Explanation of the anomalies of water

1 High melting point (0°C, c.f. CHCl$_3$ -63°C)

In ice (1h), all water molecules participate in four hydrogen bonds (two as donor and two as acceptor) an
held relatively static. In liquid water, some hydrogen bonds must be broken to allow the molecules move
around. The large energy required for breaking these bonds must be supplied during the melting process
only a relatively minor amount of energy is reclaimed from the change in volume. The free energy chang
(DG=DH-TDS) must be zero at the melting point. As temperature is increased, the amount of hydrogen
bonding in liquid water decreases and its entropy increases. Melting will only occur when there is suffici
entropy change to provide the energy required for the bond breaking. The low entropy (high organization
liquid water causes this melting point to be high. [Back]

2 High boiling point (100°C, c.f. CHCl$_3$ 61°C)

There is considerable hydrogen bonding in liquid water which prevents water molecules from being easil
released from the water's surface. This reduces the vapor pressure. Boiling cannot occur until this vapor
pressure equals the external pressure. This occurs at a consequentially higher temperature. [Back]

3 High critical point (374°C, c.f. CH$_3$CH$_3$ 32°C)

The critical point can only be reached when the interactions between the water molecules fall below a ce
threshold level. Due to the strength and extent of the hydrogen bonding, much energy is needed to cause
reduction in molecular interaction and this requires higher temperatures. Even close to the critical point,
considerable number of hydrogen bonds remain, albeit bent, elongated and no longer tetrahedrally arrang
[92]. [Back]

4 High surface tension (72.75 mJ/m^2, c.f. CCl$_4$ 26.6 mJ/m^2 at 20°C)

Water molecules at the liquid-gas surface have lost potential hydrogen bonds directed at the gas phase an
pulled towards the underlying bulk liquid water by the remaining stronger hydrogen bonds [214]. Energy
required to increase the surface area, so it is minimized and held under tension. As the forces between the
water molecules are several and relatively large on a per-mass basis, compared to those between most oth
molecules, the surface tension is large. Lowering the temperature greatly increases the hydrogen bonding
causing increased surface tension. If a small drop of water (typically 1 mm diameter) is coated in a fine
(typically 20 mm diameter) hydrophobic dust then the drop can roll and bounce without leakage [225], an
aqueous spheres can even float on water. Capillarity holds the dust at the air-liquid interface with the elas
being due to the high surface tension. The interesting absence of any apparent anomaly in the surface
tension/temperature behavior (although unexpectedly, there is no deviation associated with the density
anomaly at 4°C, but there is an inflection point at about 250°C [427]) is due to surface enrichment with
clusters that are different from those present in the bulk. These interfacial water molecules have recently
found experimentally to possess a 6% expanded but weaker hydrogen bonded structure [415], due perhap
less hydrogen bond polarization, itself caused by the missing hydrogen bonds. The affinity of chaotropic

for this expanded water structure may help explain their shallow minima in the surface tension at very lo
ionic concentrations (*i.e.* the Jones-Ray effect); higher concentrations destroying the ordered structuring
required. The greater than expected drop in surface tension with temperature increase has been quantitati
explained using spherically symmetrical water clustering [376].

It is interesting to note that surfactants lower the surface tension because they prefer to sit in the surface.
attracting the suface water molecules in competition to the bulk water hydrogen bonding and so reducing
net forces away from the surface (*i.e.* the suface tension). In contrast, most cations and anions prefer to b
fully hydrated in the bulk liquid water so adding to the attractive forces on the surface water molecules,
consequently increasing the surface tension. [Back]

5   High viscosity (0.89 cP, c.f. pentane 0.22 cP, at 25°C))

The viscosity of a liquid is determined by the ease with which molecules can move relative to each other.
depends on the forces holding the molecules together. This cohesivity is large in water due to its extensiv
three-dimensional hydrogen bonding. It should be noted that although the viscosity is high, it is not so hig
that it causes too much difficulty being moved around within organisms. The Arrhenius energy of activat
for viscous flow is similar to the hydrogen bond energy (H_2O, 21.5 kJ mol^{-1}; D_2O, 24.7 kJ mol^{-1}; T_2O,

kJ mol^{-1}, all calculated from [73]; all at 0°C and all more than doubling at -30°C) [Back]

