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A New Interpretation of Anomalous Properties of Water Based on Stillinger's Postulate

H. Kanno,*,[†] H. Yokoyama,[‡] and Y. Yoshimura[†]

*Department of Chemistry, National Defense Academy, Yokosuka 239-8686, Kanagawa, Japan, and
Department of Chemistry, Yokohama-city University, Yokohama 236-0027, Kanagawa, Japan*

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An attempt has been made to interpret the anomalous properties of supercooled water in a unified way by using Stillinger's postulate that the formation of bulky clathrate-like local structures is the main cause of the anomalous thermodynamic and transport properties exhibited by liquid water at low temperatures. Comparison of the thermodynamic properties of liquid water, tellurium, and sulfur suggests the existence of a λ-like C_p transition in supercooled water below T_H (but above T_K). It is inferred that the diverging trends of various anomalous properties with lowering temperature are preserved up to high pressures (<200 MPa) due to premature ice crystallization which conceals the expected extrema (e.g., a λ-like C_p transition) of thermodynamic properties from observation.

Introduction

In recent Raman and X-ray diffraction studies,[1−3] it has been fairly well established that local clathrate-like structures, which may exist in many varieties, are the main structural components of supercooled water at atmospheric pressure. Walrafen et al.[1] observed that the peak frequency of the Raman OH stretching contour (at 3190 cm^{-1}) in liquid water, supercooled to −33 °C at atmospheric pressure, is only 1% higher than that of the OH stretching peak (at 3160 cm^{-1}) of the type II THF clathrate hydrate crystal (THF·17H$_2$O, THF = tetrahydrofuran) and that the OD stretching component at ∼2380 cm^{-1} in cold D$_2$O liquid is assigned to the OD stretching mode of water molecules in pentagonal rings, and concluded using many other Raman data that lowering the temperature of liquid water increases the H-bonded pentagonal ring concentration to form clathrate-like polyhedral structures in supercooled water. Kanno et al.[2] have reported that the empty clathrate-like structures in liquid water are the cause of hydrophobic hydration and the unique properties of liquid water at low temperatures. Before going to the more recent X-ray diffraction study of Yokoyama et al.,[3] it is fair to point out that Stillinger[4,5] is the first to have asserted that bulky clathrate-like structures may be the cause of anomalous properties exhibited by liquid water in the supercooled temperature region. As shown by Pauling,[6] who was the first to reveal that the main structural feature of liquid water is represented by a clathrate-like structure, dodecahedron is one example of a bulky, unstrained polyhedral species dominant in supercooled water. Recently Yokoyama et al.[3] have examined their X-ray diffraction data of liquid water in detail and have revealed unequivocally that the modified Pauling model, which is based on the dodecahedron consisting of pentagonal rings of water molecules and is adapted for the number of inside water molecules to represent the density of water more precisely, is the most typical local structure in liquid water at the ambient and supercooled temperature regions under atmospheric pressure. Therefore, these reports[1−3] present an extraordinary possibility that a unified interpretation of anomalous properties of supercooled water may be possible in a simple way.

There are currently three competing typical interpretations (models) for anomalous properties of liquid water: (1) The stability limit conjecture, which was initially proposed by Speedy and Angell[7] and developed by Speedy,[8,9] states that the divergence of thermodynamic properties of supercooled water is connected to the existence of a spinodal line bounding the liquid in the superheated, stretched, and supercooled states. The crucial point of the conjecture is that with decreasing temperature the reentrance of the liquid spinodal line from the negative pressure region to the positive pressure region has not been experimentally verified. (2) The recent leading interpretation is the liquid−liquid phase transition hypothesis.[10−14] On the basis of the existence of two distinct amorphous ices {low-density amorphous ice (LDA) and high-density amorphous ice (HDA)}[15,16] and molecular dynamics simulations on the structure and equation of state of supercooled water, Poole et al.[10−12] proposed that below the hypothesized second critical point water separates into two phases, a low-density liquid water (LDL) and a high-density liquid water (HDL), the structures of which are expected to resemble closely those of the two amorphous ices. The location of the proposed critical point (the second critical point) is roughly determined to be around $P_{c2} = 100$ MPa and $T_{c2} = 220$ K from the computer simulation works. Mishima and Stanley[17] have recently reported that the hypothesis is experimentally supported by their emulsion work at high pressures in which they observed an abrupt inflection of the decompression-induced melting curve of ice IV. Despite much discussion about the possible existence of the second critical point in supercooled water,[13,14] there has been no plausible interpretation as to how typical anomalous properties of liquid water at normal pressure are caused by the existence of the second critical point, the pressure of which (most plausibly $P_{c2} > 100$ MPa) is far from the normal pressure. (3) The third is the singularity-free scenario[18−20] in which the thermodynamic anomalies are related to the presence of low-density and low-entropy structural heterogeneities. There have been many varieties of this approach. One of the early attempts is the application of the percolation theory in which water is treated

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* To whom correspondence should be addressed. E-mail: hkanno@cc.nda.ac.jp. Fax: 81-468-44-5901.
  [†] National Defense Academy.
  [‡] Yokohama-city University.

as a locally structured transient gel comprised of monomer water molecules held together by hydrogen bonds whose number increases cooperatively as temperature decreases.[18] Another notable recent interpretation is a water-like lattice model due to Sastry et al.[19,20] They have argued that the main anomalous features of liquid water are interpreted without invoking singularities such as the second critical point or the λ-like transition. More recently Sciortino and co-workers[21−23] have made another approach to interpret the dynamic properties of supercooled water using the mode coupling theory (MCT).

