

Using Heat Capacity and Compressibility To Choose among Two-State Models of Liquid Water

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We extend to heat capacity C_p the model of Vedomuthu, Singh, and Robinson (*J. Phys. Chem.* **1994**, 98, 2222). This model and that of Bartell (*J. Phys. Chem. B* **1997**, 101, 7573) fit successfully, even in the supercooled region, the temperature dependence of C_p , volume, and isothermal compressibility κ_T . The Robinson model is superior for κ_T . Tanaka's model (*J. Chem. Phys.* **2000**, 112, 799) fails for C_p even after correction of a derivational error. All three models assume that the liquid consists of low-density component 1 and high-density component 2. We conclude that Robinson's tactics, ignoring the intercomponent equilibrium constant and determining compositions solely from volumes, yield the most reliable compositions and individual-component properties. Our fits of the Robinson model to C_p yield at 0 °C $H_2 - H_1$ of (135 ± 35) J/g, $H_1 - H_{\text{ice}}$ of $0.8\Delta H_{\text{fus}}$, and $C_2 - C_1$ of (0.1 ± 0.7) J/K·g. The enthalpy difference between the components is largely responsible for the rapid change of C_p at the lowest supercooled temperatures. We propose an adjustment to Speedy and Angell's (*J. Chem. Phys.* **1976**, 65, 851) experimental values of κ_T for supercooled water.

Introduction

Water is a very unusual liquid. It has the highest heat capacity per gram of any room-temperature liquid except D₂O, and its volume increases on freezing. Its volume V , isobaric heat capacity C_p , and isothermal compressibility κ_T have minima at 4, 35, and 46 °C, respectively. In supercooled (<0 °C) water, these three properties increase markedly with decreasing temperature.¹

Water's viscosity η is also unusual. It decreases with increasing pressure (below about 33 °C), and its temperature dependence departs markedly from an Arrhenius equation.²

Many models have been invoked to explain individual properties of water. Explaining multiple properties quantitatively with a single model is much more difficult. Notably successful, even in the supercooled region, are the models of Bartell,³ Robinson and co-workers,^{2,4–8} Tanaka,^{9,10} and Kiselev and Ely.¹¹

All four of these models treat liquid water as a mixture of but two components: a more ordered, lower-density, lower-energy structural state; and a less ordered, higher-density, higher-energy state. The structural differences between these components are presumed to be short-range and transient. The local organization of the low-density component is thought to be similar to that of ice I.⁴ In accordance with Le Chatelier's principle, the mass fraction of the higher-energy, higher-density component increases with increasing temperature or pressure.

This type of model is distinctly different from two-state models based on two numbers of hydrogen bonds per individual water molecule. Models of the latter type were generally discredited by the mid-1970s. Water molecules with other than four hydrogen bonds have recently been shown to be insignificant in the liquid except as transition states.¹²

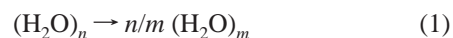
Kiselev and Ely's model reproduced very well for both H₂O¹¹ and D₂O¹³ the temperature dependence of C_p and the temperature and pressure dependence of κ_T and density ρ . We will not

consider this model further, however, since it is an equation of state and involves many more parameters than do the other models. In contrast, the other three models express properties of water as functions of properties and fractions of its two components.

We will largely ignore the two-state model of Ponyatovsky et al.¹⁴ Although it shared many features with the first three models, it differed from them considerably in its implementation and was markedly less successful than them in fitting properties of water.

The remaining three models are conceptually similar, yet Figure 1 shows that the Robinson model's values of f_2 , the mass fraction of the high-density component, are considerably lower than those of the Bartell and Tanaka models.

This disagreement may be due in part to a constraint imposed by Tanaka and (at high temperatures) by Bartell but never by Robinson. Tanaka required the equilibrium constant for the reaction



between low-density and high-density states to satisfy eq 2 with a constant value of ΔH_m .

$$\ln K_c = -\Delta H_m/RT + \text{constant} \quad (2)$$

Bartell required merely that this linearity in $1/T$ apply at high temperatures. Bartell used values of n/m from 1 to 8 in his fittings to experimental data. Tanaka tacitly assumed that $n/m = 1$. One goal of this paper is to assess the advisability of this linearity constraint.

We will also assess another difference in tactics. For determining $f_2(T)$, Robinson's group⁴ relied exclusively on fitting the model to high-precision experimental volumes. Bartell instead fitted to several properties simultaneously. However, he introduced a composite activity coefficient that guaranteed an exact fit to V . Thus both models' excellent ability to fit V is a poor criterion for assessing them.

