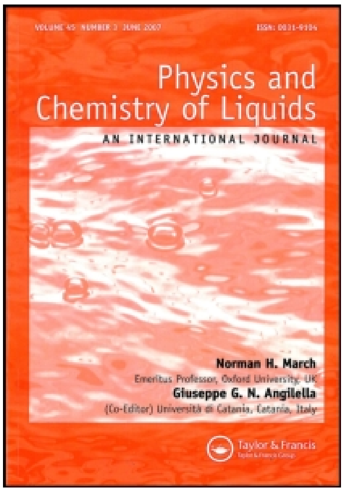

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Thermodynamic Properties of Liquid Water up to 8000 Bar and Between 25 and 150°C

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THERMODYNAMIC PROPERTIES OF LIQUID WATER UP TO 8000 BAR AND BETWEEN 25 AND 150°C

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A simple equation of state for the condensed phase, proposed by Cho, is applied to liquid water under pressure up to 8000 bar and between 25 and 150°C. The agreement between measured and calculated volumes is satisfactory over the entire range of temperatures and pressures. The equation shows that the abnormalities in the temperature and pressure dependence of the thermal expansivity, isothermal compressibility and the heat capacity are predicted quite accurately from PVT data only. The values of thermal expansivity, isothermal compressibility, and heat capacity at constant pressure are calculated, and detailed comparisons with the experimental values are made.

KEY WORDS: Thermal properties of water.

I INTRODUCTION

A simple equation of state proposed by Cho has recently been shown to represent the PVT properties of polymers[1,2] and simple liquids[3] very well. The equation of state takes the form[1,2]

$$V = V_0[K/(K + P)]^c, \tag{1}$$

where V is the volume at pressure P and temperature T, V_0 is the zero-pressure volume at T, C is a constant, and K is given by[1,2]

$$K = K_0 \exp(-k_T). \tag{2}$$

For liquids the temperature dependence of V_0 and k_T are as follows[2,3]:

$$\ln V_0 = b_0 + b_1 T + b_2 T^2 + b_3 T^3 \tag{3}$$

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and

$$k_T = k_1 T + k_2 T^2 + k_3 T^3, \tag{4}$$

where $b_0 - b_3$ and $k_0 - k_3$ are constants for specified material[1,2]. Since for most condensed phases $k_T \sim 10^{-1}$, Eq. (2) can be expressed approximately as

$$K = D_0 - D_1 T - D_2 T^2 - D_3 T^3, \tag{5}$$

where $D_0 = k_0$, $D_1 = k_0 k_1$, $D_2 = k_0 k_2$, and $D_3 = k_0 k_3$. This expression is quite useful in the temperature range of interest.

Recently, it was found that from the equation of state the thermodynamic properties of polymer can be predicted quite accurately[2,4]. In this work, the equation is used to explain the abnormal properties of liquid water up to 8000 bar in the temperature range from 25 to 150°C.

Experimental PVT data considered here include: (1) the compression data of Grindley and Lind[5](GL) in the range from 25 to 150°C and from 0 to 8000 bar; (2) the compression data of Kell and Whalley[6] (KW) in the range from 25 to 150°C and from 0 to 1000 bar; and (3) the compression data of Chen, Fine, and Millero[7] (CFM) in the range from 25 to 100°C and from 0 to 1000 bar.

II RESULTS

A Analysis of PVT data

The parameters in Eqs. (1) and (3) were first determined for water. The necessary experimental PVT data were taken from the literature. The results are given in Tables 1 and 2. Units are cm^3/g, bars, and Kelvin temperature K. The standard deviations $\sigma(V_0)$ and $\sigma(V)$ are given in the final columns of Tables 1 and 2. Figure 1 shows a comparison between experimental values of volume[5] and those calculated by using Eq. (1) with parameters based on GL data. Within the scale of the figure, there is no discernible difference between the data and the calculated values. Table 3 compares experimental and calculated zero pressure volumes and thermal expansivities by using Eq. (3) with parameters based on GL data. For Eq. (1) with Eq. (5), the PVT data of GL give

$$\begin{aligned} K &= -2.25876 \times 10^4 + 2.03807 \times 10^2 T \\ &\quad -5.06494 \times 10^{-1} T^2 + 3.93640 \times 10^{-4} T^3, \\ C &= 0.16362, \end{aligned}$$

and

$$\sigma(V) = 2.75 \times 10^{-4}.$$

Here, K is in bar and T in K.