All three interpretations describe the main features of anomalous properties of water. However, each has its own weak points because of being unable to give adequate interpretations of some important aspects and lacking unequivocal experimental evidence, although the latter is mainly due to experimental difficulties associated with the instability of liquid water at low temperatures.

In this paper, we give a new interpretation of anomalous properties of water based on the newly established water structure at atmospheric pressure.

Role of Clathrate-Like Structures for Anomalous Properties of Water

As noted in the Introduction, it is Stillinger who first pointed out that bulky cage structures may be the cause of anomalous properties exhibited by liquid water in the supercooled temperature region.[4,5] In addition to the well-known stability limit conjecture,[7−9] Speedy also developed a model similar to Stillinger's, in which he postulated that pentagonal rings of water molecules are the essential element in displaying anomalies of supercooled water.[24] However, in his more recent paper,[9] he did not mention the importance of pentagonal rings in the unified interpretation of anomalous properties of water.

Our starting point is essentially the same as the proposition of Stillinger;[4,5] namely, the concentration of the bulky, clathrate-like local structures increases cooperatively in water with decreasing temperature, causing the C_p, α (isothermal expansivity), and κ_T (isothermal compressibility) of water to diverge at around T_s (T_s = singularity point for liquid water; T_s is estimated to be $\sim$228 K at atmospheric pressure). Different from the time when he presented his idea, we have now many supporting and testable experimental data. We consider that water anomaly is very much similar to the thermodynamic behavior of liquid tellurium toward supercooling. Liquid Te also has a TMD (temperature of maximum density) very close to its melting point (450 °C) and shows a rapid volume increase, together with C_p and κ_T increases, with decreasing temperature.[25−28]

The solid tellurium has a hexagonal crystal structure in which tellurium atoms are arranged in spiral chains with axes parallel to the crystallographic c-axes. The atoms within the chains are covalently bonded to each other, whereas the bonding between the chains shows covalent as well as van der Waals character. On the other hand, the local structure of supercooled Te is described as a mixture of two and three coordinated atoms. It is reported that the concentrations of the two and three coordinated atoms are about the same at around the melting point. As the intrachain bond-stretching modes of the solid Te disappear completely in the liquid phase, it can be concluded that the chain structure has largely broken down in the liquid. Therefore, the volume increase in supercooled Te liquid with decreasing temperature is a clear manifestation that the liquid structure deviates more and more from the solid structure with decreasing temperature. These similarities between water and liquid Te are worth comparison in more detail and will be discussed in a later section.
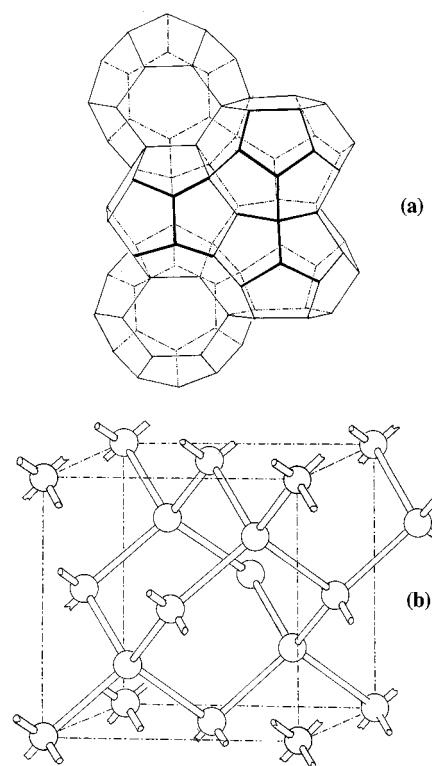

Figure 1. (a) A typical clathrate-like local structure suggested by Pauling in supercooled water (redrawn from ref 6). (b) Structure of ice Ic (redrawn from ref 29).

The apparent approach of the liquid volume of supercooled water toward the volume of ice I with a temperature decrease does not mean that the structure of liquid water approaches that of ice I. Actually it deviates rapidly from the random tetrahedral network structure to develop clathrate-like structures with a temperature decrease (Figure 1).[29]

There are ample examples[30−32] that stabilized structures in the liquid state are different from those in the solid state, although there are only a few in pure liquids. Probably liquid sulfur is the most typical one in which local structure in the liquid is much different from that in the solid.[32,33] The cyclo-S_8 species, which is the main component species in the solid state, is still the main chemical entity in liquid sulfur at around the melting point ($\sim$119 °C), and then ring cleavage and resultant formation of chain sulfur species take place with a temperature increase. A yellow transparent mobile liquid sulfur becomes brown and rapidly viscous above about 160 °C, its viscosity reaching a maximum at about 200 °C and thereafter decreasing again.

Going down from the high-temperature side ($T \le 300$ °C), the C_p of liquid sulfur shows a λ-like variation with a temperature decrease.[35] The rapid C_p decrease around 159 °C in the case of liquid sulfur is ascribed to the rapid structural changes involving the formation of cyclo-S_8 species at the expense of chain sulfur species (Figure 2). In other words, the λ-like C_p transition is due to the structural changes associated with the changes of chemical entities.[32−35] An important inference from these observations is that the liquid structure can change rather drastically with temperature. A specific local structure in a liquid has its own stable temperature range, outside of which it becomes thermodynamically unstable and of course disappears. In the case of liquid sulfur, cyclo-S_8 species rapidly disappear above 159 °C whereas chain sulfur species become unstable below 159 °C.