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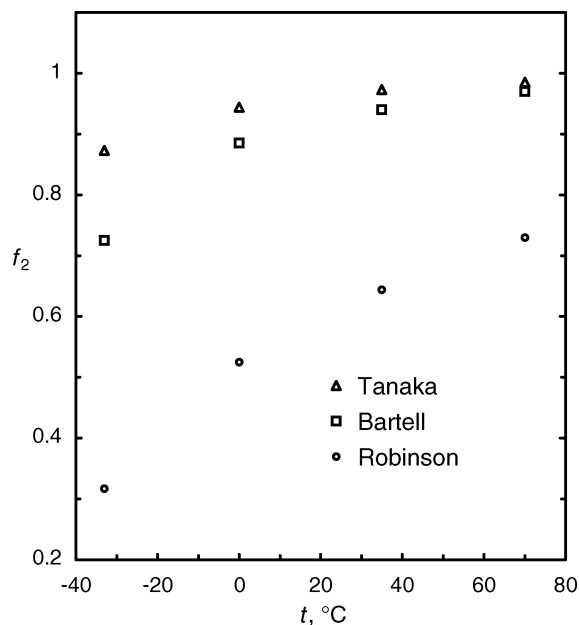


Figure 1. Mass fractions of the high-density component. Tanaka is from ref 10. Bartell is from choice B in Figure 2 of ref 3, with n/m either 1 or 5. Robinson is from fit i of ref 4.

Our principal criteria for assessing models will be their abilities to fit the temperature dependence of experimental C_p and κ_T . Heat capacity, an energetic consequence of a model, is independent of the volumetric consequence κ_T . Fitting of heat capacity (specifically C_v) had been a particular challenge for earlier mixture models of liquid water, even above supercooled temperatures.¹⁵

Bartell's model fitted well the temperature dependence of V , κ_T , and C_p .³ Tanaka's model fitted well the temperature and pressure dependence of ρ and κ_T .¹⁰ Tanaka also modeled the temperature dependence of C_p , but the results were quite unsatisfactory below -20 °C. The present paper corrects an error in Tanaka's application of his model to C_p , but agreement with experiment remains poor.

Robinson's model fitted well below ~ 70 °C the temperature and pressure dependence of V ^{4,5} and the temperature dependence of κ_T .^{5,6} but it was not tested against C_p . The present paper extends this model to C_p , which the model fits within experimental uncertainty.

This paper also reevaluates experimental values of κ_T and compares the Bartell and Robinson models' fits of this property.

Mathematical Models and Calculations

We assume that liquid water consists of only two components and that the enthalpy per gram is

$$H(T) = f_1(T)H_1(T) + f_2(T)H_2(T) + Uf_1f_2 \quad (3)$$

where f_2 (which equals $1 - f_1$) is the mass fraction of the high-density component. (This is Robinson's notation. Robinson's f_2 has the same meaning as Tanaka's $1 - \bar{S}$, Bartell's $n_M/(n_M + mn_{TN})$, and Ponyatovsky's c .) The term Uf_1f_2 approximates the energy of interaction between the two components.

The isobaric heat capacity derived from eq 3 is

$$C_p = dH/dT = f_1C_1 + f_2C_2 + (df_2/dT)[H_2 - H_1 + (f_1 - f_2)U] \quad (4)$$

where all derivatives are at constant pressure. Thus, C_p of the liquid includes a relaxation term in addition to the weighted

heat capacities of the two components. The relaxation term represents the contribution to C_p of interconversion between the components. Ponyatovsky et al. included the U term in their expression for C_p , but Bartell did not. Ponyatovsky, however, tacitly assumed that C_1 equals C_2 .

Tanaka¹⁰ omitted the U term, claiming that it would be unimportant except at temperatures well below those at which supercooling occurs.

If we assume that C_1 and C_2 are independent of temperature, then

$$C_p(T) = C_1 + f_2\Delta C + (df_2/dT)[\Delta H(T_r) + \Delta C\Delta T + (1 - 2f_2)U] \quad (5)$$

where T_r is a reference temperature, ΔT is $T - T_r$, and ΔC is $C_2 - C_1$. If we assume instead that $U = 0$ and that C_1 and C_2 depend linearly on temperature, with

$$C_i(T) = C_i(T_r) + \alpha_i\Delta T \quad (6)$$

then

$$C_p(T) = C_1(T_r) + \alpha_1\Delta T + f_2[\Delta C(T_r) + \Delta\alpha\Delta T] + (df_2/dT)[\Delta H(T_r) + \Delta C(T_r)\Delta T + \frac{1}{2}\Delta\alpha(\Delta T)^2] \quad (7)$$