From the temperature dependence of the zero-pressure bulk modulus, we have[1,2]

$$\frac{d \ln K}{dT} = -\delta\alpha_0 + q(T) \tag{6}$$

$$= -(k_1 + 2k_2 T + 3k_3 T^2) + q(T), \tag{7}$$

Table 1 Parameters in Eqs. (1) and (2).

	Ref.	C	k_0	k_1	k_2	k_3	*Range/kbar*	*Range/°C*	$\sigma(v) \times 10^4$
GL	5	0.16362	18.52985	-3.86785×10^{-2}	8.73581×10^{-5}	-5.66043×10^{-8}	0–8	25–150	2.79
KW	6	0.15281	2.47344	-5.42908×10^{-2}	1.28057×10^{-4}	-9.08016×10^{-8}	0–1	25–150	0.63
CFM	7	0.15901	73.94775	-2.40077×10^{-2}	3.71341×10^{-5}		0–1	25–100	0.45

Units are cm^3/g, bars, and K.

Table 2 Parameters in Eq. (3).

	Ref.	b_0	b_1	b_2	b_3	*Range/°C*	$\sigma(v_0) \times 10^5$
GL	5	0.307905	-2.60388×10^{-3}	6.21718×10^{-6}	-3.06811×10^{-9}	25–150	6.53
KW	6	0.31772	-2.68653×10^{-3}	6.44678×10^{-6}	-3.27946×10^{-9}	25–150	6.67
CFM	7	0.49624	-4.28375×10^{-3}	1.11916×10^{-5}	-7.95998×10^{-9}	25–100	1.36

Units are cm^3/g and K.

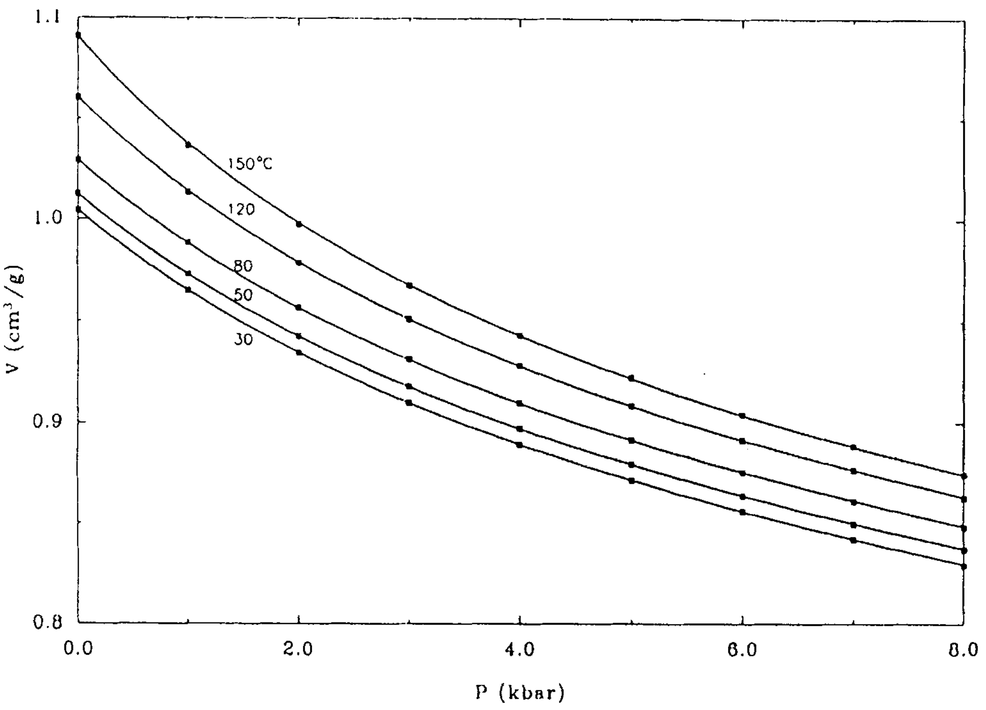

Figure 1 Comparison of experimental isotherms (■) of water with theoretical isotherms (solid lines).

Table 3 Comparison of experimental and calculated values of V_0, α_0, and β_0.

