THERMODYNAMIC PROPERTIES OF BULK AND OCCLUDED SUPERCOOLED WATER AND IONIC SOLUTIONS

by

C. A. Angell

January 1976

PURDUE UNIVERSITY
WATER RESOURCES RESEARCH CENTER
WEST LAFAYETTE, INDIANA
THERMODYNAMIC PROPERTIES OF BULK AND OCCLUDED SUPERCOOLED WATER AND IONIC SOLUTIONS

by

C.A. Angell

The work upon which this report is based was supported in part of funds provided by the United States Department of the Interior, Office of Water Research and Technology, as authorized by the Water Resources Research Act of 1964 (PL 88-379 as amended), and the Purdue University Research Foundation.

Period of Investigation: July 1, 1972 - December 30, 1975

Completion Report for Project No. OWRT 13 051-IND
THERMODYNAMIC PROPERTIES OF BULK AND OCCLUDED SUPERCOOLED
WATER AND IONIC SOLUTIONS

C.A. Angell
Department of Chemistry
Purdue University

ABSTRACT

Techniques have been developed for performing quantitative determinations, of the heat capacity, compressibility, and near infrared spectra, of pure water, D₂O, and their electrolyte solutions under conditions of supercooling amounting to as much as 38°C in the case of pure water and > 120°C for certain concentrated electrolyte solutions. In the latter cases glasses form, and some of their properties have been determined. In the case of pure water, which has been the focus of this study, remarkable anomalies are encountered in the supercooled regime. The heat capacity, compressibility, and negative expansivity are increasing exponentially with decreasing temperature according to a function which suggests the existence of a thermodynamic singularity at -45°C. This phenomenon is dependent on extended water-water interactions since it is rapidly eliminated by addition of electrolytes such as LiCl. Alternative interpretations of these phenomena are discussed, with focus on the possible existence of internal liquid phase lambda transitions associated with open hydrogen bonded networks or the existence a low temperature limit on the mechanical stability of water as a liquid phase.

A concentrated aqueous electrolyte solution, 5.5 m lithium acetate, is found to form a glass for which the glass transition temperature pressure dependence is negative, the first such example on record.
THERMODYNAMIC PROPERTIES OF BULK AND OCCLUDED
SUPERCOOLED WATER AND IONIC SOLUTIONS

1. PROJECT AIMS

The purpose of this project has been to explore methods for determining
the thermodynamic and non-equilibrium properties of water in supercooled
liquid state to the lowest possible temperatures. Fundamental thermodynamic
properties such as the heat capacity and compressibility had never been de-
termined below 0°C before, and some evidence was available to suggest that
such properties would exhibit very unusual anomalies at temperatures approach-
ing the homogeneous nucleation temperature known to occur at -40°C. It was
intended to extend these measurements, should the results prove as inter-
esting as expected, to a series of aqueous solutions with the object of using
the findings to give new information on the structural character of such solu-
tions.

It was expected that success in performance of these measurements would
greatly enhance our understanding of liquid water.

As work proceeded, it became obvious that certain non-thermodynamic measure-
ments should be included in the study. These will be outlined in the following
section.

2. PROPERTIES STUDIED AND EXPERIMENTAL METHODS

(a) General Methods of Preparing Supercooled Samples For Study

The primary obstacle to the study of water at temperatures substan-
tially below 0°C is the relatively high probability of crystallization to ice
1. This probability can be reduced by scrupulously removing all foreign par-
ticles from the water sample, or by otherwise preparing samples in such a way
that the probability of the sample containing foreign surfaces suitable for ice
1 crystal nucleation is made small. The chance of contamination decreases log-
arithmically with decreasing sample size, hence most supercooled water studies
have been based on the use of very small samples of clean water. Isolation of
small samples both in fine glass capillaries (1,2) and in emulsion droplets
has proven effective in this respect. Decrease in sample size also reduces
the probability of homogeneous nucleation.

(b) Measurements On Pure Water and D₂O

(1) Heat Capacity of Supercooled Water and D₂O

Heat capacity measurements have been made using a Perkin Elmer dif-
fferential scanning calorimeter which records the amount of energy necessary to keep
the temperature of a small sample of water the same as that of a reference. In
the early stages of this project the technique adopted for avoiding crystallization
of water on cooling below 0°C was to isolate small samples of the liquid in very
thin capillary tubes. This technique had been successfully used in earlier in-
vestigations of the density of water under super-cooled conditions. This technique, while proving successful for the study of proton magnetic resonance of water down to -35°C in order to obtain information on the changes in bonding, did not prove capable of adaption for specific heat studies. The reason for this lay in the mechanical difficulty of stacking capillaries of useful dimensions in the very small space available in the differential scanning calorimeter sample pans. Following contact with Rasmussen and McKenzie at the Cryobiology Research Institute, Madison, Wisconsin, we adopted the use of certain emulsions of water in hydrocarbons which are stable at temperatures down to the homogeneous nucleation temperatures of water, -40°C. Measurements of the heat capacity of the emulsion before and after freezing of the water have allowed the confirmation and extension of heat capacity measurements made concurrently using conventional drift calorimetry by Rasmussen and McKenzie[3]. Using these emulsions, it has proved possible to measure, with and accuracy of ±4%, the heat capacity of water down to a low temperature limit of -38°C - an extension of 38°C in the temperature range over which this important property is known.

(ii) Compressibility of Normal and Supercooled Water.

A simple technique in which the length of a column of pure water in a fine capillary, small enough in diameter to inhibit crystallization to -26°C, was measured as a function of pressure up to 120 atmospheres, was developed and from a series of measurements at different temperatures the compressibility of water was determined over the range +30 to -26°C.

