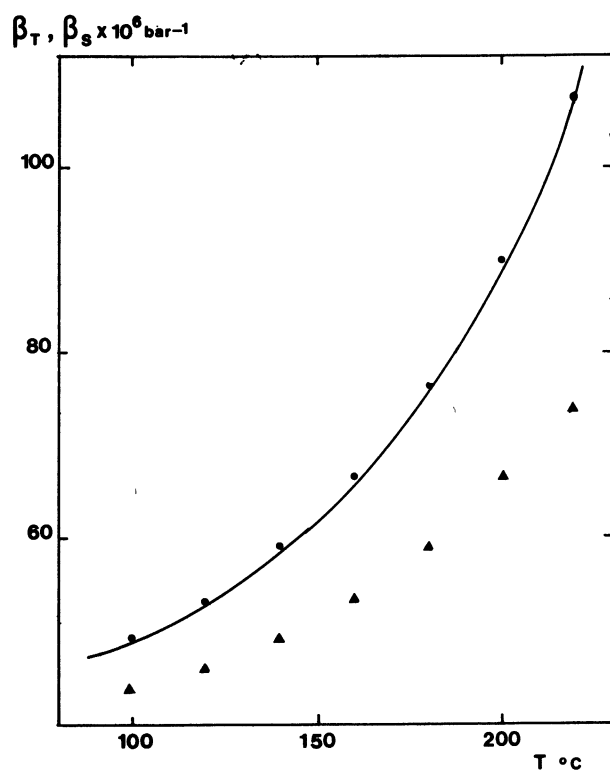
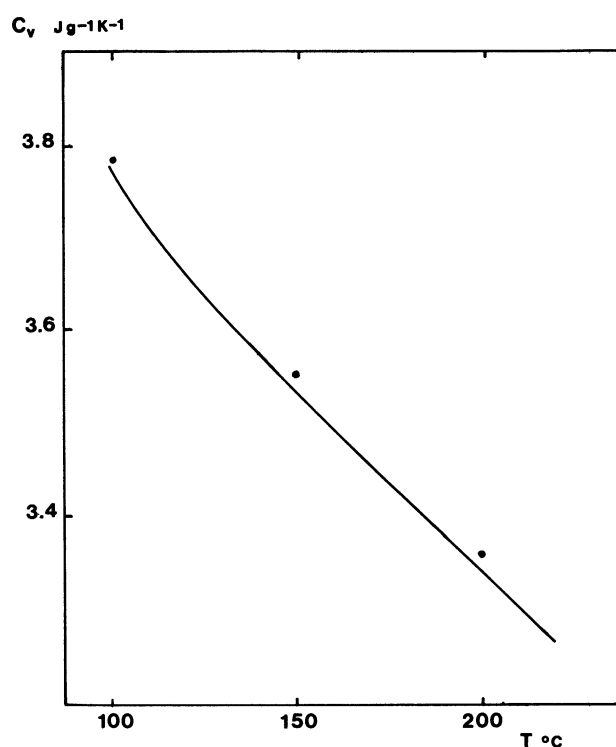
Fig. 5. — The isothermal and adiabatic compressibilities at one bar as a function of temperature : β_T (● ref. 23; — ref. 17); β_S (▲ ref. 23).

Fig. 6. — Temperature dependences of the specific heat at constant volume : ● from ref. 32; — our estimate.

2.1 NORMAL COMPONENTS OF THE THERMAL EXPANSIVITY AND THE ISOTHERMAL COMPRESSIBILITY OF WATER AT ONE BAR. — In the mixture models, the structural effects are taken into account supposing that the neighbouring structure of an oxygen atom depends on the number of bonds j emanating from it [8, 33, 34]. If we consider a local quantity such as the volume per oxygen atom, v_j , it is plausible that v_j will depend on the number of bonds j .

At a simplified level, it may be supposed that the structural effects are essentially due to the presence

of the 4-hydrogen bonded molecules and consequently, following Stanley and Teixeira [33] we will suppose that

$$\begin{aligned} v_3 &\simeq v_2 \simeq v_1 \simeq v_0 = V_N \\ v_4 &= V_S \text{ with } V_S > V_N \end{aligned} \quad (5)$$

where V_N is the molecular volume of monomeric or « normal » water and V_S is the molecular volume of « structured » water.