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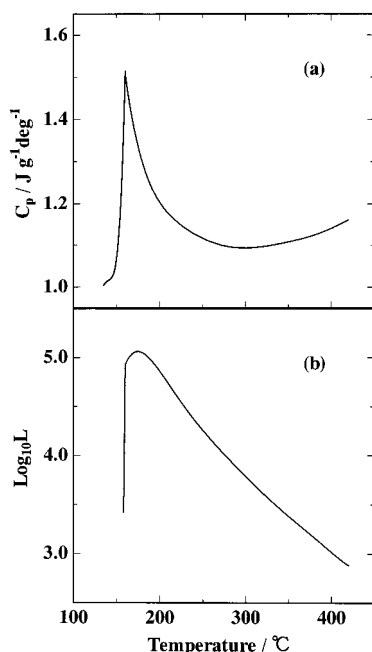
Figure 2. Heat capacity (C_p) (a) and chain length (L) (b) changes of liquid sulfur as a function of temperature (redrawn with modifications from ref 33).

In the case of liquid water the rapid volume increase with decreasing temperature is the clear indication that it will go to a certain catastrophic point not far from T_H (T_H = homogeneous nucleation temperature). As pointed out by Angell,[36,37] the excess entropy of liquid water ΔS_l (= $S_l - S_s$, S_l = entropy of the liquid, S_s = entropy of the solid) rapidly decreases with decreasing temperature to the point where ΔS_l becomes zero (so-called Kauzmann's paradox,) if the C_p of liquid water continues to rise in the same way as the temperature region just above T_H. There are three possibilities to avoid this absurd situation that ΔS_l becomes zero at T_K (T_K = Kauzmann temperature; the entropy of liquid water becomes smaller than that of ice I below T_K; in the case of water $T_K \approx -65$ °C):[36,37] (1) liquid water shows a glass transition at a certain temperature above T_K, (2) it gives a λ-like C_p transition not far from T_H ($T > T_K$), and (3) it always crystallizes before arriving at T_K. It is important to point out that if the diverging trend of thermodynamic properties of liquid water would continue unchanged to lower temperatures ($T < T_H = -38$ °C) without crystallization, there should be a glass transition, below which temperature a glassy water with clathrate-like structures should be obtained. As there has been no glassy water showing a glass transition as high as $T_g \approx 220$ K, which is expected from the C_p behavior of liquid water above T_H, the first possibility should be a marginal one. However, there is a temptation to expect that there may be a glassy water with clathrate-like structures below T_H (but higher than T_K) which may be only short-lived and may instantly transform into a more stable crystal form, i.e., ice Ih. Seeing the facts that amorphous solid water gives a glass transition at ~135 K[38] and that there is no pure substance having two glass transitions, we can discard the first possibility at the moment.

In the X-ray and neutron scattering studies[39-44] of hyperquenched glassy water (HGW), LDA, and HDA, it is shown that the local structure of HGW is similar to that of a low-density amorphous ice either made by heating a HDA or obtained by vapor deposition onto a cold substrate, although there are several small differences between these three amorphous ices. However, the similarity of the local structure of HGW to that of LDA made from high-density amorphous ice

clearly indicates that the local structure of HGW resembles that of ice I. The natural consequence of the structural differences between supercooled water above T_H, in which bulky clathrate-like structures are dominant, and HGW, in which hexagonal rings of water molecules are the building unit of the local structures, leads to the following conclusion that liquid water with dominant clathrate-like structures becomes increasingly unstable with decreasing temperature and inevitably crystallizes even if there might be a certain C_p transition (a λ-like transition is one example) taking place just below T_H as proposed by Angell a long time ago.[37]

Glass Formation of Water and Aqueous Solutions

From the observed C_p of supercooled water, T_g is expected to be around −60 °C because it must be higher than the so-called T_K. However, ASW, HGW, and LDA all give a very weak glass transition at around 135K. There have been repeated arguments for and against the possibility that there is a continuity between metastable liquid water just above T_g and water at around 273 K.[45-49] It is generally accepted that the structures of ASW and glassy water prepared by hyperquenching small liquid droplets (HGW) are essentially the same when both of the amorphous solid waters are annealed at about 130 K.

The cooling rate of 10^6–10^7 K/s is necessary to bring a water droplet to a glassy state.[50-52] This high cooling rate may eliminate, at least in part, the development of open clathrate-like structures in supercooled water in passing through the temperature region where bulky clathrate-like structures are thermodynamically stable and dominant. Thus, it is expected that the quenched glassy state resembles ice I in structure. In fact, the close similarity of glassy water and ice I has been verified by X-ray and neutron diffraction studies.[39-44]

In Speedy's interpretation of the stability limit conjecture,[8] he expected that the liquid water becomes a rigid gel at some temperature, $T_{gel} = T_s(1 \text{ atm}) \simeq 228$ K, when quenched at 10^6–10^7 K/s. He considered that the rigid state of water at T_s is better described as a gel rather than a glass because the rigidity (the diverging viscosity at T_s) has its origin in the long-range correlations in supercooled water. On the other hand, we consider that, in the ultrafast quenching process, the open clathrate-like structure is not developed as much in the temperature region of 0 to −45 °C, though this anticipation has not been experimentally confirmed, and that when clathrate-like structures are developed to become dominant liquid water becomes very unstable so that it will always crystallize before reaching a hyperquenched glassy state.