The apparatus is shown schematically in Fig. 1. The water sample was isolated in a pyrex capillary, 15 cm long and about 20 μm i.d., by means of a small plug of mercury. A cross-wire was attached to the capillary with epoxy resin. The capillary was subjected to hydrostatic pressure in a 20 cm long pyrex pressure tube fabricated from 6mm o.d., capillary tubing. The pressure tube was attached to a stainless steel adapter with epoxy resin. Pressure from a hydraulic pump was transmitted to the pressure tube by pentane, and was measured to ±2 bar by a Haase Bourdon Tube gauge. A thermostating fluid (1:1 methanol:ethanol) was circulated through a pyrex thermostat tube which surrounded the pressure tube. Temperatures were measured to ±0.1°C by a Cr/Al thermocouple immersed in the thermostat fluid and attached to the pressure tube.

A traveling microscope was used to measure the length \( l = x - x_0 \) between the cross wire at \( x \) and the mercury-water meniscus at \( x_0 \). The capillaries were drawn and selected to ensure a constant diameter over the range of \( x \) so that the volume of the water sample was proportional to \( l \) and \( (\varepsilon l/\varepsilon p) \propto \varepsilon V/\varepsilon p \). The compressibility at temperature \( T \), relative to that at some reference temperature \( T_r \), was calculated from

\[
\kappa_T = V^{-1} \left( \varepsilon V/\varepsilon p \right)_T = \kappa_{Tr} V_T \left( \varepsilon V/\varepsilon p \right)_r/(V_T \left( \varepsilon V/\varepsilon p \right)_r)
\]

where \( V \) is the molar volume of water. Corrections estimated for the effects of the thermal expansion and compressibility of the pyrex capillary were negligible.
Measurements on a particular sample were made until it froze or until the pressure tube burst. Freezing occurred at about -26°C. The pressure tubes were reliable to 120 bar but always burst below 220 bar. Plots of $I$ vs. $p$ were linear within the scatter of ±10μm and the slope was obtained graphically with an estimated error of ±1.5%. For each run, a value of $T$ was chosen to scale the experimental values of $\tau$ onto the literature (4)$^R$ values of $\kappa_f$ between 30°C and 40°C. Attempts to extend the range of measurements by measuring the velocity of sound in a supercooled emulsion were made both in the Physics Department at Purdue University and at Catholic University, Washington, D.C. using the "sing-around" apparatus of Professor T.A. Litovitz. In neither case did it prove possible to overcome the serious problems arising from the scattering of sound waves from the heterogeneous liquid. Although it appeared that suitable cell design could overcome this problem, the financial resources both for the apparatus, and for the post-doctoral associate who tackled this problem, were not available. Thus compressibility measurements have been limited to a lower temperature of -26°C.

(iii) Proton Chemical Shifts in Supercooled Water

In order to investigate whether anomalies in the thermodynamic properties of water in the supercooled condition could be associated with changes in hydrogen bonding, the variation of the proton chemical shift with decreasing temperature was studied using the departmental Varian A60NMR spectrometer. These measurements were made on water in two sub-divided states, (i) in micro-columns within fine glass capillaries, and (ii) in microglobules in the same emulsion in which the heat capacity studies were performed. In capillaries, temperatures of -35°C could be reached before crystallization occurred, while the emulsion could be studied down to -39°C.

(iv) Homogeneous Nucleation Temperature of Supercooled Water at High Pressures

In order to determine the complete range of additional studies made available by the use of the supercooled regime for water, determinations of the homogeneous nucleation temperature were made at different pressure up to a limit of 3 kbars. The technique used was simple, involving only a differential thermal analysis arrangement held in a stainless steel high-pressure tube subjected to pressure by an oil injection pump. The temperature of homogeneous nucleation was readily detected during the steady cooling of the stainless steel container tube.

(v) Infrared Spectra of Supercooled Water and $D_2O$

The near infrared spectra of water are sensitive to structural changes in the bonding arrangements of water molecules, and these spectra have been much studied in attempts to deduce the effects of temperature on hydrogen bonding. Although the emulsions which permit supercooling of water to -38°C appear opaque, it proves possible to obtain quite good spectra in the near infrared region using samples of thickness approximately 0.2 cm. The spectra are slightly broadened with respect to the corresponding spectra of pure water but that is a minor effect and does not vitiate the use of these spectra for structural diagnosis purposes. Spectra have been obtained in water and water + deuterium oxide mixtures over ranges of temperature between +20 and -36°C using a 0.2 cm. standard optical cell in conjunction with a Cary 14R spectrophotometer.
(c) Measurements on Aqueous Salt Solutions

(i) Heat Capacity

The emulsion technique has also been employed to study the heat capacity of aqueous electrolyte solutions of various compositions, the interest lying in the effect that the water-orientating charged particles have on the nature of the heat capacity anomaly observed for pure water. A number of different salt additives in various concentrations were tried on a qualitative basis, to see if in any case a maximum in the heat capacity could be observed prior to homogeneous nucleation. The case of lithium chloride was studied in detail, with compositions up to 11 mole %, lithium chloride being included, no maximum being found.

Measurements which have been performed on additional solutions since support under this grant was terminated have shown the presence of weak maxima in C_p shortly before crystallization commences.

(ii) Glass Transition Temperatures and Their Dependence on Pressure

One of the most unusual features of supercooled water is the negative expansion coefficient. If water could be supercooled into the glassy state, a consequence of the negative expansivity would be that the glass transition temperature would decrease with increasing pressure, behavior which has never been observed before. Unfortunately water cannot easily be obtained in the glassy state. However, a great many concentrated aqueous solutions are easily vitreified. It was therefore deemed worthwhile to determine whether such a phenomenon could be observed in an aqueous solution in which some residuum of the expansivity anomaly could be retained.