Note that V_N and V_S are equivalent to V_{gel} and V_{ice} in reference 33 or to V_c and V_0 in reference 8.

We will write :

$$\alpha_{P_N} = \frac{1}{V_N} \left(\frac{\partial V_N}{\partial T} \right)_P \quad \text{and} \quad \beta_{T_N} = \frac{1}{V_N} \left(\frac{\partial V_N}{\partial P} \right)_T. \quad (6)$$

Where the subscript N denotes the « normal » components of the thermal expansivity and the isothermal compressibility of water respectively. We propose an estimate of α_{P_N} and β_{T_N} at one bar based on the two following assumptions :

a) The experimental values of α_P and β_T at $T > 160$ °C can be assumed to be the « normal » components.

The molecular volume v of H_2O is a linear function of f_4 , the mole fraction of the molecules involved in 4-bonded interaction

$$v = V_N + f_4(V_S - V_N). \quad (7)$$

f_4 was obtained directly from intermolecular Raman intensity data [16, 35] (Fig. 7). At $T > 160$ °C, f_4 is less than 0.04 [35, 36]; so the contribution of the 4-bonded molecules is weak and can be ignored. Consequently, according to equation 7, one obtains for $T > 160$ °C, $v \simeq V_N$ and thus

$$\alpha_{P_N} \simeq \alpha_P \quad \text{and} \quad \beta_{T_N} \simeq \beta_T.$$

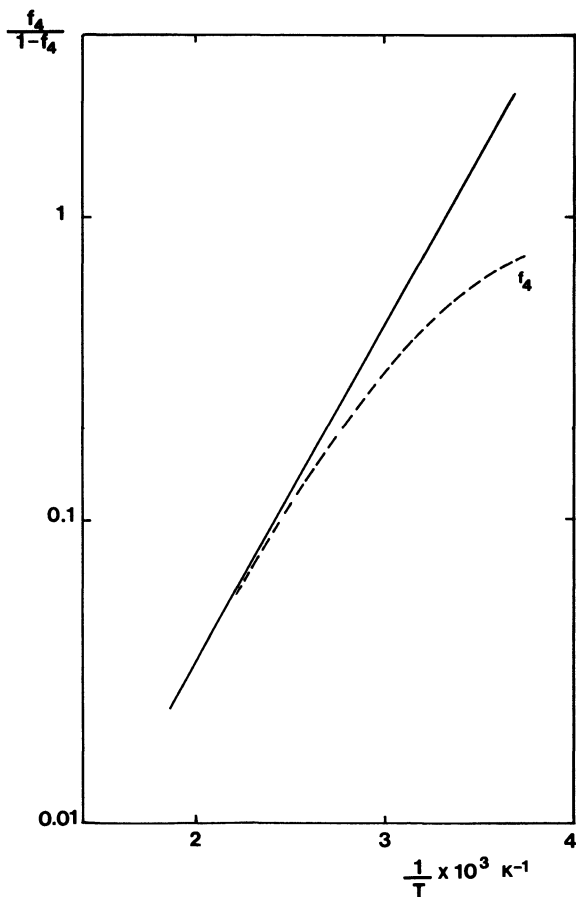


Fig. 7. — Mole fraction f_4 of H_2O molecules involved in 4-bonded interactions as function of temperature (from ref. 36), — $\frac{f_4}{1-f_4}$, - - - f_4 .

b) The isobaric evolution of the normal components of α_P and β_T can be fitted with the following formulae :

$$\beta_{T_N} = \beta_0(T_S - T)^{-\gamma} \quad (8)$$

$$\alpha_{P_N} = \alpha_0(T_S - T)^{-\alpha}$$

where T_S is the temperature corresponding to the limit of the stability for the liquid state. For water, at one bar this temperature T_S is estimated to be 325 °C [37]. The experimental evidence for these formulae is given in the appendix in the case of unassociated mono or polyatomic liquids : argon, CO_2 and n-hexane.

Remark. — At a simplified level, the isobaric heat capacity C_P can be considered as the sum of three terms [34] :

$$C_P = C_{P_N} + C_{P_B} + C_{P_S}. \quad (9)$$

— C_{P_N} is the normal term :

$$C_{P_N} = \left(\frac{\partial h_N}{\partial T} \right)_P \quad (10)$$

where $h_N = u_N + PV_N$, and u_N is the normal energy contribution corresponding to the vibrations and librations of the molecule.