T(°C)	V_0, *cm³/g*		$\alpha_0 \times 10^3$, *deg*$^{-1}$		$\beta_0 \times 10^4$, *bar*$^{-1}$	
	Expt[a]	*Calc*[c]	*Expt*[b]	*Calc*[c]	*Expt*[b]	*Calc*[d]
30	1.00442	1.00443	0.3135	0.3197	0.4494 (0.4482)	0.4523
50	1.01215	1.01224	0.4581	0.4531	0.4423 (0.4418)	0.4467
70	1.02279	1.02275	0.5840	0.5791	0.4502 (0.4473)	0.4528
90	1.03598	1.03591	0.6965	0.6978	0.4767 (0.4615)	0.4697
110	1.05165	1.05165	0.8041	0.8091	0.5103 (0.4838)	0.4974
130	1.06985	1.06993	0.9125	0.9130	0.5566	0.5363
150	1.09080	1.09072	1.0232	1.0096	0.6234	0.5869

[a] Data from Ref. 5.
[b] Data from Ref. 9, bracketed values represent the data of Ter Minassian *et al.*, Ref. 8.
[c] Calculated from Eq. (3).
[d] Calculated from Eq. (13).

where δ is the zero-pressure Anderson–Gruneisen constant, α_0 is the zero-pressure thermal expansivity $\alpha_0 = (\partial \ln V_0/\partial T)_P$, and $q(T)$ is a function of temperature only. For most condensed phases, the second term on the right-hand side of Eq. (7) is ordinarily much smaller than the first term. Therefore, a good approximation is[1,2]

$$\frac{d \ln K}{dT} = dk_T/dT \tag{8}$$

$$= -(k_1 + 2k_2 T + 3k_3 T^2). \tag{9}$$

In this work, we use Eq. (9) for the temperature dependence of $d \ln K/dT$.

B Thermal expansivity

From Eq. (1) we have[1,2]

$$\alpha = \alpha_0 - \frac{CP}{K+P}\frac{dk_T}{dT}. \tag{10}$$

From this we have

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = -\frac{CK}{(K+P)^2}\frac{dk_T}{dT}. \tag{11}$$

Letting $\alpha \to \alpha_m$ as $P \to \infty$, it follows from Eq. (10) that

$$\alpha_m = \alpha_0 - C(dk_T/dT). \tag{12}$$

Equation (11) shows that the rate of change of α with pressure is rapid at low pressures and becomes less rapid at high pressures, and as the pressure becomes infinite α approaches the limiting value α_m. According to the result calculated from Eq. (9) based on the PVT data of GL, $dk_T/dT = 0$ at $T_k = 322.65$ K, and $dk_T/dT < 0$ below T_k and $dk_T/dT > 0$ above T_k. Thus, it follows from Eq. (11) that $(\partial\alpha/\partial P)_T > 0$ below T_k and $(\partial\alpha/\partial P)_T < 0$ above T_k, and at T_k $(\partial\alpha/\partial P)_T = 0$. Therefore, α increases with increasing pressure below T_k and decreases with increasing pressure above T_k, and at T_k, α is independent of pressure. These agree with the experimental results[8,9]. Using the PVT data of CFM[7], we have $T_k = 323.31$ K, and using the PVT data of KW[6], we have $T_k = 320.75$ K which is much smaller than others. According to the experimental results of Ter Minassian *et al.*[8], the corresponding temperature is 322.3 K.

Figure 2(a) shows the general aspect of the isotherm of α as a function of pressure calculated from Eq. (10). As shown there, at high pressures the isotherms intersect, so that at higher pressures α at the higher temperatures is lower than it is at the lower temperatures. Such behavior has been observed experimentally[8]. The isobars as a function of temperature are shown in Figure 2(b). All calculations in Figures 2(a) and 2(b) are based on the parameters obtained from the PVT data of GL. As shown in Figure 2(b), all isobars intersect at T_k, since α at T_k is independent of pressure over the entire range of pressure. The sign of the derivative $(\partial\alpha/\partial T)_P$ changes in the vicinity of 5.2 kbar. The thermal expansivity increases with increasing temperature