The glass transition temperatures of lithium acetate solutions were determined using a differential thermal analysis technique in which the sample and reference thermocouples were arranged colinearly in the pressure tube, the pressure-transmitting fluid (methylcyclohexane) also serving as the DTA reference sample material. The glass transitions were readily detected. A typical trace is shown in the inset to Fig. 9 below for the case of lithium acetate solution.

(iii) Expansion Coefficients

The expansivity of the lithium acetate solutions, the pressure dependence of whose glass transition temperature has been measured as described in the previous sections, was measured by a simple volumetric technique.

3. RESULTS

(a) Pure Water

(ii) Heat Capacity

Results for our various heat capacity measurements are tabulated at 5-K intervals in Table I. Data for water are plotted together with literature data above 273 K in Figure 2a. The difference between the heat capacity of ice and that of water, ΔC_p, which is the experimentally determined quantity, is plot-
ted in Figure 2b. We include in Figure 1b some data currently being report-
ed by Rasmussen and MacKenzie, obtained by conventional drift calorimetry on
emulsified water. Agreement with Rasmussen and MacKenzie's measurements is
fairly good but the uncertainty in their data, particularly at their lowest
temperature of -34°C, is somewhat in excess of ours. It is important to note
that our emulsion data superimpose within experimental error on the bulk water
data which extend to -20°C. This shows that the state of subdivision of the
water does not strongly affect the measurement; hence it is very improbable
that the exponential increase in ΔC with decreasing temperature is an arti-
fact of the experiment. Certainly this large increase is not observed in the
behavior of emulsions of NaCl solutions when the NaCl concentration is
sufficient (>7m) to break up the water structure.

The findings are in any case very compatible with the equally dramatic
increase in negative expansivity assessed from Zheleznyi's density measurements
on water in a 10-μ capillary (2). For comparison, the latter data and
the current emulsion data of Rasmussen and MacKenzie, (3b ) together with
bulk water data calculated to -20°C by Kel1 (4) using a curve-fitting func-
tion obtained from measurements above 0°K, are displayed in Figure 2c.

(ii) Compressibility of Pure Water

Results obtained from four independent runs using, in total, 3
different capillaries, 3 different pressure tubes, 2 different travelling micro-
scopes and 2 different water samples (double distilled deionized and Abbot ster-
ile water), are plotted in Fig. 3. The combined results show a standard dev-
iation of 2% about a smooth curve drawn through the data. The dashed curve in
Fig. 3 is a polynomial extrapolation by Kel1 (4) of kₚ data from measurements
above 0°C. The extrapolation is surprisingly successful, though it slightly
underestimates the rate of increase of kₚ at the lowest temperatures. Since
our measurements are calibrated using the known value at 30°C, the concordance
of the present data with the dashed curve between 30°C and 0°C serves as an in-
dication of reliability of the present measurement technique. The full curve
passing through the experimental points at low temperatures is an analytical
function to be discussed below.

(iii) Proton Nuclear Magnetic Resonance Proton Chemical Shifts

In Figure 4a the pmr chemical shifts, δ, are presented as raw
data referenced as indicated in the legend. Because the susceptibility cor-
rections for capillary and emulsion experiments are different, the different
data sets do not superimpose.

In Figure 4b we show the data after susceptibility corrections have been
introduced all data being reduced first to shifts relative to methane at 7atm
and then finally plotted as shifts relative to that of bulk water at 0°C. The
susceptibility of the emulsion was taken to be a volume fraction weighted aver-
age of heptane and water. Since capillary data and bulk water data coincide at
high temperatures, it was assumed that the bulk water susceptibility correction
was applicable to both. The susceptibility correction for water was made
using an extrapolation of Auer's susceptibility data and Zheleznyi's density
data.
Susceptibility corrections are all a little uncertain, especially at low temperatures, because the susceptibility of water is sensitive to extent of hydrogen bonding which is evidently changing particularly rapidly at low temperatures. It is clear, however, that the susceptibility corrections must render even more pronounced the curvature in the $\delta$ vs. $T$ plot already present in the raw data. Since this curvature is of prime interest we demonstrate, in Figure 4b inset, that the curvature cannot be associated with the high-pressure methane reference by showing that $\delta(CH_4, 37 \text{ atm}) - \delta(\text{cyclopentane})$ varies quite linearly with temperature.

We find Figure 4b, which summarizes data gathered in many individual runs over the temperature range, quite pleasing. The emulsion data in particular are found in very good accord with the data on bulk water from $+40^\circ C$ (at which the emulsion breaks down) to $-15^\circ C$ the lowest temperature accessible with bulk samples. There appear to be some real differences between results for bulk water and for water in capillaries, though the departures from the bulk water plot are similar for capillaries differing by about an order of magnitude in internal diameter. The discrepancies may therefore originate in the corrections rather than in the actual water structure. Because the emulsion data which extend to lower temperatures, proved quite satisfactory we chose not to pursue the capillary problem.

The accelerating nonlinear downfield chemical shift temperature dependence is common to both measurement sets and is therefore unambiguously established by these measurements. It is notable that it occurs in the same temperature region in which the great increases in heat capacity and (negative) expansivity magnitudes occur.

(iv) Homogeneous Nucleation Temperature of Supercooled Water at High Pressures

Results are shown in Fig. 5 for emulsions of water in n-heptane and in a mixture of methylcyclohexane (MCH) plus methylcyclopentane (MCP), the latter dispersant phase being necessary for temperatures below the freezing point of n-heptane. Some earlier results obtained with a more massive pressure cell and larger samples are included (points denoted under "cell 1" in Fig. 5).

The most significant finding is the very wide region of additional PTX space in which properties, $X$, of water can be studied using techniques suitable for the dispersed nature of the sample. It will be possible to investigate somewhat less extensive regions with samples of fine-bore capillary tubes. Use of glass capillary tubing treated to withstand high internal pressure (~3 kbar) should greatly simplify the exploration of this region.