We separately fitted eqs 5 and 7 to experimental values of C_p (at atmospheric pressure) by nonlinear least-squares, using Microsoft Excel Solver. Each fit used 21 experimental values. Ten were those measured below 0 °C by Archer and Carter.¹⁶ The remaining 11 (at equally spaced temperatures from 0 °C to t_{\max}) were determined from the equation fitted by De Haas to data of Osborne et al.¹⁷ Experimental uncertainties ϵ decreased from 0.003 to 0.001 J K⁻¹ g⁻¹ from 0 °C to t_{\max} but were 0.014–0.052 J K⁻¹ g⁻¹ below 0 °C. To prevent the least-squares fits from being unduly dominated by data below 0 °C, the quantity that was minimized was not $\sum\Delta^2$, the sum of squares of the residuals, but the weighted measure of error

$$\text{WME} = \sqrt{\sum(\Delta/\epsilon)^2/d} \quad (8)$$

where d is the number of degrees of freedom. Parameter values determined by this procedure were unaffected (to within their statistical uncertainties) by the choices of initial parameter values.

Our fits of C_p used analytical functions for $f_2(T)$ (and from them df_2/dT) that had been determined either by the Robinson group or by Tanaka. The Robinson f_2 function which we used (and which was used in that group's fitting of most other properties) was the one whose parameters they determined by "fit i," an exact algebraic fit of the function

$$V(T) = [1 - f_2(T)]V_1(T) + f_2(T)V_2(T) \quad (9)$$

to 8 highly precise values of specific volume between -30 and $+4$ °C.⁴ The Robinson group used this same f_2 function in their fits to all other properties.

Tanaka assumed a 1:1 equilibrium between states 1 and 2. He therefore constrained $f_2(T)$ (i.e., $1 - \bar{S}$ in his notation) to satisfy eq 10.¹⁰

$$\frac{1 - f_2}{f_2} = \frac{g_1}{g_2} \exp\left[\frac{H_{m2} - H_{m1}}{RT}\right] \quad (10)$$

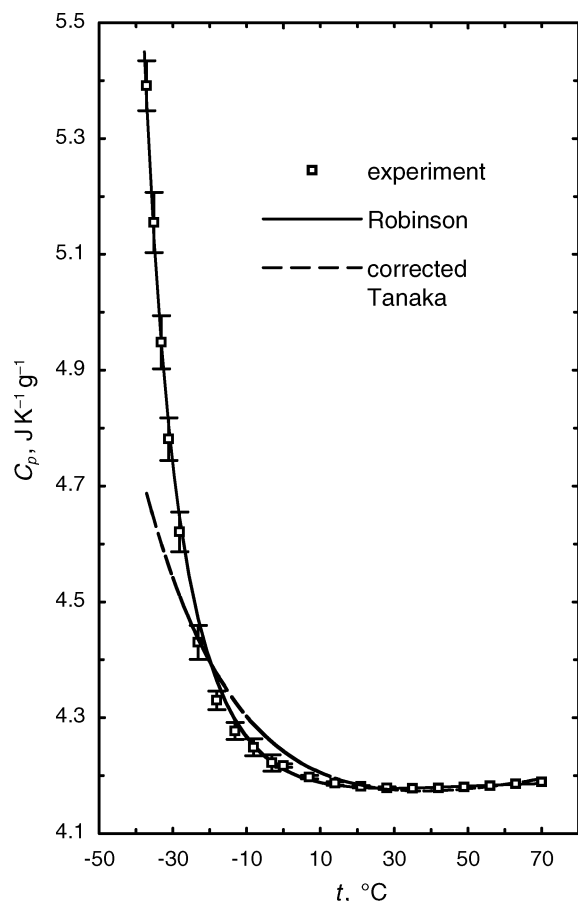


Figure 2. Robinson and Tanaka models fitted to experimental heat capacity of liquid water from -37 to 70 °C. Experimental uncertainties above 30 °C (0.001 J K $^{-1}$ g $^{-1}$) are not shown.