— C_{P_B} is the « bonding » term :

$$C_{P_B} = - 2 E_{HB} \left(\frac{\partial p_B}{\partial T} \right)_P \quad (11)$$

where E_{HB} is the energy necessary to break a hydrogen bond and p_B is the probability for two neighbour molecules to be hydrogen bonded.

— C_{P_S} is the « structural » term, which depends only on f_4 and $(\partial f_4 / \partial T)_P$ ($f_4 = P_0$ in reference 34). At high temperatures ($T \gtrsim 160$ °C), $f_4 \lesssim 0.04$ and the structural effects can be neglected :

$$C_{P_S} \ll C_{P_N}.$$

However p_B and its derivative with respect to the temperature are still important because : $p_B \simeq 0.45$; $dp_B/dT \simeq 0.002 \text{ K}^{-1}$ in reference 36. So that C_{P_S} is expected to be of the order of magnitude of C_{P_N} . Thus at $T > 160$ °C

$$C_P \simeq C_{P_N} + C_{P_B}.$$

It is interesting to note that, in alcohols where one generally neglects the structural effects ($C_{P_S} = 0$), the abnormal component of C_P (often called configurational heat capacity) arises only from the breaking of hydrogen bonds [38], as in water at high temperatures.

To define the normal components α_{P_N} and β_{T_N} we took the experimental values of α_P and β_T measured at $T > 160$ °C and adjusted the parameters α_0 , α , β_0 , γ to fit the evolution of α_P and β_T . Thus the « normal » components α_{P_N} and β_{T_N} are taken as :

$$\alpha_{P_N} = 6.121 \times 10^{-2} (325 - t)^{-0.787} \text{ K}^{-1} \quad (12)$$

$$\beta_{TN} = 1.495 \times 10^{-2} (325 - t)^{-1.061} \text{ bar}^{-1} \quad (13)$$

with t in °C.

Starting with α_{PN} it is now possible to define a hypothetical « normal » water or « unbonded » water, for which the specific volume would be :

$$V_N = 2.587 \exp - [0.2875(325 - t)^{0.2129}] \text{ cm}^3/\text{g} \quad (14)$$

($V_N = 1.1927 \text{ cm}^3/\text{g}$ at 220 °C [25].)

In figures 8 and 9, plots of α_{PN} and β_{TN} versus temperature are shown and can be compared with the previous estimates deduced from the studies of aqueous solutions.

2.2 THE ISOCHORE HEAT CAPACITY OF THE « NORMAL » WATER. — Or « what should the heat capacity of water be without hydrogen bonds ? »

In this case the specific heat C_{VN} is reduced to a vibrational contribution [1]; it can be calculated using the Debye model with vibration frequencies deduced from the infra-red or Raman measurements. According to Kauzmann, each molecule has six modes of vibration, the frequencies of which are distributed on two Debye spectra centred at 654 cm^{-1} and 168 cm^{-1} . The vibration frequencies derived from infra-red experiments between 0° and 100 °C [15] are slightly dif-