In the glass-formation studies of aqueous solutions,[53-55] it has often been noted that glass formation is only possible at a normal cooling rate (~10^3 K/min) when the intrinsic water structure is completely destroyed. From an X-ray diffraction study, Narten et al.[53] reported that below $Y = 10$ (Y = moles of water/moles of salt) the intrinsic water structure completely disappeared in aqueous LiCl solution, which is glass-forming below $Y = 11$ at the cooling rate of ~10^3 K/min. When these glass transition temperatures are extrapolated to zero solute concentration, a temperature of $T_g = 138 \pm 2$ K is obtained. This is reasonable because there are no or few clathrate-like local structures in anomaly-free aqueous solutions.

It is now appropriate to discuss the fragile-to-strong transition observed between water at around 273 K and supercooled water just above the glass transition temperature (~136 K).[56,57] Here we can give a clear-cut explanation of this seemingly anomalous behavior (the fragile-to-strong transition) of supercooled water. On going from room temperature to a lower

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temperature (> -45 °C), the open clathrate-like structures are developed in water with an attendant C_p increase, which is the major anomaly rendering water as "the most fragile liquid" of all the liquids examined so far. Ito et al.[57] have examined the fragility of water by comparing the properties of many glass-forming liquids and concluded that water is the most fragile above -38 °C and, on the other hand, strong just above its glass transition temperature ($T_g \simeq 135$ K). This fragile-to-strong transition is now regarded as a natural consequence of the structural changes of supercooled water since the water above T_H has many clathrate-like structures while the water just above T_g is very close to LDA in structure.

There has been ample experimental evidence[58-61] that there is close similarity between LDA and ice I. Tse et al.[58] reported that the transformation of ice Ih to HDA is caused by a mechanical instability imposed by high pressure and concluded that HDA does not have a liquid-like structure (HDA is not thermodynamically connected to a liquid state). They also noted that the vibrational profile for LDA is almost identical to that of ice Ih but differs from that of a fast quenched glassy water. Kanno et al.[59] also reported that from the Raman spectra of ice I and LDA the structure of LDA is very close to that of ice I.

It is well-known that the thermodynamic and kinetic properties of a glass are more or less affected by its thermal history.[62,63] Therefore, it is expected that a glassy water made by rapidly quenching bulk water above 300 K (namely, HGW) may have a structure different from that of LDA or ASW because there may be some residual clathrate-like structures trapped in HGW. In the calorimetric study of HGW, ASW, and LDA, Johari et al.[64] reported that HGW and ASW have a higher T_g ($\simeq 136$ K) than that ($\simeq 129$ K) of LDA. Furthermore, it is reported[64] that the supercooled liquid obtained by heating LDA does not convert, on cooling, to HGW and the liquid obtained by heating LDA does not produce, on cooling, HGW as if the two liquids retain the structural distinction of their amorphous solid states.

Taking into account the foregoing discussion, the observation that the T_g of HGW ($T_g = 136 \pm 1$ K) is higher than that of LDA ($T_g = 129 \pm 2$ K) is now nicely explained in the same line of the interpretation. The rapidly quenched glassy state usually reflects a liquid structure at higher temperatures than its glass transition temperature, and therefore, HGW should in part contain clathrate-like structures, which invite a temperature rise in its glass transition.

Johari et al.[64-66] also reported that the T_g of ASW is almost identical to the T_g of HGW. This may be interpreted as the indication that ASW also contains clathrate-like structures in a small quantity. In fact, it is reported that as-deposited ASW is very porous in structure and therefore clathrate-like structures may be formed during sintering (thermal annealing) as ASW was usually subjected to thermal annealing before a T_g measurement. Another additional effect may come from the fact that ASW contains a small amount of gas molecules in its porous structure. Water molecules around encapsulated gas molecules must form clathrate-like structures so that a T_g rise is expected as shown soon.

In aqueous solution systems, there have been many experimental data[67-70] showing that aqueous solutions with clathrate-like structures tend to give higher glass transition temperatures than those without clathrate-like structures. Kanno and co-workers[67-70] made a number of reports that aqueous solutions of tetraalkylammonium halides give much higher T_g values than the corresponding aqueous solutions of lithium halides (Figure 3). Aqueous solutions of highly hygroscopic salts are usually glass-forming in certain composition regions at a cooling rate
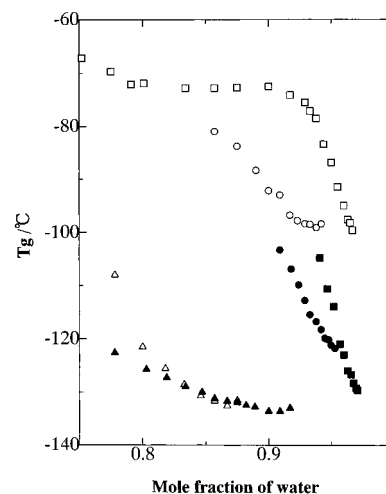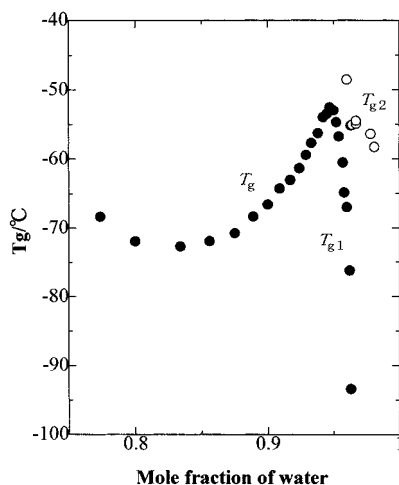