By fitting eq 11 to experimental densities, he determined the values 8.1×10^{-5} for g_1/g_2 and 1800 K for $\Delta H_m/R$.^{9,10}

$$\rho(T) = \rho_2(T) + f_1(T)[\rho_1(T) - \rho_2(T)] \quad (11)$$

Thus Tanaka's function $f_2(T)$ was

$$f_2(T) = 1/[1 + 8.1 \times 10^{-5} \exp(1800/T)] \quad (12)$$

When Tanaka tested his model against experimental values of C_p , he incorrectly omitted from eq 7 the term that involves df_2/dT . He allowed C_2 to be a linear function of T but made C_1 temperature-independent. To fit Tanaka's model to C_p , we used eq 7 with α_1 fixed at zero and with $df_2(T)/dT$ the derivative of eq 12.

We obtained Bartell's fitted values of isothermal compressibility κ_T from the $n = 6$ curve of his Figure 6.³ We calculated values of κ_T for the fitted Robinson model from Table 1 and eq 5 of Cho et al.⁵ [By fitting the corrected values of $\kappa_I(T)$ and $\kappa_{II}(T)$ from Table 1 of Cho et al., we determined that the corrected values for parameters $\kappa_I(T_0)$, $\kappa_{II}(T_0)$, γ_I , and γ_{II} from Table 2 of Vadamuthu et al.⁶ are 51.6210×10^{-6} bar $^{-1}$, 13.8920×10^{-6} bar $^{-1}$, 0.0027654 K $^{-1}$, and 0.012032 K $^{-1}$, respectively.]

Results

Figure 2 shows Robinson and corrected Tanaka models fitted to the experimental heat capacity of liquid water. Both models have three adjustable parameters. The Robinson model is the

simple version (eq 5) with temperature-independent C_1 and C_2 and with $U = 0$. The corrected Tanaka model uses eq 7 with U and α_1 but not α_2 fixed at zero and with $\Delta H(T_f)$ fixed at 138.5 J K $^{-1}$ g $^{-1}$.

Tanaka tacitly assumed that the molecular species in the high- and low-density states of water are both $(H_2O)_n$. Thus, the 1800 K in eq 12 corresponds to ΔH_m of 14.97 kJ per mole of $(H_2O)_n$. However, ΔH in eq 7 needs to be per gram, not per mole, since the value of n is unknown and experimental values of C_p must therefore be per gram. Our tests of Tanaka's model fixed ΔH at $831/n$ J K $^{-1}$ g $^{-1}$ for values of n from 1 to 9. The Tanaka function in Figure 2 has $\Delta H(T_f)$ fixed at 138.5 J K $^{-1}$ g $^{-1}$, which corresponds to 6 as the value of n , but the standard deviation changed negligibly for n values from 3 to 9.

With $U = 0$, fitting of Robinson's model to C_p was straightforward with eq 5 but unsatisfactory with eq 7 if all five remaining parameters [$C_1(T_f)$, $C_2(T_f)$, $\Delta H(T_f)$, α_1 , and α_2] were optimized simultaneously. In the latter case, the value of $\Delta H(T_f)$ was negative, which is incompatible with the underlying model, and its standard deviation was huge, 155 J g $^{-1}$. We chose to optimize instead the remaining four parameters for selected fixed values of $\Delta H(T_f)$. Unless these fixed values were in the range 120 – 170 J g $^{-1}$, the optimizations gave physically unreasonable results. Below about 120 J g $^{-1}$, $\Delta H(T)$ became negative for some temperatures below 100 °C. Above about 170 J g $^{-1}$, one or both temperature coefficients α_1 and α_2 became negative.

Table 1 shows that these acceptable fixed values of $\Delta H(T_f)$ in five-parameter C_p functions are considerably smaller than the optimized $\Delta H(T_f)$ values in three-parameter functions with constant C_1 and C_2 . The quality of fit by these three-parameter functions deteriorated rapidly as t_{\max} , the highest temperature of the data being fitted, increased above 70 °C. Such deterioration was insignificant for five-parameter functions.

With the five-parameter functions, optimized parameter values varied negligibly with t_{\max} for a fixed value of $\Delta H(T_f)$, but varied significantly with $\Delta H(T_f)$ for a fixed value of t_{\max} . Indeed, the sign of $\Delta C(T_f)$ reversed when $\Delta H(T_f)$ changed from 120 to 170 J g $^{-1}$.

Table 1 shows that with C_1 and C_2 independent of T , optimizing U with $\Delta H(T_f)$ fixed at zero is slightly superior to optimizing $\Delta H(T_f)$ with U fixed at zero. Still better fits result from optimizing both $\Delta H(T_f)$ and U , but with the drawback of greatly increased standard deviations for all four optimized parameters.