$\alpha_p \times 10^4 \text{ K}^{-1}$

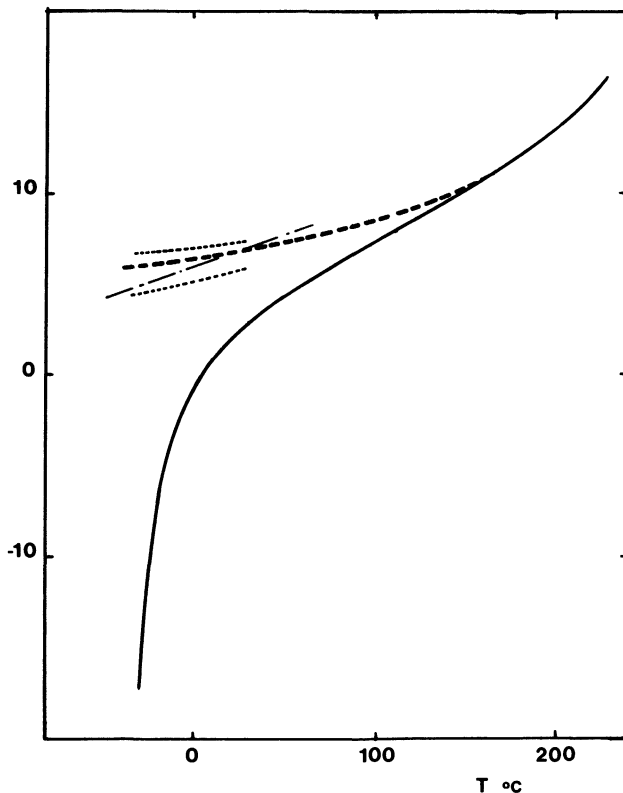


Fig. 8. — Expansivity of water as a function of temperature, — measured data ref. 17, ---- our estimation of the « normal » component α_{PN} , - - - estimation of α_{PN} from ref. 13, estimation limits of α_{PN} from ref. 14.

$\beta_T \times 10^6 \text{ bar}^{-1}$

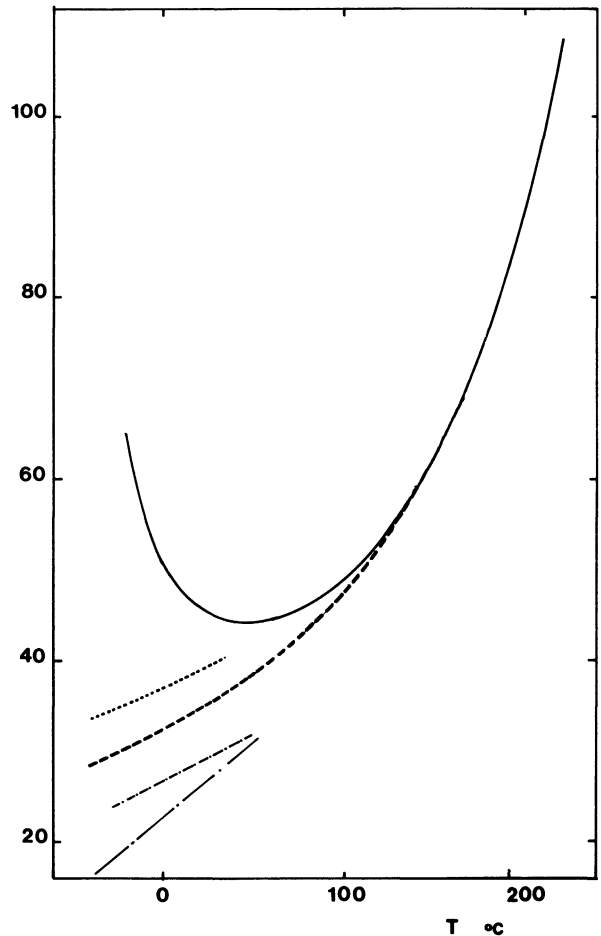


Fig. 9. — Isothermal compressibility of water as a function of temperature — ref. 16, ---- our estimate of the « normal » component β_{TN} , — estimate of β_{TN} from ref. 10, - - - estimate of β_{TN} from ref. 12, estimate of β_{TN} from ref. 14.

ferent from those obtained from Raman measurements [16]. However, in both cases, the thermal evolution can be represented by a linear equation

$$\nu (\text{cm}^{-1}) = \nu_0 - \Delta \nu \times (t - 30) \quad (15)$$

see table II.

Table II. — *Vibration frequencies of H₂O.*

Frequencies (cm ⁻¹)	Infra-red (a)	Raman (b)
ν_{0L}	193	168
$\Delta \nu_L$	$- 0.2 \pm 0.1$	$- 0.2 \pm 0.1$
ν_{0T}	685	654
$\Delta \nu_T$	$- 0.7 \pm 0.1$	$- 0.7 \pm 0.1$

The subscripts L and T refer respectively to the longitudinal and transverse vibration.

- (a) Reference 15.
- (b) Reference 16.

The values of C_{V_N} derived from both data are represented in figure 10.