Figure 3. Variation of T_g values for aqueous LiCl, MgCl$_2$, AlCl$_3$, Me$_4$NCl, Et$_4$NCl, and Pr$_4$NCl solutions with the mole fraction of water (N): (▲) aqueous LiCl solution, (●) aqueous MgCl$_2$ solution, (■) aqueous AlCl$_3$ solution, (△) aqueous Me$_4$NCl solution, (○) aqueous Et$_4$NCl solution, (□) aqueous Pr$_4$NCl solution. As the Et$_4$NCl solution gives two T_g phenomena above $N = 0.91$ ($Y = 10$), the average T_g values were used for plotting. Sources of T_g data: aqueous LiCl, MgCl$_2$, and AlCl$_3$ solutions, from ref 55 and unpublished data in this laboratory; aqueous R$_4$NCl solutions, from refs 67 and 68.

of about 6×10^2 K/min.[55] There are clear trends[55] that aqueous solutions of monovalent cation salts such as LiCl, CH$_3$COOLi, etc. are glass-forming up to about $Y = 10$ ($N = 0.91$), those of divalent cation salts such as CaCl$_2$, Mg(ClO$_4$)$_2$, etc. are vitrifiable up to about $Y = 20$ ($N = 0.95$), and those of trivalent cation salts such as AlCl$_3$, La(ClO$_4$)$_3$, etc. can be quenched in glassy states up to about $Y = 30$ ($N = 0.97$). In view of these trends, the glass-forming composition region of aqueous tetrapropylammonium chloride (Pr$_4$NCl) solution is extraordinarily large because aqueous Pr$_4$NCl solution is glass-forming up to about $Y = 29$. This wide glass-forming composition region may be ascribed to the high stability of clathrate-like structures because there are many pentagonal rings of water molecules, which are inhibitors in ice I nucleation, in the solution. In fact, hydrogen bonds in clathrate-like structures are reported to be strong and comparable in strength to those in amorphous solid ice at low temperatures.[2]

An interesting contrast is that aqueous tetrabutylammonium chloride (Bu$_4$NCl) solution is not glass-forming in any composition region at a normal cooling rate of 6×10^2 K/min despite the fact that the glass-forming composition region grows from $Y = 7$ for aqueous tetramethylammonium chloride (Me$_4$NCl) solution, to $Y = 15$ for aqueous tetraethylammonium chloride (Et$_4$NCl) solution, and to $Y = 26$ for aqueous Pr$_4$NCl solution.[67,68] It is well-known that Bu$_4$NCl forms a stable clathrate hydrate of the composition Bu$_4$NCl·32H$_2$O whereas none of the above three R$_4$NCl compounds (R = Me, Et, and n-Pr) have been reported to form stable clathrate hydrate.[71] Accordingly, it is considered that the strong driving force for clathrate hydrate formation prevents an aqueous Bu$_4$NCl solution from glass formation at a cooling rate of $\sim 10^3$ K/min.

Glass formation of aqueous butyltripropylammonium chloride (BuPr$_3$NCl) solution is very suggestive in this respect.[69] The T_g of an aqueous solution of a hydrophilic solute or a metal electrolyte monotonically decreases with decreasing solute concentration toward 135 K at zero solute concentration.[55] As seen in Figure 4, the T_g of aqueous BuPr$_3$NCl solution increases with a decrease in salt concentration. This T_g increase is clear experimental evidence that the clathrate-like structure formation

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Figure 4. Variation of T_g (T_{g1} and T_{g2}) values for aqueous BuPr₃NCl solution with the mole fraction of water (N). Souce of data: from ref 69. Above $N = 0.96$ ($Y = 23$) the solution gives two glass transitions due to phase separation. The rapid T_{g1} decrease indicates that the first glass transition heads for the glass transition of water ($T_g \approx 136$ °C) with increasing water content. On the other hand, the second glass transition seems to head for the expected glass transition for a hypothetical glassy state of the water with clathrate-like structures.

invites a T_g increase due to an attendant viscosity increase arising from the strong hydrogen bonds in the clathrate-like structures and their connectivities.

Here some comment must be made about the third possibility that supercooled water always crystallizes before arriving at T_K. This is the stability limit conjecture of Speedy.[8,9] Actually supercooled water crystallizes at a T_H (at ∼−41 °C at atmospheric pressure) slightly higher than the expected T_s (∼−45 °C). As compared with other molecular liquids, super-cooling of water at low pressures (≪200 MPa) is much shallower than those of other molecular liquids (normally the $\Delta T_H/T_m$ ratio ranges from 0.2 to 0.3, $\Delta T_H = T_m - T_H$).[72,73] This shallow supercooling ($\Delta T_H/T_m = 0.14$ at atmospheric pressure) is mainly attributed to the formation of open clathrate-like structures in supercooled water. In fact, at 200 MPa, the $\Delta T_H/T_m$ ratio grows to 0.28 ($\Delta T_H = 70$ K, $T_m = 253$ K), which is now in the normal range.[36] In the supercooled temperature regime at low pressures (<200 MPa), the supercooling limit of water is now understood to be closely related to the catastrophic failure of bulky clathrate-like structures which are only stable in the limited P–T range. Accordingly, the concept that supercooled, superheated, and stretched waters are all grouped in a single overall spinodal line is not appropriate.

Pressure Dependence of Local Structures in Liquid Water

One of the most peculiar features of liquid water is the pressure dependence of viscosity at low temperatures: the viscosity of water decreases with an increase in pressure up to about 150 MPa and then increases with a further increase in pressure as do the normal liquids.[74,75] It is important to point out that anomalous behavior is limited to the low-temperature region: above about 30 °C, the viscosity of water shows normal behavior with pressure.