(v) Infra Red Spectra of $H_2O$

Spectra obtained in the region 1 to 1.5 microns are displayed in Fig. 6. Comparisons of emulsion spectra with those of pure water or pure ice at the same temperature are given in Fig. 7 to demonstrate the extent to which the particulate nature of the emulsion sample causes distortion of the spectra. It is seen these distortions are not so pronounced as to invalidate the use of spectra for analysis. Progressive shifts in the
the spectra to longer wave lengths, in concert with increase in intensity are
are observed with decreasing temperature. Such changes are in the direction
of the ice spectrum but an extrapolation of the spectra to lower temperatures
indicates that the spectra of ice itself would never be obtained by con-
tinued decreasing of water temperatures. This implies that the structural
temperatures are not due to the formation of microcrystallites of ice.

(b) Measurements on Aqueous Salt Solutions

(i) Heat Capacity Measurements on LiCl Solutions

Qualitative heat capacity measurements were made on a number of
of electrolyte solutions to see if, in any instance, a maximum in the heat
capacity like that predicted for water at -45°C could be observed directly.
None were found, although in further studies made since expiration of this
grant, some cases with weakly defined maxima have been encountered. In the
present work the case of the LiCl + H₂O system was selected for detailed study.
Results are shown in Fig. 8. A systematic depression of the anomalous part
of Cₚ is observed as the lithium chloride content is increased. The increase in Cₚ
finally disappears completely at a composition of 11 mole % lithium chloride.
It appears that lithium chloride, which is known as a strong "structure maker"
according to conventional aqueous solution jargon, is simultaneously a strong
"water structure breaker".

(ii) Glass Temperatures and Their Dependence on Pressure.

Results of our pressure dependence study are shown in Fig. 9
and contrasted with data for a typical anhydrous salt system obtained with our
apparatus. The values of dTg/dP found for these liquids may be compared with
values of 22 and 24 deg kbar for poly(vinyl acetate) and polyisobutene, re-
spectively. Assuming a linear dependence of Tg on P, the data yield a value
for dTg/dP of -0.60 ± 0.20 deg kbar for the LiOAc-10 H₂O solution. To the
authors knowledge, this is the first time that a negative value of dTg/dP has
been found.

(iii) Expansion Coefficient

Expansivities of the same concentrated lithium acetate solution
in (ii) in the temperature range +80 to -35 C using two different dilatometers,
are shown in Fig. 10. Below -35°C the sample froze during the long period need-
ed for equilibration. A modified, less accurate, technique in which beads of
the glass are introduced into a dilatometer filled with a pentane dilatometric
fluid, was used to obtain data in the glass transition region (∼115°C). These
data are included in Fig. 10. A small decrease in α at Tg is observed. Also
included is a plot of the heat capacity of the same solutions to demonstrate
the presence of large positive changes in this quantity at the same tempera-
ture.

The value of Δα observed at Tg is, within the large uncertainty of measure-
ment, the same as the value -4.1 x10⁻⁵ predicted from the measured dTg/dP
(Fig. 9) and ΔCₚ (Fig. 10 inset) using the Ehrenfest-like relation

\[ \frac{dTg}{dP} = Tg \frac{\Delta\alpha}{\Delta C_p} \]
4. DISCUSSION AND INTERPRETATION

The almost exponential increase in the heat capacity of water at temperatures below -15°C (Fig. 1) is a remarkable phenomenon, of which very few parallel examples exist in the chemical literature. It has some implications of immediate significance, particularly when viewed against the observation that, on warming to -135°C, vitreous ice (the amorphous material formed by depositing water molecules from the vapor state onto a substrate at liquid nitrogen temperature) briefly becomes a supercooled liquid at -135°C before crystallizing to ice 1c(5).

In this section, therefore, we will discuss the heat capacity anomaly first, before examining the behavior of the compressibility and other properties. Later we will consider the information obtained on solutions.

(a) The Heat Capacity Anomaly and its Implications

Let us consider the implications of the heat capacity behavior by asking the question, "What is in store for liquid water at lower temperatures if we extract its thermal energy at a rate sufficiently high that nuclei of ice are unable to form and grow?". The practical possibility of achieving such conditions depends on the molecular mobility at the homogeneous nucleation temperature which in water, has evidently become quite small. These conditions are reached quite commonly in the quenching of viscous liquids and the result is that glassy solids are produced at temperatures not too far below TH. Since vitreous or at least X-ray amorphous water can be obtained by vapor deposition procedures and by splat-quenching of liquid water, we are led to ask whether the glass formation event can be predicted from now-available data on water and, if so, at what temperature it would occur.

We attempt to answer this question by plotting, in Fig. 11a, the total heat capacities of supercooled water and ice are plotted against log T so that the area under the heat capacity curve for a given phase corresponds to an entropy generated in (or lost from) that phase over any chosen temperature interval. Permissible extensions to lower temperature of the water heat capacity are governed by the third-law requirement, discussed in more detail elsewhere (6), that the area between the supercooled liquid and crystalline solid C0 between 273 and 0 K amount to no more than that representing the entropy of fusion ΔSf (since the total entropy of a disordered phase at 0 K can never underlie that of the stable crystal).

From Figure 11a we find that if the heat capacity of water supercooled below -38°C continues to increase at the rate observed between -30 and -38°C then all the excess entropy gained on fusion (i.e., ΔSf shown as an area in Fig.11a) would be lost by 205-210 K (≈ -65°C). This is shown more clearly by Fig. 11b in which the calculated entropy difference between water and ice, which is ΔSf at 273 K, is plotted as a function of decreasing temperature. The difference tends to zero as T → -65°C. At ≈ -65°C, then, assuming the residual entropy of ice due to proton disorder would also be present in glassy water, a precipitous decrease in the water heat capacity to that of ice would have to occur to avoid thermodynamic embarrassment. The state of the substance at this temperature could be described as an "ideal glass" in which structural change, hence viscous flow, is proscribed.
This result, although consistent with the observed transport behavior, is paradoxical because experimentally it is found that vitreous water passes through the glass transition (i.e., exhibits a heat capacity increase and a relaxation time to the order of seconds which permits crystallization) at a temperature of about $-130^\circ$.