The correlation coefficient between the variables df_2/dT and $(df_2/dT)(1 - 2f_2)$ (corresponding to the parameters $\Delta H(T_f)$ and U , respectively, in eq 5) is 0.9943 for t_{\max} of 70 °C. A correlation coefficient so close to 1.0000 indicates that one of the parameters $\Delta H(T_f)$ and U is redundant. This is demonstrated by the first six rows of Table 1. Fits of comparable quality are obtained from the extreme $\Delta H(T_f) = 0$ to the extreme $U = 0$, and $\Delta H(T_f)$ and U sum to ~ 210 J g $^{-1}$.

The variables corresponding to $\Delta H(T_f)$ and $\Delta C(T_f)$, that is, df_2/dT and $f_2 + (df_2/dT)\Delta T$, are also strongly correlated. Their correlation coefficient is -0.9829 . This strong correlation is responsible for the change in sign of $\Delta C(T_f)$ when $\Delta H(T_f)$ changes from 120 to 170 J g $^{-1}$ in the bottom 4 rows of Table 1.

Table 2 summarizes our thermodynamic results at 0 °C and compares them with the heat of fusion of ice. Values of $H_1 - H_{ice}$ were obtained from eq 13, which divides the melting of ice into two contributions: the conversion of the entire sample to liquid component 1; and the conversion of a fraction f_2 of

TABLE 1: Parameters^a from Fits of Robinson Model to Experimental^b Heat Capacity

t_{\max} , °C	$\Delta H(T_r)^c$, J/g	U , J/g	$C_1(T_r)$, J/K·g	$C_2(T_r)$, J/K·g	α_1 , J/K ² ·g	α_2 , J/K ² ·g	WME ^d
70	200 (6) ^a	0 ^e	2.81 (6)	3.896 (7)	0 ^e	0 ^e	1.4
100	223 (5)	0 ^e	2.58 (5)	3.883 (6)	0 ^e	0 ^e	5.4
70	0 ^e	205 (11)	4.08 (4)	4.43 (3)	0 ^e	0 ^e	1.3
100	0 ^e	197 (12)	4.09 (4)	4.42 (3)	0 ^e	0 ^e	1.5
70	102 (48)	104 (51)	3.43 (31)	4.16 (13)	0 ^e	0 ^e	0.5
70	102 ^e	104 (6)	3.43 (2)	4.16 (2)	0 ^e	0 ^e	0.5
100	41 (54)	168 (56)	3.82 (36)	4.33 (14)	0 ^e	0 ^e	1.1
70	120 ^e	0 ^e	4.01 (11)	3.45 (10)	0.014 (4)	0.0040 (4)	0.9
100	120 ^e	0 ^e	3.96 (10)	3.49 (9)	0.012 (4)	0.0039 (4)	1.2
70	170 ^e	0 ^e	3.17 (13)	3.81 (12)	0.002 (5)	0.0011 (4)	1.1
100	170 ^e	0 ^e	3.08 (12)	3.90 (11)	-0.002 (5)	0.0010 (5)	1.9

^a Standard deviations of optimized parameters are in parentheses. ^b Experimental values range from -37.15 °C to t_{\max} . ^c $T_r = 273.15$ K. ^d WME, the weighted measure of error of the fit, is $\sqrt{[\sum(\Delta/\epsilon)^2]/d}$, where ϵ is the uncertainty of an experimental value, Δ is the corresponding error, and d is the number of degrees of freedom. ^e Fixed parameter.

TABLE 2: Thermodynamic Values at 0 °C^a

	$U = 0$ J/g	$U = 104$ J/g
$H_2 - H_1$, J/g	145 ± 25	102
$H_1 - H_{\text{ice}}$, J/g	258 ± 13	254
$H_2 - H_{\text{ice}}$, J/g	403 ± 12	356
ΔH_{fus} , J/g	334 ^b	334 ^b
$C_{p2} - C_{p1}$, J/K·g	0.0 ± 0.6	0.7

^a Values other than ΔH_{fus} were determined from fits of Robinson-based C_p functions (eq 7 for $U = 0$, eq 5 for $U = 104$) to experimental values from -37 to 70 °C. ^b Experimental value.