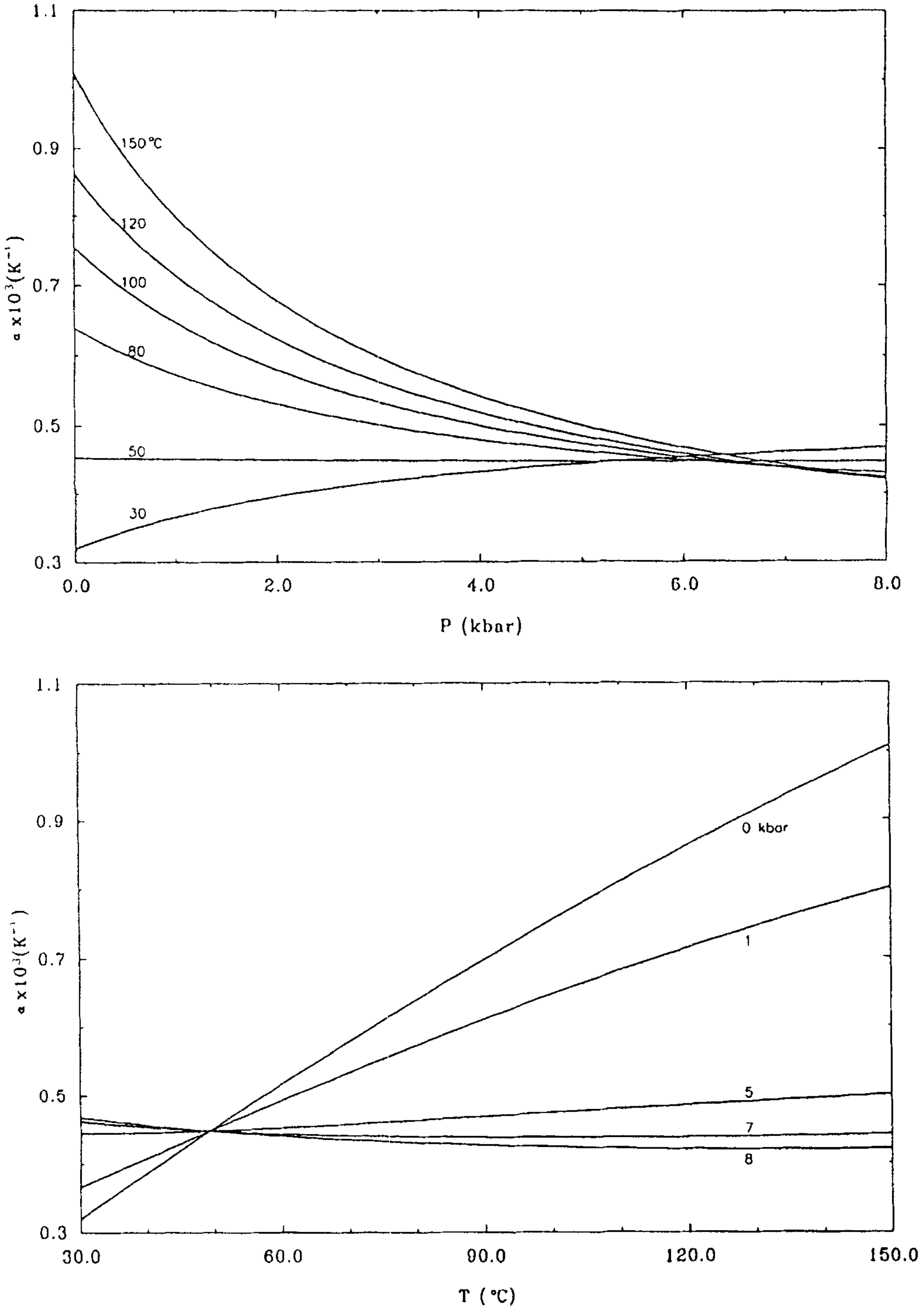

Figure 2 General aspect of the behavior of the thermal expansivity of water, (a) as a function of pressure, (b) as a function of temperature. The number indicated on the isobars is in kbar.

Table 4 Comparison of experimental[a] and calculated [b] values of α.

	$\alpha \times 10^3$, k^{-1} deg^{-1}							
P(bar)	*30°C*		*50°C*		*100°C*		*150°C*	
	Expt	*Calc*	*Expt*	*Calc*	*Expt*	*Calc*	*Expt*	*Calc*
200	0.3248 (0.3257)	0.3311	0.4547 (0.4677)	0.4527	0.7182 (0.7314)	0.7282	0.9551 (0.9811)	0.9565
600	0.3486 (0.3527)	0.3504	0.4543 (0.4669)	0.4520	0.6672 (0.6883)	0.6838	0.8562 (0.8712)	0.8691
1000	0.3728 (0.3757)	0.3664	0.4581 (0.4661)	0.4514	0.6304 (0.6492)	0.6474	0.7851 (0.7817)	0.8002
3000	0.4328 (0.4410)	0.4175	0.4572 (0.4639)	0.4496	0.5264 (0.5256)	0.5339	0.5968 (0.5474)	0.5986
5000	0.4500 (0.4653)	0.4449	0.4508 (0.4630)	0.4486	0.4747 (0.4741)	0.4745	0.5081 (0.4672)	0.5005
7000	0.4470 (0.4754)	0.4620	0.4409 (0.4627)	0.4479	0.4407 (0.4517)	0.4380	0.4577 (0.4347)	0.4424
8000	0.4448 (0.4779)	0.4683	0.4378 (0.4626)	0.4477	0.4277 (0.4461)	0.4245	0.4420 (0.4269)	0.4215