6   High heat of vaporization (40.7 kJ mol^{-1}, c.f. H$_2$S 18.7 kJ mol^{-1})

There is still considerable hydrogen bonding (~75%) in water at 100°C. As effectively all these bonds ne
be broken (very few indeed remaining in the gas phase), there is a great deal of energy required to conver
water to gas, where the water molecules are effectively separated. The increased hydrogen bonding at low
temperatures causes higher heats of vaporization (e.g. 44.8 kJ mol^{-1}, at 0°C). The high heat of vaporizatio
also causes water to have an anomalously low ebullioscopic constant (i.e. effect of solute on boiling poin
elevation, 0.51 K kg/mol, c.f. CCl_4 4.95 K kg/mol). Water also has an anomalously high entropy of

vaporization (109 J K^{-1} mol^{-1}, cf. Trouton's constant 85 J K^{-1} mol^{-1}) due to the additional hydrogen-bon
order lost on vaporization. As both values are anomalously high, their ratio (DH$_{vap}$/DS$_{vap}$) is not anoma
The high heat of vaporization also gives rise to an anomalously high heat of sublimation. [Back]

7   Shrinks on melting

When water freezes at 0°C, at atmospheric pressure, its volume increases by about 9%. If the melting poi
lowered by increased pressure, the increase in volume on freezing is even greater (e.g. 13% at -20°C). Th
structure of ice (1h) is open with a low packing efficiency where all the water molecules are involved in f
straight tetrahedrally-oriented hydrogen bonds; for comparison, solid hydrogen sulfide has a face centere
cubic closed packed structure with each molecule having twelve nearest neighbors [119]. On melting, sor
these ice (1h) bonds break, others bend and the structure undergoes a partial collapse. This is different fro
what happens with most solids (but similar to other tetrahedrally arranged solids such as silicon and silica
where the extra movement available in the liquid phase requires more space and therefore melting is
accompanied by expansion. If the increase in volume on freezing is prevented, an increased pressure of u
25 MPa may be generated; easily capable of bursting pipes in Winter[4]. Melting ice, within a filled and se
fixed volume, may result in an apparently superheated state where the metastable iso-dense liquid water i
stretched, relative to its equilibrium state at the effectively-negative pressure, due to its cohesiveness.

Consequently, the ES⇌CS equilibrium is shifted towards the more-open ES structure.

In contrast, it should be noted that the high pressure ices (ice III, ice V, ice VI and ice VII) all expand on melting to form liquid water (under high pressure). [Back]

8   High density that increases on heating (up to 3.984°C); the density anomaly
The high density of liquid water is due mainly to the cohesive nature of the hydrogen-bonded network. T reduces the free volume and ensures a relatively high-density, compensating for the partial open nature of hydrogen-bonded network. Its density, however, is not as great as that of closely packed, isoelectronic, li neon (1207 kg m^{-3} at 27 K). The anomalous temperature-density behavior of water can be explained as previously [13, 14] utilizing the range of environments within whole or partially formed clusters with dif degrees of dodecahedral puckering. The density maximum is brought about by the opposing effects of increasing temperature, causing both structural collapse that increases density and thermal expansion that lowers density. At lower temperatures there is a higher concentration of ES whereas at higher temperatur there is more CS and fragments, but the volume they occupy expands with temperature. The change from to CS as the temperature rises is accompanied by positive changes in entropy and enthalpy due to the less ordered structure and greater hydrogen bond bending respectively.

A similar but unrelated phenomena occurs in hexagonal, cubic and amorphous ices which all expand slig with cooling below about 50 K. This appears to be due to alteration in the net bending motion of three tetrahedral hydrogen bonded molecules with temperature, as higher frequency modes are reduced [209].

A further strange anomaly in water is that at a temperature below the maximum density anomaly there m a minimum density anomaly so long as no phase change occurs. This is expected to lie just below the minimum temperature accessible on supercooling (232 K, [215]) and close to where both maximum ES structuring and compressibility occur, with the liquid density close to that of hexagonal ice. [Back]

9   The number of nearest neighbors increases on melting
Each water molecule in hexagonal ice has four nearest neighbors. On melting, the partial collapse of the hydrogen bonded network allows unbonded molecules to approach more closely so increasing this numb Normally in a liquid the movement of molecules, and the extra space they find themselves in, means that becomes less likely that they will be found close to each other; e.g. argon has exactly twelve nearest neig in the solid state but only an average of about ten on melting. [Back]

10   Nearest neighbors increase with temperature
If a water molecule is in a fully hydrogen-bonded structure with strong and straight hydrogen bonds (suc hexagonal ice) then it will only have four nearest neighbors. In the liquid phase, molecules approach mor closely due to the partial collapse of the open hydrogen bonded network. As the temperature of liquid wa increases, the continuing collapse of the hydrogen bonded network allows unbonded molecules to approa more closely so increasing the number of nearest neighbors. This is in contrast to normal liquids where th increasing kinetic energy of molecules and space available due to expansion, as the temperature is raised, means that it becomes less likely that molecules will be found close to each other. [Back]

11   Pressure reduces its melting point (13.35 MPa gives a melting point of -1°C)

Increasing pressure normally promotes liquid freezing, shifting the melting point to higher temperatures. [...] is shown by the forward sloping liquid/solid line in the phase diagram. In water, this line is backward slo[...] As the pressure increases, the water equilibrium shifts towards a collapsed structure (e.g. CS) with highe[...] entropy. This lowers the melting free energy change (DG=DH-TDS) such that it will be zero (i.e. at the melting point) at a lower temperature. The minimum temperature that liquid water can exist without ever[...] freezing is -21.985°C at 209.9 MPa; at higher pressures water freezes at higher temperatures. Stretching i[...] has the reverse effect; ice melting at +6.5°C at about -95 MPa negative pressure within stretched microsc[...] aqueous pockets in mineral fluorite [243].