The observations are not reconciled by supposing, unrealistically, that at $-40^\circ$C, reaches its maximum value and remains constant thereafter until the entropy of fusion is exhausted at $-79^\circ$C (curve 2 Figure 11a).

In order to resolve the paradox it is necessary to suppose that not far below $-40^\circ$C supercooling water passes through a $\lambda$-type heat capacity anomaly not unlike that due to a ring-chain equilibrium exhibited by liquid sulfur at $159^\circ$. This alternative is illustrated by curve 3 of Figure 11a. A qualitative theory for such behavior based on the cooperative bond lattice model is available (7). We will consider in a later paper the possible appropriateness of a branched-chain $\neq$ connected-ring equilibrium treatment suggested by Gibbs' polymer approach to the water problem, and by the empirical similarities of liquid sulfur and supercooled water properties in their anomalous temperature ranges.

Because viscous liquid transport property temperature dependences generally follow changes in configurational entropy or enthalpy contents, the $\lambda$ transition would presumably be accompanied by a sharp drop in viscosity and diffusivity temperature dependences which would postpone the temperature at which the glass transition occurs to the experimental value.

(b) The Compressibility Anomaly and Density Fluctuations

The existence of a hidden $\lambda$ transition at $-45^\circ$C suggested by the above discussion implies the existence of a number of related anomalies in other physical properties associated with the presence of anomalous fluctuations in the equilibrium properties.

The anomalous behavior of the compressibility for instance is evidence for the existence of anomalous fluctuations in the volume (or density) since the two are related according to the expression

$$\kappa_T = \frac{\Delta V^2}{kT}$$

(1)

The temperature dependence of the compressibility is of considerable interest. Below $-10^\circ$C we find that the compressibility, hence $\frac{\Delta V^2}{V^2kT}$, can be described within measurement uncertainty by the equation

$$\kappa_T = A \varepsilon \nu$$

(2)

where $A$, and $\nu$ are constants and $\varepsilon = (T/T_c - 1)$, $T_c$ being a singular temperature. The full line drawn through the experimental points in Fig. 2 is the plot of this function for the parameters $A = 29.65 \times 10^{-6}$, $1 \text{bar}^{-1}$, $\nu = 0.39$ and $T_c = 228^\circ$. The latter temperature coincides with the value suggested for the $\lambda$ temperature.
Eq. 2 is of the form known to describe the variations of thermodynamic properties in the immediate vicinity of a critical point or lambda-type singular point when \( \varepsilon \) is sufficiently small for the first term in a series expansion for the property to be dominant (8). In the present instance the data to which Eq. 2 has been fitted have been obtained relatively far from \( T_c \), so the significance of the fit should be viewed with some caution. On the other hand, the case for Eq. 3 type functions for water may be strengthened by examination of their power to describe the temperature dependence of other properties, some of which are known more accurately and/or to lower temperatures than the present \( \kappa_T \) data.

Expansivity data for water extend to \(-34^\circ C (\varepsilon = 0.05)\) and are of good precision. To analyze these data adequately it must first be observed that whenever abnormal (cooperative) fluctuations are observed they are found to occur superimposed on the "normal" fluctuations characteristic of the property. Thus, Eq. (2) for the expansivity should be tested after separation of \( \varepsilon \) from a "normal" component \( \alpha_0 \) which increases linearly with temperature

\[
\frac{\varepsilon}{\alpha} = \alpha_{\text{tot}} - \alpha_0
\]  

(3)

The necessity for a normal component is particularly clear in the case of the expansivity since the passage through \( \alpha = 0 \) at \( 4^\circ C \) could never be accounted for by Eq. (2) alone. Fig. (12) shows a decomposition of the concordant expansivity data of Zelinski (2), and Rasmussen and McKenzie (3b) into a part which obeys Eq. (2) with parameters \( A_1 = 127.1 \times 10^{-6} \text{ K}^{-1} \gamma = -1.025 \) and \( T_c = 228K \) up to \( 100^\circ C \), and a residual part. As anticipated, the residual part is of normal magnitude and increases linearly with increasing temperature. Fig. 12 includes a comparison with the expansivity of liquid \( H_2O \) which is also hydrogen-bonded but which lacks the open network character of \( H_2O \).

\( C_p, C_v \), and energy fluctuations

Since \( \Delta E = (\frac{\partial E}{\partial V})_T \Delta V + (\frac{\partial E}{\partial T})_V \Delta T \), fluctuations in the energy of a body may be written (15') as the sum of contributions arising from volume fluctuations and from temperature fluctuations,

\[
\overline{\Delta E^2} = (\frac{\partial E}{\partial V})^2_T \overline{\Delta V^2} + (\frac{\partial E}{\partial T})^2_T \overline{\Delta T^2}
\]  

(4)

Substituting for \( \overline{\Delta V^2} \) using Eq. (2) and for \( \overline{\Delta T^2} \) using the relation (15')

\[
\overline{\Delta T^2} = kT^2 / C_v
\]  

(5)

we obtain

\[
\overline{\Delta E^2} = (\frac{\partial E}{\partial V})^2_T \kappa_T V_kT + C_v kT^2
\]  

(6)

The first term, arising from volume fluctuations, reduces to \( kT^2(C_p - C_v) \) for low pressures, and therefore we find, in view of the observed \( p_C \), divergence, that water is subject to anomalously increasing energy fluctuations as
$T \to 45^\circ C$. However, the energy fluctuation increases all originate in the volume fluctuation term as can be shown using the present $\kappa_T$ data to obtain $C_v$ and thereby the temperature fluctuation-based contribution to $\Delta E^\infty$.