[a] Data from Ref. 9, bracketed values represent the data of Ter Minassian *et al.*, Ref. 8.
[b] Calculated from Eq. (10) based on the PVT data of GL.

below this pressure, but above this pressure a minimum in α is predicted to occur at a certain temperature T_B, whose value depends on the pressure. For a given pressure, α decreases with increasing temperature below T_B and increases with increasing temperature above T_B. These results agree with experimental results[9].

In Table 4, the values calculated from Eq. (10) using the parameters based on GL data are compared with the experimental values[9]. Values in brackets represent the calculated values by using the empirical equation of Ter Minassian *et al.*[8] with the coefficients reported in Ref. 8.

C Isothermal compressibility

From Eq. (1) the isothermal compressibility, $\beta = -(\partial \ln V/\partial P)_T$, is represented by[1,2]

$$\beta = \frac{C}{K + P}. \tag{13}$$

From this we have

$$\left(\frac{\partial \beta}{\partial T}\right)_P = \frac{CK}{(K + P)^2} \frac{dk_T}{dT}. \tag{14}$$

By comparing Eq. (11) with Eq. (14), we have

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = -\left(\frac{\partial \beta}{\partial T}\right)_P, \tag{15}$$

which is the Maxwell relation.

Since $dk_T/dT < 0$ below T_k and $dk_T/dT > 0$ above T_k, it follows from Eq. (14) that $(\partial\beta/\partial T)_P < 0$ below T_k and $(\partial\beta/\partial T)_P > 0$ above T_k. Thus, as a function of temperature, a minimum in β is predicted to occur at T_k, and the temperature of minimum compressibility T_k is independent of pressure since $dk_T/dT = 0$ at T_k. Equation (14) also shows that for a given temperature, $(\partial\beta/\partial T)_P$ decreases with increasing pressure. These predictions have been confirmed by experiment.[8–11] In Table 5, values calculated from Eq. (13) with the parameters based on the PVT data of GL are compared with experimental values[9]. Values in brackets represent the experimental values of Ter Minassian *et al*[8]. For zero-pressure values, we compare in Table 3. The agreement is seen to be good.

D Heat Capacity

The calculation of the heat capacity at constant pressure is based on the thermodynamic equation

$$(\partial C_P/\partial P)_T = -T(\partial^2 V/\partial T^2)_P. \tag{16}$$

Applying Eq. (1) to Eq. (16), we have

$$\begin{aligned}\Delta C_P &= C_P(T, P) - C_P(T, 0)\\ &= -T\Bigg[\left(\frac{d\alpha_0}{dT} + \alpha_0^2\right)V_0 K R_1 + \left(2\alpha_0\frac{dK}{dT} + \frac{d^2K}{dT^2}\right)C V_0(R_1 + R_3)\\ &\quad + \frac{C(C-1)V_0}{K}\left(\frac{dK}{dT}\right)^2(R_1 + 2R_3 - R_2) - \frac{2CV_0}{K}\left(\frac{dK}{dT}\right)^2(R_2 - R_3)\Bigg],\end{aligned} \tag{17}$$

where

$$R_1 = \frac{1}{1-C}\left[\left(\frac{V_0}{V}\right)^{(1-C)/C} - 1\right],$$

$$R_2 = \frac{1}{1+C}\left[\left(\frac{V}{V_0}\right)^{(1+C)/C} - 1\right],$$

and

$$R_3 = \frac{1}{C}\left[\frac{V}{V_0} - 1\right].$$

Values of ΔC_P were calculated from Eq. (17) based on the PVT data of GL. In Table 6, a comparison is made of their values with those obtained by Ter Minassian *et al.*[8] and Vedam and Holton[12]. The agreement is seen to be good except for values at high pressures. According to Eq. (17), $(\partial C_P/\partial P)_T$ undergoes a sign change at a certain pressure, whose value depends on the temperature. For a given temperature, C_P decreases with increasing pressure below this pressure and increases with increasing pressure above this pressure. The pressure of the minimum C_P increases with increasing the temperature. Such behavior has been observed experimentally[8].