TABLE 3: Adjustment of Experimental Values of Isothermal Compressibility

t , °C	$10^6 \kappa_T$, bar ⁻¹			
	S&A ^a	S&A - 1.20	Kell ^b	adj. S&A - Kell
-25	69.14	67.94	70.94	-2.99
-20	64.00	62.80	64.25	-1.45
-15	60.07	58.87	59.44	-0.56
-10	56.94	55.74	55.83	-0.09
-5	54.36	53.16	53.06	0.10
0	52.18	50.98	50.885	0.09
5	50.30	49.10	49.169	-0.07
10	48.66	47.46	47.809	-0.35

^a Function from Table 1 of ref 18. ^b Equation 20 from ref 17; values below 0 °C are extrapolated.

the latter to component 2, which also gives rise to an interaction energy. The Robinson value of f_2 at 0 °C is 0.5254.

$$\Delta H_{\text{fus}} = H_1 - H_{\text{ice}} + (H_2 - H_1)f_2 + Uf_1f_2 \quad (13)$$

Despite the strong influence of U on $\Delta H(T_r)$ and of $\Delta H(T_r)$ on $\Delta C(T_r)$, Table 2 shows that $\Delta H(273)$ is (135 ± 35) J g⁻¹, $\Delta C_p(273)$ is (0.1 ± 0.7) J K⁻¹g⁻¹, and $H_1 - H_{\text{ice}}$ is $0.8\Delta H_{\text{fus}}$ both for the 4-parameter function with $\Delta H(273)$ and U optimized and for the 5-parameter functions with $U = 0$.

We reevaluated the best published experimental data for isothermal compressibility, κ_T , of supercooled water. The Speedy and Angell κ_T function¹⁸ is based on direct measurements from -26 to +10 °C in glass capillaries. The Kell κ_T function¹⁷ is far more precise but is based solely on experiments at and above 0 °C. Table 3 shows that subtracting 1.2×10^{-6} bar⁻¹ from the Speedy and Angell function for κ_T reduces its disagreement with the Kell function in the range -10 to +5 °C to less than 10% of the original disagreement. This 2% adjustment of the Speedy and Angell function is no greater than its reported uncertainty: a standard deviation of 2.2% and an experimental error of 2%. We propose that below -10 °C, the adjusted Speedy and Angell function is more reliable than either their unadjusted function or the extrapolated Kell function.

TABLE 4: Experimental and Fitted Values of Isothermal Compressibility

t , °C	$10^6 \kappa_T$, bar ⁻¹		
	expt ^a	Bartell ^b	Cho ^c
-25	67.94	66.1	67.887
-20	62.80	62.0	62.978
-15	58.87	59.1	58.970
-10	55.83	56.5	55.703
-5	53.06	54.1	53.050
0	50.885	51.9	50.903
5	49.169	50.2	49.178
10	47.809	48.5	47.802
20	45.892	46.0	45.877
30	44.771	44.5	44.774
40	44.239	43.8	44.251
50	44.173	43.5	44.143
60	44.496	44.0	44.337
70	45.162	44.9	44.757

^a Below -10 °C, experimental values are adjusted S&A values from column 3 of Table 3; otherwise, eq 20 from ref 17. ^b Estimated from the $n = 6$ curve of Figure 6 of ref 3. ^c From ref 5.

Table 4 and Figure 3 compare the Robinson model of Cho et al.⁵ and the Bartell³ model with experimental values of κ_T . The Bartell model was fitted to κ_T values of Kell and of Speedy and Angell (S&A). Nevertheless, it agrees much better below -10 °C with our adjusted S&A values than with the original S&A values. This shows that our adjustment is not biased against the Bartell model.

Discussion

Figure 3 shows that the Robinson model, as implemented by Cho et al.,⁵ fits κ_T much better than does the best ($n = 6$) Bartell³ model.

Figure 2 shows that even a 3-parameter Robinson model is markedly superior to the corrected Tanaka model in fitting C_p . The Robinson model is no better than the Bartell model in fitting C_p . Fits from -37 to 100 °C by 5-parameter Robinson models with $\Delta H(273)$ of 120 or 160 J g⁻¹ have errors as large as 0.05 or 0.06 J K⁻¹ g⁻¹, respectively. On the basis of Figure 5 of Bartell,³ his best fit ($n = 6$) from -33 to 92 °C likewise has errors as large as 0.05 or 0.06 J K⁻¹ g⁻¹.