2.3 ISOBARIC SPECIFIC HEAT OF THE « NORMAL » WATER. — This specific heat C_{P_N} has been determined using the relation

$$C_{P_N} = C_{V_N} + \frac{\alpha_N^2 V_N T}{\beta_{T_N}} \quad (16)$$

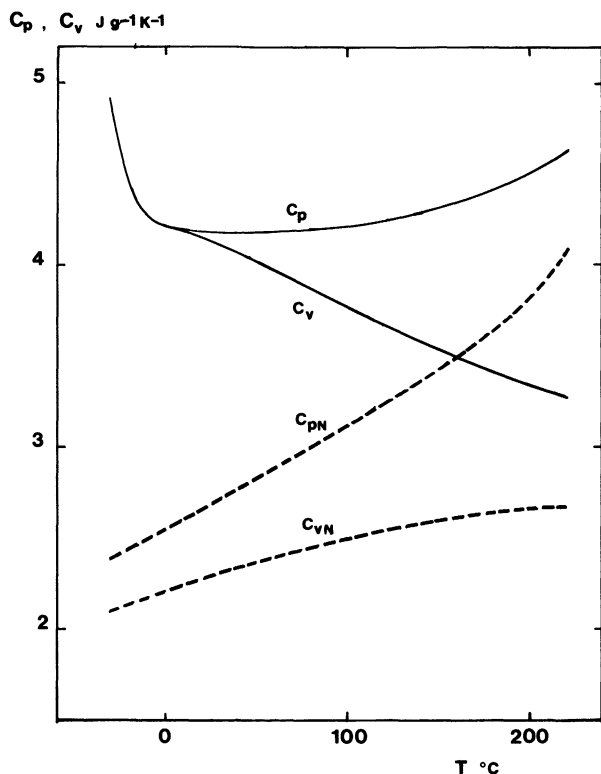


Fig. 10. — Isobaric and isochore specific heats of water at one bar, — C_p and C_v , - - - - estimate of the « normal » components C_{P_N} and C_{V_N} .

where the subscript N corresponds to the « normal » component of water, i.e. to a hypothetical unbonded water.

The evolution of C_{P_N} with temperature is presented in figure 10. Finally, all the « normal » components of the physical properties of water are gathered in table III.

3. Concluding remarks.

We presented and discussed the physical properties of superheated water up to 220 °C; the data were obtained from the measurements of density and sound velocity in superheated water, and by extrapolation from C_p measurements at high pressure.

Starting from these data, we have presented for water estimates of the « normal » components of the thermal expansivity and of the isothermal compressibility which can be used as a background in the analysis of the « abnormal » contributions.

Our analysis is based on the two following assumptions :

a) The structural effects are essentially due to the presence of the 4-hydrogen bonded molecules. An interesting consequence is that above 160 °C the structural effects can be neglected since the mole fraction of the molecules involved in 4-bonded interaction is very low ($f_4 < 0.04$): the water can then be considered as « normal ».

b) Below 220 °C, the temperature dependence of the « normal » components α_p and β_T on the temperature can be fitted with the following simple formula :

$$X = X_0(T_s - T)^{-x}$$

which has been tested on argon, CO₂ and n-hexane.

In figures 8 and 9, the « normal » components derived from our analysis are summarized together

Table III. — Physical properties of the « normal » water.

t (°C)	$\alpha_N \times 10^4$ (K ⁻¹)	$\beta_N \times 10^6$ (bar ⁻¹)	v_N (cm ³ /g)	C_{V_N} (J/gK)	C_{P_N} (J/gK)
- 40	5.89	28.65	0.942 7		
- 20	6.155	30.41	0.944 2	2.13	2.43
0	6.452	32.40	0.966 3	2.20	2.54
20	6.78	34.66	0.979 1	2.27	2.66
40	7.15	37.25	0.992 9	2.33	2.76
60	7.58	40.23	1.007 6	2.39	2.87
80	8.06	43.73	1.023 5	2.45	2.99
100	8.62	47.86	1.040 6	2.50	3.10
120	9.27	52.82	1.059	2.54	3.18
140	10.05	58.90	1.080	2.58	3.35
160	11.00	66.50	1.103	2.61	3.48
180	12.18	76.26	1.129	2.64	3.64
200	13.69	89.27	1.158	2.66	3.81
220	15.7	107.4	1.193	2.71	4.06

with those from the other analysis based on studies of aqueous solutions. It is interesting to point out that, in the case of the thermal expansivity (Fig. 8), all the estimates are in good agreement. Concerning the isothermal compressibility (Fig. 9), the results derived from the studies of aqueous solutions obviously depend on the type of mixture chosen, so that no comparison can be made.