Table 5 Comparison of experimental[a] and calculated[b] values of β.

	$\beta \times 10^4$, bar^{-1}									
P(bar)	*30°C*		*50°C*		*100°C*		*120°C*		*150°C*	
	Expt	*Calc*	*Expt*	*Calc*	*Expt*	*Calc*	*Expt*	*Calc*	*Expt*	*Calc*
200	0.4273 (0.4270)	0.4286	0.4213 (0.4207)	0.4236	0.4621 (0.4505)	0.4554	0.4968 (0.4772)	0.4849	0.6702	0.5476
600	0.3809 (0.3886)	0.3879	0.3822 (0.3830)	0.3838	0.4103 (0.4108)	0.4098	0.4352 (0.4355)	0.4335	0.4883	0.4830
1000	0.3549 (0.3553)	0.3543	0.3494 (0.3505)	0.3509	0.3705 (0.3751)	0.3724	0.3898 (0.3967)	0.3920	0.4304	0.4320
3000	0.2471 (0.2467)	0.2472	0.2463 (0.2449)	0.2456	0.2549 (0.2553)	0.2559	0.2624 (0.2641)	0.2650	0.2778	0.2827
5000	0.1885 (0.1911)	0.1899	0.1902 (0.1904)	0.1889	0.1962 (0.1948)	0.1949	0.2016 (0.1986)	0.2002	0.2107	0.2101
7000	0.1545	0.1541	0.1555	0.1534	0.1603	0.1574	0.1638	0.1608	0.1700	0.1672
8000	0.1406	0.1408	0.1429	0.1403	0.1473	0.1436	0.1489	0.1464	0.1544	0.1517

[a] Data from Ref. 9, bracketed values obtained by Ter Minassian *et al.*, Ref. 8.
[b] Calculated from Eq. (13) based on the PVT data of GL.

Table 6 Comparison of experimental and calculated values of ΔCp.

	$-\Delta Cp, JK^{-1}\,g^{-1}$										
P, bar	*30°C*			*50°C*			*80°C*			*100°C*	
	Expt A	*Expt B*	*Calc*	*Expt A*	*Expt B*	*Calc*	*Expt A*	*Expt B*	*Calc*	*Expt A*	*Calc*
200	0.053		0.040	0.044		0.042	0.041		0.044	0.042	0.045
600	0.140		0.110	0.121		0.115	0.113		0.121	0.116	0.124
1000	0.207	0.200	0.166	0.183	0.160	0.175	0.172	0.190	0.185	0.176	0.188
2000	0.313	0.300	0.268	0.291	0.240	0.287	0.279	0.310	0.304	0.280	0.308
3000	0.363	0.360	0.329	0.350	0.280	0.359	0.344	0.380	0.383	0.342	0.388
4000	0.384	0.410	0.361	0.382	0.310	0.403	0.382	0.420	0.435	0.378	0.440
5000	0.388	0.440	0.374	0.396	0.330	0.427	0.404	0.440	0.468	0.399	0.474
5600			0.374			0.434			0.480		0.488
6000		0.460	0.372		0.340	0.436		0.440	0.486		0.495
6600			0.365			0.435			0.491		0.502
7000		0.470	0.358		0.340	0.433		0.440	0.492		0.505
7600			0.345			0.427			0.492		0.506
8000			0.335		0.340	0.421		0.440	0.490		0.506

Expt A: Data from Ref. 8.
Expt B: Data from Ref. 12.
Calc: Calculated from Eq. (17).

Unfortunately, for values at higher pressures and temperatures, detailed comparisons are not made for the lack of experimental data.

III CONCLUSIONS

It has been shown that for water up to 8000 bar and between 25 and 150°C, Eq. (1) can be used to represent the volumetric data and to explain the thermodynamic anomalies. From the equation the following are predicted: (1) The thermal expansivity increases with increasing pressure below $T_k = 322.65\ \mathrm{K}$ and decreases with increasing pressure above T_k, and at T_k the thermal expansivity is independent of pressure over the entire range of pressure. (2) At higher pressures the thermal expansivity at higher temperatures is lower than it is at the lower temperatures. (3) As a function of temperature, a minimum in the isothermal compressibility occurs at T_k and the temperature of minimum compressibility T_k is independent of pressure. (4) As a function of pressure, a minimum in the heat capacity at constant pressure is predicted to occur at a certain pressure, and the pressure of the minimum heat capacity increases with increasing the temperature.

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