We obtain $C_v$ at each volume for which $C_v$ has been measured by combining $\kappa_T$ with earlier $C_p$ (3a, 6) and (3b) data using the relation

$$C_v(V) = C_p(V) - \frac{\alpha^2 VT}{\kappa_T} \tag{7}$$

The behavior of $C_v$ at a single value of volume can then be deduced from the relation

$$\frac{\partial C_v}{\partial T} = \frac{\partial C_v}{\partial T} - (\alpha C_v/\partial V)_T \alpha V \tag{8}$$

$C_v$ of Eq. (7) which represents $C_v$ at a constant pressure of one atmosphere, proves to remain constant (at 18.1 cal mole$^{-1}$ deg$^{-1}$) within experimental uncertainty between 5$^\circ$ and 26$^\circ$C, and this constancy would be maintained to 38$^\circ$C (the lowest temperature to which $C_v$ has been measured) if $\alpha$ and $\kappa_T$ at temperatures between -26$^\circ$C and -38$^\circ$C conform to the type (2) equations. At a constant volume of 18 cc mole$^{-1}$, $C_v$ evidently has a weak maximum at 4$^\circ$C since at $P = 1$ atm $\alpha = 0$ at this temperature. From extrapolation of available PVT data it appears that at this volume ($\alpha C_v/\partial T$) must be positive between -35 and 4$^\circ$C. Thus at low temperature $C_v$ decreases with decreasing temperature reversing its high temperature behavior and giving a Schottky-type heat capacity function essentially as predicted (for the configurational contribution to $C_v$) by the non-cooperative case of the bond lattice model (9).

Temperature fluctuations in water (which are statistically independent of volume fluctuations) therefore show no anomalies, in contrast with the case for most cooperative systems in which $C_v$ diverges (8). Likewise, the temperature fluctuation-based term in Eq. (6) makes no contribution to the anomalous increase in energy fluctuations which therefore must be correlated with, and dependent on, the anomalous increase in density fluctuations. The latter increases are almost as pronounced at constant volume as at constant pressure (at least at large volumes) since the linear column length vs. pressure (0-120 bar) plots, whose slopes yield $\kappa_T$, all included the length corresponding to the density maximum, i.e. within measurement uncertainty $\kappa_T$ increases as rapidly with decreasing temperature at a constant volume of 18 cc as it does at a constant pressure of 1 bar.

5. SOURCES OF COOPERATIVITY AND THE STATE OF THE SYSTEM AT -45$^\circ$C

It is clear from the above that a phenomenon of the first order of interest has been revealed, and the challenge now is to provide a molecular explanation for the cooperative behavior observed, and an interpretation of the state of the system at the temperature of the singularity, -45$^\circ$C.

We will first outline some possible alternative interpretations, and then examine the extent to which they are consistent with observations of (i) high pressure behavior; and (ii) behavior in presence of second components in solution.
The present phenomenon is qualitatively distinguished from critical phenomena of the gas-liquid or ferromagnet-paramagnetic type by the absence of any divergence in $\gamma$. The fact that in the present case anomalous increases in energy fluctuations only occur in association with anomalous increases in density fluctuations suggests that the geometrical factors which determine the volume associated with a given energy state are of primary importance to the manifestation of the cooperative behavior. Thus the source of the cooperative behavior should reside in the topological aspects of the tetrahedral network. The density fluctuations presumably arise and decay by the migration of large O----H-O angle ($\rightarrow 180^\circ$) hydrogen bonds which "prop open" the expanded structure when present in high local concentrations but allow collapsed dense regions to form when local concentrations are smaller. The concomitant energy fluctuations occur because bonds characterized by large O----H-O angles are also bonds of low energy, as many calculations have shown (10).

It is consistent with the importance of geometrical factors in the observed phenomenon for water that related behavior, at least to the extent that a density maximum is observable, is found for liquid SiO$_2$(H). SiO$_2$ is also a network liquid in which tetrahedral coordination of silicon centers (through oxygen bridges in this case) is the key structural feature. A primarily geometrical, as distinct from energetic, origin for the cooperative phenomenon in water is also indicated by the finding of Rahman and Stillinger (12) that a density maximum and a strong negative expansion coefficient (for $T > 210^\circ$C) may be produced by computer simulation of water using only pairwise additive "effective" interaction potentials.

A quantitative analysis of this type of cooperativity will be difficult and will necessitate a recognition of the manner in which, with decreasing temperature, a given large bond angle can enhance the probability of other large bond angles in its neighborhood. Ring statistics analyses of the type made possible by the current computer simulation studies of water structure and dynamics (12) will presumably be central to the development of understanding in the area. There are however, serious computing economics problems in the way of extension of these calculations into the temperature (and equilibration time) range of the cooperative domain.

Qualitatively, the accelerating increase in compressibility seen in the present work can be reproduced by a lattice model which recognizes only two types of molecule site, viz. centers and corners of a basic body centered cubic cell, and two distinct bonding interactions. In this model formulated by Bell (13) the density maximum and compressibility maximum are predicted to disappear when an energy penalty, imposed on the hydrogen bonding of molecules on body centered (close-packed) sites, is overcome by increases of external pressure above a critical value. At a simpler and more empirical level, low temperature compressibility increases can also be obtained from the zeroth order bond lattice model of Angell (9) if the geometrical cooperativity concept is introduced by requiring the volume increment per "on" bond to be proportional to the fraction of "on" bonds. No additional parameters are required. However, in neither case is a singularity predicted, and as the tendency of thermodynamic properties and related relaxation times (e.g. for shear viscosity, and diffusion) to diverge at -45°C is the most significant finding of
the present work, we will limit further discussion to the projected state of the system at -45°C.