The inability of the Tanaka model to fit C_p at low temperatures shows that one or both of the constraints inherent in this model are too restrictive. These are (1) that n/m in eq 1 equals 1 and (2) that eq 2 be satisfied with a constant value of ΔH_m . Robinson⁴ did not impose either of these constraints. Bartell³ did not impose constraint 1, and he imposed constraint 2 only at high temperatures. At lower temperatures, he compensated for the inadequacy of eq 2 by introducing a temperature-

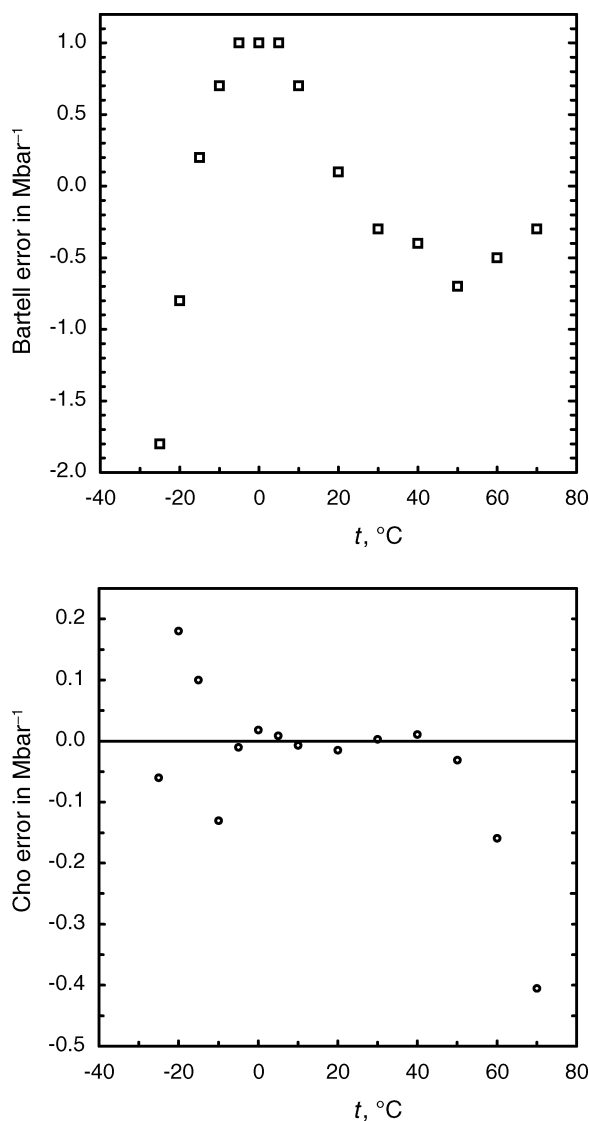


Figure 3. Fitted minus experimental values of isothermal compressibility. Data are from Table 4.

dependent correction factor K_c/K that guaranteed an exact fit to V . K_c calculated from Bartell's mass fractions satisfied eq 2 down to about -10 °C for n/m of 1 or 5. (He did not report the extent of linearity for n/m of 6, the value that provided his best fits to experimental data.)

We calculated K_c from the Robinson⁴ mass fraction function f_2 and several choices of n/m . We then tested the ability of these K_c to satisfy eq 2 from 70 to -36 °C. With n/m values of 6 and 1, graphs of $\ln K_c$ versus $1/T$ were linear down to $+7$ and -12 °C, respectively, but departed markedly from linearity at lower temperatures. With n/m of 0.1, the graph was linear down to -32 °C. These results contrast with those of Bartell, who obtained the best fits to experimental data with the n/m value 6. Note that an n value less than m is physically implausible, since it would mean that the molecular species in the low-density, more ordered state had fewer H_2O molecules than the one in the less ordered state.

These Bartell and Robinson results show that constraint 2 is inadvisable. Bartell's imposition of constraint 2 over a limited temperature range was not helpful. Furthermore, invoking K_c obliges one to choose a value of n/m for eq 1. This elusive quantity does not arise with Robinson's completely empirical approach, which is based on quantities per gram not per mol.

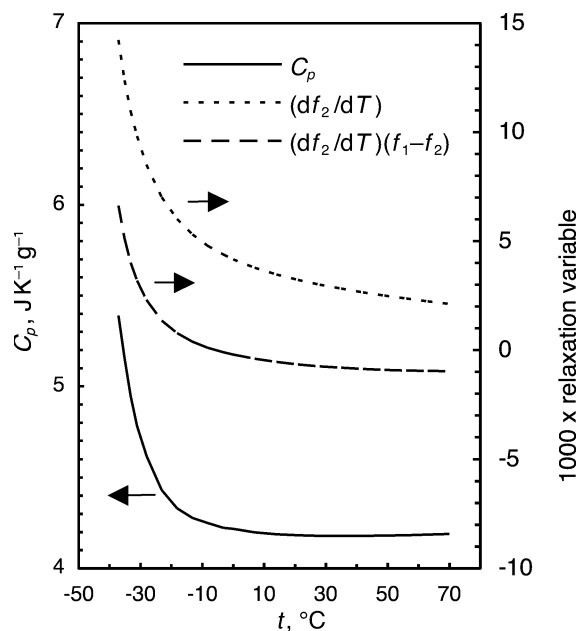


Figure 4. Temperature dependence of experimental heat capacity and of the two functions of f_2 that contribute to the relaxation term of eq 4. The f_2 function is from fit i of ref 4.