There have been a number of reports[76−78] that pressure application exerts the same effects on water structures as does the addition of common salts which disrupt the intrinsic water structure. In fact, pressure application exhibits the same trend in the number of properties of water as the addition of salts such as NaCl; e.g., TMD moves to lower temperatures with an

increase in either pressure or salt concentration,[79,80] and T_H decreases similarly with pressure or salt concentration.[81] Therefore, a decrease of T_H with pressure demonstrates that clathrate-like structures are distorted and disrupted to become a water structure at high pressures. Although there have been many X-ray and neutron diffraction studies,[82−86] a clear-cut structural picture has not been elucidated. Okhulkov et al.[84] obtained X-ray diffraction data of liquid water at 20 °C from 1 atm up to 770 MPa. They interpreted their X-ray scattering data by assuming that the liquid structure fluctuations can be represented by several structures of solid water phases. Of course, the preferential local structures in water at high pressures depend on which of the ice phases the liquid water is most close to at a given temperature and pressure. Actually in the present interpretation a clear-cut picture of the water structure at high pressures is desirable but not indispensable.

There have been only a few cases in which thermodynamic or transport properties of supercooled water have been measured over wide pressure and temperature ranges.[75,76,87,88] In an early attempt to interpret the anomalous properties of supercooled water in a unified way, Speedy and Angell[7] proposed that a large number of thermodynamic and other transport properties of water at low temperatures are well described by a critical type of equation

$$X = A\epsilon^{\gamma} + X_0 \tag{1}$$

where $\epsilon = (T - T_s)/T_s$, X_0 is the background component, A and γ are constants, and T_s is a singularity temperature.

Kanno and Angell[87] extended the earlier κ_T measurements by Speedy and Angell to higher pressures up to 190 MPa and at temperatures in the range of +25 to −30 °C. An important result is that pressure application on water causes the anomalous regions to be displaced to lower temperatures. Analyzing the κ_T data by eq 1, it is shown that the singular temperature (T_s) falls in a way parallel to that of the T_H curve up to 190 MPa, implying that the diverging trend of thermodynamic properties of water continues up to high pressures (∼190 MPa). Lang and Lüdemann[88] measured the longitudinal deuterium relaxation time in D₂O and the longitudinal ¹⁷O relaxation times in supercooled D₂O and H₂O. They compared the applicability of eq 1 and a well-known VTF equation,[56] which is reported to describe various thermodynamic and transport properties of glass-forming liquids quite well, and reported that the temperature dependence of the spin−lattice relaxation times T_1 of the ¹⁷O isotope in H₂O and D₂O can be better represented by eq 1 than the VTF equation at low pressures ($P < 150$ MPa) whereas at high pressures ($P > 150$ MPa) the T_1 data can only be fitted by the VTF equation. In the same line of NMR works, Prielmeier et al.[76] measured the self-diffusion coefficients D in H₂O and D₂O at pressures up to 400 MPa and temperatures down to 200 K. Application of eq 1 to the D data at higher pressures ($P > 150$ MPa) yields T_s values higher than the respective T_H values, indicating that the results are in contradiction to the stability limit conjecture. These results are also in accord with the present interpretation that clathrate-like structures are dominant in the low-pressure region and that they are gradually converted into high-pressure local liquid structures with an increase in pressure. The initial decrease of viscosity with increasing pressure is clearly interpreted by the disruption and distortion of strongly-hydrogen-bonded clathrate-like structures in liquid water at low temperatures. Figure 5 gives the summarized T_s data as a function of pressure. An important conclusion obtained from these data is that although the anomalous regions are displaced to lower temperature regions the diverging trends of the

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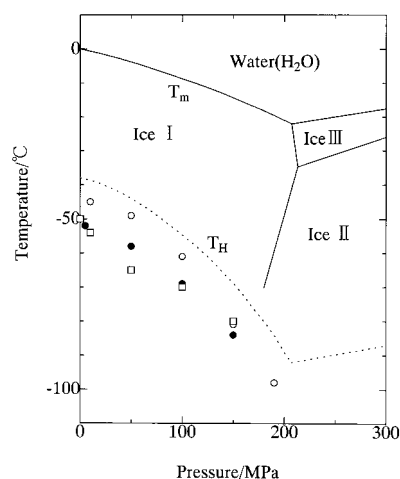
Figure 5. Pressure dependence of T_s: (○) T_s from the isothermal compressibility data from ref 87, (●) T_s from the self-diffusion data from ref 76, (□) T_s from the correlation times τ_θ derived from ^{17}O T_1 data from ref 88.

anomalous properties are preserved up to high pressures (<150 MPa). This strongly indicates that cooperative growth of the clathrate-like local structures in supercooled water is displaced to lower temperatures with increasing pressure. Another is that the pressure dependence of T_s is similar to that of T_H, signifying the close correlation of them.

In the high-pressure DTA study[89] of aqueous LiCl solutions of $Y = 20$, the T_g of the glassy solutions vitrified above 250 MPa and decompressed to atmospheric pressure is reported to be around −137 °C. This observation is very suggestive because an aqueous solution with high-density local water structures also gives a glass transition at around −137 °C when T_g is measured at normal pressure and when the solute concentration is extrapolated to zero. Similar T_g results were also obtained in the T_H measurements for emulsified aqueous alkali-metal chloride solutions at high pressures.[81] From these T_g data[81,89] it is expected that the T_g of glassy high-density water may be around 140 K at 300 MPa.