Two qualitatively distinct interpretations of \( T_s \), each having certain advantages deserve consideration: (a) The singularity may correspond to the \((p = 1 \text{ bar})\) point on a line of \( \lambda \) transitions which traverses the liquid free energy surface or (b) it may correspond to the \((p = 1 \text{ bar})\) point on a line along which the free energy surface terminates.

The former possibility was adopted by Angell et al. (7) in their attempt to link supercooled water and vitreous ice in a continuity of states. These authors drew attention to the phenomenological parallel provided by the \( \lambda \) transition in liquid sulfur at 150°C (1 bar). Additional examples of such transitions (damped to various degrees) are provided by liquid Ge-Te and related alloys at \( T > 300°C \) (14). In water such a transition could correspond to the completion of a process of bond angle optimization and strain minimizing amongst energetically similar molecular configurations, with the concomitant establishment of some type of long range order in the random network hydrogen bonding patterns (12). (Here "long range order" need not imply strict spatial periodicity in the usual sense, as the existence of amorphous ferromagnets and antiferromagnets can verify.) Such an interpretation explains naturally why \( \eta, T_p \), and \( D^{-1} \) which respond to extent and strength of bonding should tend to diverge with \( \kappa_T, C_P \), and \( \alpha \).

The second possibility can be restated as an assertion that topological changes occurring as the tetrahedral network structure is established with decreasing temperature, lead the molecular system to a condition akin to that of an excessively supercooled vapor in which the mechanical stability criterion, \((\partial P/\partial V)_{T,T} > 0 \) (or \( \kappa_T < 0 \)) (15) is violated. At this point the system must become unstable to any fluctuation, and a change of phase must occur. A line of such points would therefore define the boundary of the liquid water free energy surface. The principal support for this interpretation of \( T_s \) is the explanation it can provide for the close empirical correspondence between \( T_s \) and the temperature \( T_H \) below which crystallization of water always occurs.

It is recognized that mechanical instability must set a low temperature limit on the conceivable supercooling of a saturated vapor, and a high temperature limit on the superheating of a liquid since equations of state for the fluid predict negative compressibilities \((\partial P/\partial V)_{T,T} > 0 \) for excessively supercooled and superheated states respectively. By contrast, no established body of opinion exists on the possibility, raised from time to time (16), that the supercooling range of liquids in general may be limited by their becoming mechanically, as well as thermodynamically, unstable. Since this notion is unfamiliar a brief discussion of the related liquid-vapor case is warranted.

In the liquid-vapor case, the mechanical stability limits for supercooling and superheating are fixed by the extrema in the van der Waals type \( V-T \) loop, see Fig. 5(a), since at any temperature \( T_s \) at which \((\partial T/\partial V)_{s} \) on an isobar goes negative, \((\partial P/\partial V)_{T,T} \) on the \( T_s \) isotherm goes positive, violating the stability criterion. The \( \kappa \) of these liquid and vapor instability points meet at the gas-liquid critical point, and jointly they define a curve known as the "spinodal" curve. In laboratory superheating and supercooling experiments, phase transformation occurs by the kinetic process, homogeneous nucleation, at a temperature in the stable region shortly before the mechanical limit is reached (except at the critical point where the mechanical and thermodynamic instability temperatures coincide).
The fact that no physically realizable critical point exists for the liquid-to-crystal transition does not exclude the possibility that the liquid itself may become mechanically unstable at low enough temperatures. The present observations could be taken as evidence that in the right circumstances it can and does. It must be recognized, however, that among real systems (see below) the association of thermodynamic anomalies with homogeneous nucleation is, so far, unique to the case of water.

Some additional, but qualified, support for association of anomalous fluctuations with crystal nucleation may be obtained from the results of a molecular dynamics study on a 2-dimensional hard disc system (870 discs, periodic boundary conditions). In this finite system Alder and Wainwright (17) found that points of positive \( (\partial P/\partial A) _T \), for which pressure fluctuations were extremely large, connected the mechanically stable fluid and ordered-solid branches of the P-A diagram. The fluctuations, which were associated with a dynamic coexistence of regions of fluid-like and crystal-like order, did not disappear until volumes well onto the mechanically stable branches were reached. Unlike liquid-vapor critical fluctuations, which require attractive forces, the hard disc system fluctuations must be entropy-driven, hence are basically geometric in origin as we believe is the case for water. A comparable van der Waals type P-V loop could not be constructed for \( \text{H}_2\text{O} \), however, because of the inversion of the normal liquid-crystal density relations.

**High Pressure Studies**

The effect of pressure on the homogeneous nucleation temperature is quite striking. At 2 kbar pressure it is seen (Fig. 5) that water can be supercooled to \(-92^\circ\text{C}\), before crystallization commences. Such an extension of the range of temperatures in which experiments on liquid properties can be performed should prove very valuable to our attempts to understand the nature of this liquid, and the origin of its anomalous characteristics.