The Robinson model is not only more successful than the Bartell model in fitting κ_T but uses fewer adjustable parameters in fitting κ_T , V , and C_p . In both models, these properties for the high- and low-density components are expressed as polynomials in temperature (with the exception of the Bartell model's low-density contribution to C_p). Each Bartell polynomial for κ_T and V has one more term than the corresponding Robinson polynomial. The Bartell polynomial for high-density C_p has five terms versus only two terms each in our Robinson-based C_1 and C_2 . (In the Bartell model, the low-density contribution to C_p is not a polynomial. It is expressed instead in terms of the temperature rate of change of the slope of $\ln K$ versus $1/T$.)

This great flexibility of the Bartell polynomial for the high-density component's C_p calls into question the significance of this model's success in fitting water's C_p . Does this success really help to validate the model, or does it rely in large part on that flexibility?

Figure 1 shows that Robinson's values for the mass fraction f_2 differs markedly from those of Bartell and Tanaka. We have used the fitting of V , κ_T , and C_p as evidence for the superiority of Robinson's $f_2(T)$. Robinson also used the same $f_2(T)$ to fit within experimental uncertainty the temperature dependence of viscosity² η and refractive index^{8,19} and to provide a simple basis for correlating quantitatively between H_2O and D_2O the temperature dependence of ρ^{20} and η^{21} .

Vedamuthu et al.⁴ determined this superior f_2 . Their tactics for determining f_2 differed from Bartell's in two ways besides the ignoring of K_c . Vedamuthu et al. relied solely on fitting of the most precisely known property, V . Bartell, however, fitted his model simultaneously to C_p , κ_T , and the cubic expansion coefficient α , thereby making his f_2 function vulnerable to errors from the least correct data being fitted.

The remaining tactical difference was the upper temperature limit of the data used in determining f_2 . This limit was 4 °C for Vedamuthu et al. but was 100 °C for Bartell. Isosbestic points indicate that two structural states suffice to interpret Raman spectra of water to at least 72 °C.^{22,23} (Isosbestic points for additional properties of water have been reported, but no data above 40 °C were available for them.²⁴) Should an additional

state happen to be significant between 72 and 100 °C, it might affect values of Bartell's f_2 function even below 72 °C. On the other hand, there was no intrinsic virtue in using an upper limit as conservative as 4 °C. Vadamuthu et al. used 4 °C for a pragmatic reason: to control the total number of adjustable parameters needed for $V_1(T)$ and $V_2(T)$ in the determination of $f_2(T)$.

The sharp increase of C_p at the lowest supercooled temperatures is due to the relaxation contribution

$$(df_2/dT)[\Delta H + (f_1 - f_2)U] \quad (14)$$

(cf. eq 4), not to the remaining contribution

$$f_1 C_1 + f_2 C_2 = C_1 + f_2 \Delta C \quad (15)$$

which changes too gradually at low temperatures. Figure 4 shows that both terms of the relaxation contribution increase sharply with decreasing temperature in the same general temperature range as does C_p . C_p has a minimum at 35 °C because only above that temperature does the increase of $f_1 C_1 + f_2 C_2$ outweigh (just slightly) the decrease of the relaxation contribution.

Conclusions

Several models express the properties of liquid water in terms of contributions from low-density and high-density components. The most successful of these models is that of the Robinson group, as indicated by its superior fitting of the temperature dependence of κ_T and C_p , even at supercooled temperatures where water behaves anomalously. The Robinson model's mass fractions for the two components are quite different from those of the Bartell and Tanaka models, the best competing models of this type. We attribute this difference to Robinson's tactics for determining the mass fractions. He relied solely on the high-precision experimental data available for volume, and he did not presume any quantitative regularity in the temperature dependence of the intercomponent equilibrium constant.

The contribution that the relaxation term

$$(df_2/dT)[H_2 - H_1 + (f_1 - f_2)U]$$

makes to C_p of liquid water is small at normal temperatures but is responsible for the rapid increase of C_p with decreasing T at the lowest supercooled temperatures.

We propose an adjustment to Speedy and Angell's¹⁸ experimental values of κ_T for supercooled water.

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