Comparison of Liquid Te and Water

As noted in the previous section, liquid tellurium shows behavior very similar to that of supercooled water in the temperature dependences of volume, C_p, κ_T, and α.[25-28] Below T_m the volume of liquid tellurium exhibits a large increase with a temperature decrease in a manner just like that of supercooled water. Other properties such as C_p, κ_T, and α also show a diverging trend down to about 350 °C and then give a transitional behavior indicating a rapid structural change taking place toward another different liquid structure. Although there are some ambiguities in the liquid Te structure, there is a common agreement that rapid local structural changes are the cause of peculiar V, C_p, κ_T, and α behavior in the supercooled temperature region. This common consensus will suffice for the present discussion.

Figure 6 shows temperature dependences of the various thermodynamic properties of the two liquids (water and liquid tellurium) on a reduced temperature (T/T_m) scale. When comparison is made on reduced scales, it is remarkable that both liquids behave very similarly down to a certain degree of supercooling. In the case of liquid water, supercooling is rather shallow so that we cannot observe experimentally the fate of the structural changes, exhibited by anomalous V, C_p, κ_T, and α behavior, to lower temperatures ($T < T_H$). However, inferring from the data from liquid tellurium, we are tempted to consider
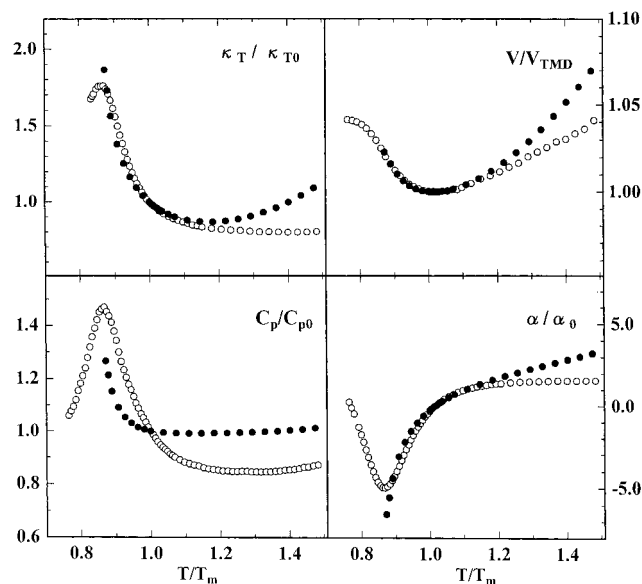
Figure 6. Comparison of the anomalous thermodynamic properties of liquid water and tellurium on a reduced scale: (●) liquid water, (○) liquid tellurium. Sources of data: liquid Te, all numerical V, C_p, α, and κ_T data were supplied by Y. Tsuchiya (ref 25); liquid water, refs 9 and 100. C_{p0} and κ_{T0} are the values at T_m, α_0 is the value at $1.1T_m$ so that the sign of the α/α_0 ratio is kept the same as that of α, and V_{TMD} is the value at the temperature of maximum density.

that supercooled water would show a λ or some similar structural transition at temperatures not far from T_H as just proposed by Angell.[36,37] To our regret, the expected transition exists in the inaccessible temperature region ($T < T_H$) and cannot be proved or disproved experimentally. From Figure 6, we can obtain one important conclusion that the cooperativity of the structural change is stronger for supercooled water than for supercooled liquid tellurium because the volume (V/V_{TMD}) and thermodynamic (κ_T/κ_{T0} and α/α_o) changes with reduced temperature are narrower for liquid water than for liquid tellurium.

To interpret these anomalous thermodynamic properties of liquid tellurium, various models have been proposed. Tsuchiya and Seymour[90] presented an inhomogeneous structure model in which liquid tellurium is assumed to consist of two kinds of domains (one is metallic with three coordinated atoms, and the other is nonmetallic with two coordinated atoms), and the structural change associated with various anomalous behaviors is considered to be brought about by the change in the mole fractions of the two domains with temperature.

Here we compare two more properties between water and liquid tellurium. The glass transition temperature (T_g) of glassy tellurium is reported to be 300 K,[91] meaning that the T_g/T_m ratio is 0.42 while the T_g/T_m ratio for water is 0.49 ($T_g = 135$ K when HGW is used). There is a well-known empirical rule, i.e., $T_g/T_m = 2/3$, for many glass-forming liquids.[92,93] Therefore, both liquids have very low glass transition temperatures as compared with normal glass-forming liquids. It is to be stressed that simple marginally-glass-forming liquids such as CCl_4, $CHCl_3$, and isopentane have very low T_g/T_m ratios ($T_g/T_m = 0.24$ for CCl_4, 0.38 for $CHCl_3$, and 0.58 for isopentane).[94] In this respect, water and liquid Te are both classified as the poor glass-forming group. The other interesting comparison is the difference in the manner of the entropy loss in the supercooling process between the two liquids. Ito et al.[57] have recently shown that water is assigned to the most fragile liquid when compared with other liquids in the $\Delta S_l/\Delta S_m$ vs T/T_m plots (ΔS_m = excess entropy of a liquid at T_m, ΔS_l = excess entropy at $T < T_m$). When only the C_p data above 630 K are used for the $\Delta S_l/\Delta S_m$ vs T/T_m plot for liquid

T_e, it is evident that liquid Te is much stronger than liquid water (strictly speaking, the liquid water above T_H) and is classified as a strong liquid in the strong−fragile classification scheme. This difference may be a cause of the big difference of the supercooling ability between the two liquids because supercooled water rapidly approaches T_K with decreasing temperature.