Unfortunately, the effect of pressure on the homogeneous nucleation temperature cannot be used to distinguish between the two possible interpretations of \( T_\lambda \), since decreases in \( T_\lambda \) with increasing pressure would be expected in either case. If \( T_\lambda \) is a mechanical stability limit, then \( T_\lambda \) will necessarily vary with \( T_\text{cr} \) because of their close connection. \( T_\lambda \) in turn should decrease with pressure because pressure increases opposite the formation of the open network which seems necessary to promote instability. On the other hand, if \( T_\lambda \) is a lambda transition temperature then its pressure dependence can be predicted from thermodynamic relations (see below) and this dependence should probably be reflected by \( T_\lambda \) since (i) nucleation requires an abnormal order (entropy) fluctuation, (ii) the mean square entropy fluctuations \( \Delta S^2 \) scales is proportional to the heat capacity \( C_p \), according to (15)

\[
(\Delta S)^2 = kC_p
\]

and (iii) \( C_p \) is increasing rapidly as \( T \to T_\lambda \). The pressure dependence of \( T_\lambda \) should be given by an Ehrenfest-like relation,

\[
\frac{dT_\lambda}{dp} = TV \frac{C_p}{C_p,\varepsilon}
\]
where $T$ and $V$ are the temperature and volume at a temperature near $T_c$ and $C_p$ and $\alpha$ are the contributions to $\alpha$ and $C_p$ from the cooperative fluctuations, in appropriate units. Using data from Figs. 12 and 2 at $-34^\circ$, we would therefore expect $dT_H / dp$ to be approximately $20 \times 237 \times (22 + 5) \times 10^{-4}$ \begin{equation*}
(26 - 12) \times 41.3
\end{equation*}
or $-23$ deg. Kbar$^{-1}$ if $T_c$ occurs at a constant value of $C_p$. The initial slope of the experimental plot (Fig. 5) is $-10^\circ$ C kbar$^{-1}$, which is only of the same order of magnitude as the predicted value.

The thermodynamic properties of spinodal points have not been properly elucidated to date, but it is probable that an expression similar or identical to Eq. (10) would describe their pressure dependence. Thus either interpretation of $T_S$ is probably consistent with the $T_H$ vs $P$ observations.

Solution Studies

The rapid disappearance of most of the heat capacity anomaly with additions of LiCl, seen in Fig. 8, shows clearly how important is the freedom to build extended water-water interacting arrangements in the manifestation of thermodynamic anomalies. In this respect the effect of second components is reminiscent of the effects of iodine or chlorine additions on the properties of sulfur near the $\lambda$ transition temperature in that substance.

On the other hand, a residue of the anomalous behavior seems quite persistent with composition change and it is presumably such a residual component which is responsible for the unusual glass-forming behavior of the lithium acetate solution seen in Fig. 9. Unfortunately, heat capacity data up to ambient temperatures are not available for this solution so that proper comparisons with the LiCl solution measurements cannot be made at this point. It is likely that the possibility of forming strong hydrogen bonds between acetate ions and water molecules may lead to some significant differences in behavior.

The behavior of the lithium acetate solution is, however, of considerable interest in its own right in connection with theories of the temperature dependence of relaxation processes in viscous liquids. For many years it has been popular particularly among polymer chemists, to believe that liquids become less viscous with increasing temperature because, above $T^*$, the liquid volume increases with the introduction of free space or "holes". The fact that, at least near $T^*$, lithium acetate solution can decrease in viscosity despite a decrease of $\gamma$ expansion coefficient, means that the above popular idea cannot be completely general.

Conclusions

Clearly a great deal of additional work needs to be done before the true nature of the cooperative process occurring in water will be properly understood. Nevertheless, the information provided by the present ONRT-supported study has given a very useful start to this promising line of investigation into the nature of science's most thoroughly studied liquid.
REFERENCES

b. N. Muller and J. A. Schufle, ibid, 73, 3345 (1968)
c. J. A. Schufle and Nai Teng Yu, J. Colloid Interface Sci., 46, 395 (1968)


Figure 1. Apparatus for determination of compressibility of supercooled water.
Figure 2. (a) Heat capacity of H$_2$O between 70 and $-35^\circ$C. (b) Difference in heat capacity between supercooled water and ice and supercooled D$_2$O and D$_2$O ice, as a function of temperature. (c) Total expansion coefficients of water and D$_2$O between 10 and $-35^\circ$C.
Figure 3. Compressibility of water in normal and supercooled conditions. Dashed line is polynomial extrapolation of data on water above 0°C by Kell (ref. 4). Solid line is plot of Equation 2.
Figure 4: (a) Uncorrected proton chemical shifts for bulk water, water in fine capillaries, and in emulsion form, in the temperature range -46 to 80°C relative to the reference proton resonances indicated in legend (right-hand ordinate scale). (b) Corrected shift values all referred to the resonance frequency for bulk water at 0°C (left-hand ordinate scale). Inset: shift of methane reference against pentane over temperature range of the present measurements.
Figure 5. Homogeneous nucleation and equilibrium melting temperatures for water in emulsion carrier fluids are distinguished as follows: (a) neptane, (b) heptane, (c) methycyclohexane, (d) methycyclopentane + methycyclohexane. Results obtained with different pressure cells are indicated as follows: cell 1: (o) heptane, (□) neptane, (△) methycyclohexane, (●) methycyclopentane + methycyclohexane.
Fig. 7. Comparison of emission and bulk sample near infrared spectra for water and ice.
Figure 6. Near Infrared spectra of emulsified water and ice at low temperatures.
Figure 8. Effect of lithium chloride concentration on the heat capacity anomaly in water and electrolyte solutions.
Fig. 9 Pressure dependence of $T_g$ for lithium acetate + water solution of mole ratio 1:10. Data for the anhydrous ionic glass 40 mol% Ca(NO$_3$)$_2$ + 60 mol% KNO$_3$ is included for comparison. Inset: A typical DTA trace obtained from a LiOAc·10 H$_2$O sample under a pressure of 1.3 kbar.

Fig. 10 Expansion coefficients for the liquid and glassy states of lithium acetate + water solution of mole ratio 1:10, as a function of temperature. Inset: A typical DSC trace obtained from a LiOAc·10 H$_2$O sample.
Figure 11(a) Heat capacities of water and ice as a function of log T, showing relation between entropy of fusion (5.213 cal mol⁻¹ deg⁻¹) and thermodynamically admissible extensions to lower temperature of liquid water heat capacity. (b) Difference in total entropies of water and ice as a function of temperature below the equilibrium melting point.