Appendix.

In unassociated liquids, the temperature dependence of the expansivity α_p and the pressure dependence of the compressibility β_T are correctly represented by the following simple expressions :

$$\alpha_p = (T^* - T)^{-\alpha} \quad (1')$$

and

$$\beta_T = \beta_0(P - P^*)^{-\beta}. \quad (2')$$

We have tested these relations below the critical point ($T < T_{cr}$ and $P < P_{cr}$) in a large range of pressures and temperatures; good agreement has been obtained in all the range of the stable or metastable states accessible to the experiments. For argon and CO_2 , α_p and β_T have been deduced from the state equation proposed by Bender [39] and for n-hexane we used an equation given by Ermakov and Skripov [40]. So below the critical point, one can define a curve, $T^*(P)$ such that $\ln \alpha_p$ is linearly dependent on $\ln(T^*(P) - T)$. In the same way, one can find $P^*(T)$ such that $\ln \beta_T$ is linearly dependent on $\ln(P - P^*(T))$.

One can see in figures 11a and b that these curves $P = P^*(T)$ and $T = T^*(P)$ coincide with a pseudo spinodal curve determined by a linear extrapolation of the isochores (the pseudo spinodal being the envelope of the isochores [37]).

Now we must point out that the empirical formulae used here to fit α_p and β_T hold over an unexpectedly wide range of data, far from the pseudo spinodal curve. In fact, a simple power law could only be expected in the close vicinity of a spinodal point. [In mean-field calculations, the expansion of the Helmholtz potential leads to an exponent 1/2 for α_p , β_T and C_p , either on isotherms or isobars [41].]

Remarks. — Below the critical pressure, one can find a value $T^{**}(P)$ such that the isobaric evolution of

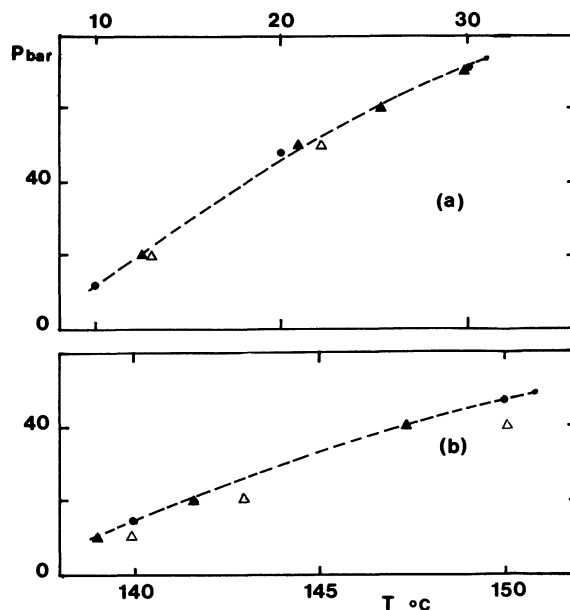


Fig. 11. — Spinodal curves : (a) for liquid CO_2 , (b) for liquid argon, ----- $T_s(P)$ (the spinodal), ● $T^*(P)$, ▲ $P^*(T)$, △ $T^{**}(P)$.

$\ln \beta_T$ versus $\ln(T^{**}(P) - T)$ is linear. However, this value is generally different from the spinodal temperature $T_s(P)$. The difference

$$\Delta T_s = T^{**} - T_s$$

is in the order of few degrees near the critical point, it decreases with the pressure and becomes negligible far from the critical point. For instance, in argon, $P_c = 48$ bar ($P_c =$ critical point).

P (bar)	10	20	40
ΔT_s (°C)	1	1.6	2.4

Consequently we conclude that at pressures far below the critical pressure the isobaric evolution of α_p and β_T versus temperature, in un-associated liquids, can be well fitted by :

$$\begin{aligned} \alpha_p &= \alpha_0(T^* - T)^{-\alpha} \\ \beta_T &= \beta_0(T^* - T)^{-\gamma}. \end{aligned} \quad (3')$$

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