Concluding Remarks

We have already seen that most of the anomalous thermodynamic properties of supercooled water have been successfully explained in terms of the clathrate-like structure formation in supercooled water at low pressures. In addition to X-ray and Raman studies,[1−3] there are several pieces of supporting experimental evidence that clathrate-like structures are dominant in supercooled water. Xie et al.,[95] using the small-angle X-ray scattering method, measured the absolute structure factor of liquid water in the wavenumber range $0.05 < \nu < 0.30$ Å^{-1} and temperature range $-34 < T < +25$ °C and concluded that the increase in density fluctuations in water with supercooling is ascribed to an increasing fraction of water molecules participating in cluster formation. Walrafen and Chu[96] added another piece of evidence for the existence of high concentrations of strongly-hydrogen-bonded clathrate-like structures in highly supercooled water by analyzing shear viscosity and self-diffusion data. Sorensen and co-workers[97] also interpreted their viscosity data of aqueous ethanol solution as an indication that cage-like structures are formed in aqueous solution and liquid water at low temperatures. Thus, we now have many experimental data warranting us to claim that the clathrate-like structure formation is the main cause of the diverging increases of volume, C_p, and κ_T in supercooled water. Furthermore, it is to be noted here that there have been several computer works in favor of the assertion advanced here. Geiger et al.,[98] using an ST2 pair potential, made MD simulations of supercooled water and reported the existence of numerous clathrate-like holes in the metastable region of water. More recently Sciortino and co-workers,[21−23] using the extended simple point charge model, SPC/E, have examined the MCT predictions for the single-particle dynamics of supercooled water. The important results of their simulation works are that (1) the apparent power-law-type behavior of the temperature dependence of transport coefficients in supercooled water is traced to the formation of long-lived cage-like local structures and (2) the SPC/E water undergoes a kinetic glass transition about 50 K below the TMD. In relation to the present interpretation, the latter result is very interesting and provocative because the glassy state below the suggested kinetic glass transition may correspond to the glassy state with local clathrate-like structures which was taken up as the first possibility in our interpretation although discarded in real water.

Although the existence of a λ-like or some similar C_p transition in supercooled water is inferred from the thermodynamic behavior of liquid tellurium, which shares many of the anomalous properties of supercooled water and shows a λ-like C_p transition, it must be pointed out that except in only one case there has been no other direct experimental evidence showing suggested λ-like behavior in any thermodynamic and transport property of liquid water. Trinh and Apfel[99] measured the sound velocity down to -33 °C and observed a minimum at around -31 °C. On the other hand, two types of observations have been reported for aqueous solution systems.[97,101−103] In one type,[101,102] the diverging trend of the "anomalous" property is preserved until the anomalous property is wiped out with increasing solute concentration, while in the other type,[97,103] the
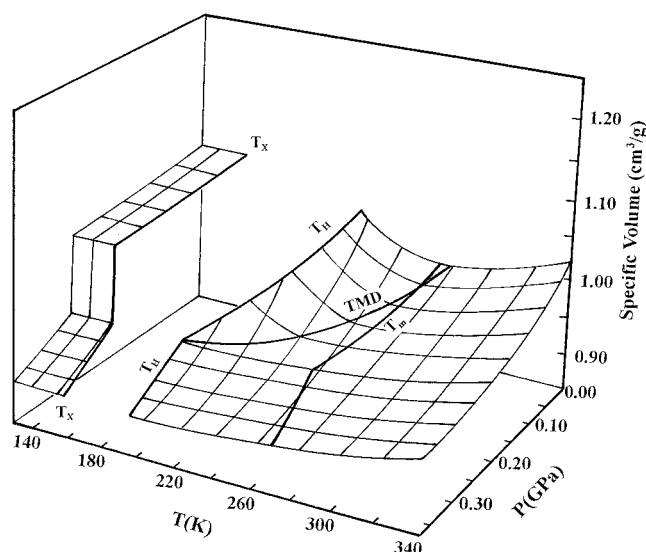
Figure 7. PVT surface for liquid water. Data are from refs 9, 17, 80, and 100. The PVT surface below the T_H curve is rather tentative due to the deficiency of experimental data. As there have been no T_g data for HDA, the boundary between HDA and HDL is uncertain so that distinction is not made in this figure. The liquid−liquid transition, which is expected to occur in supercooled water at high pressure and low temperature,[10−12] is a big issue still unresolved,[13,14] and here we adopt the boundary proposed by Dougherty[104] recently and our unpublished data.[105]

clear maximum (or minimum) is observed before the anomalous property is lost with increasing solute concentration. Despite only a few available data, it seems that only a hydrophobic solute can give rise to a λ-like extremum in an "anomalous" thermodynamic or transport property of the resultant aqueous solution.

Summarizing all these considerations and available experimental data, the PVT surface of liquid water is given in Figure 7, and the conclusions are given as follows: (1) The anomalous properties of water at low temperatures and pressures (≤ 200 MPa) are brought about by cooperative growth of clathrate-like local structures in water with decreasing temperature. (2) The apparent diverging trends of anomalous properties of liquid water with decreasing temperature are preserved up to high pressures (≤ 200 MPa) due to premature ice crystallization which conceals the expected extrema inferred from the anomalous behavior of liquid tellurium from observation. (3) It is expected that a hydrophobic solute can stabilize the intrinsic clathrate-like local structures in liquid water, thereby giving rise to an extremum in the "anomalous" property (e.g., a λ-like C_p transition) in the resultant aqueous solution if only the solute concentration is not high.

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