It should be noted that ice skating does not produce sufficient pressure to lower the melting point significantly; the slipperiness being generated by frictional heating. [Back]

12   Pressure reduces the temperature of maximum density

Increasing pressure shifts the water equilibrium towards a more collapsed structure (e.g. CS). So althoug[...] pressure will increase the density of water at all temperatures (flattening the temperature density curve), i[...] have a disproportionate effect at lower temperatures. The result is a shift in the temperature of maximum density to lower temperatures. At high enough pressures the density maximum is shifted to below 0°C (~[...] MPa) and, at above 200 MPa, it cannot be observed. A similar effect may be caused by increasing salt concentration, which behaves like increased pressure in breaking up the low-density clusters. Thus in 0.3[...] Molal NaCl the temperature of freezing and maximum density coincide at -1.33°C. Higher salt concentra[...] reduce the temperature of maximum density such that it is only accessible in the supercooled liquid. The stronger hydrogen bonding in D_2O gives rise to a smaller shift in the temperature of maximum density w[...] respect to increasing pressure.

At very high negative pressures (i.e. increased stretching of liquid water), the temperature of maximum density may be reduced as the hydrogen bonds are stretched to breaking point; the temperature of maxim[...] density showing a maximum with respect to pressure in the negative pressure region [419]. [Back]

13 D_2O and T_2O differ significantly from H_2O in their physical properties

These heavier forms of water hydrogen. bond more strongly than normal water. This causes many of thei[...] properties (such as the viscosity, self-diffusion coefficient, protein solubility and toxicity [424]) to be dif[...] from those expected from a simple consideration of their increased mass (e.g. the D_2O/H_2O viscosity rati[...] rises from about 1.16 at 100°C to around 2.0 in deeply supercooled water [23b]. This difference appears [...] shift in the equilibrium position equivalent to a slight increase in temperature [425]; e.g. viscosity data ha[...] been reconciled if the temperatures are shifted by 6.498°C and 8.766°C for D_2O and T_2O respectively [7[...]

Mixtures of H_2O and D_2O equilibrate to form HDO:

$$H_2O + D_2O \rightleftharpoons 2HDO \qquad K_{eq} = 3.76, 25°C$$

which is close to a total randomisation of the hydrogen atoms (i.e. equal concentrations of HOH, HOD, [...] and DOD giving $K_{eq} = 4$). Even the properties of HDO deviate from those expected from a consideration[...] the properties of H_2O and D_2O [126]. [Back]

14   Large viscosity increase as the temperature is lowered

The water cluster equilibrium shifts towards the more open structure (e.g. ES) as the temperature is lowe[...]

This structure is formed by stronger hydrogen bonding. In turn, this creates larger clusters and reduces th
ease of movement (increasing viscosity). Self-diffusion is also greatly reduced at lower temperatures whe
anomalously decreases as the density decreases (see below). [Back]

15   Viscosity decreases with pressure (at temperatures below 33°C)

Viscous flow occurs by molecules moving through the voids that exist between them. As the pressure
increases, the volume decreases and the volume of these voids reduces, so normally increasing the viscos
Water's pressure-viscosity behavior can be explained by the increased pressure (up to about 150 MPa) ca
deformation, so reducing the strength of the hydrogen-bonded network, which is also partially responsibl
the viscosity. This reduction in cohesivity more than compensates for the reduced void volume. At higher
pressures water behaves as a normal liquid; viscosity increasing with pressure. Self-diffusion is also affe
by pressure where (at low temperatures) both the translational and rotational motion of water anomalousl
increase as the pressure increases (see below). [Back]

16   Low compressibility (0.46 GPa^{-1}, c.f. CCl$_4$ 1.05 GPa^{-1}, at 25°C)

It may be thought that water should have a high compressibility ($k_T = -[\P V/\P P]_T/V$) as the large cavities i
liquid water allows plenty of scope for the water structure to collapse under pressure without water mole
approaching close enough to repel each other. The deformation causes the growth in the radial distributio
function peak at about 3.5 Å with increasing or pressure [51] (and temperature [50]), due to the collapsin
structure. The low compressibility of water is due to water's high-density, again due to the cohesive natu
the extensive hydrogen bonding. This reduces the free space (compared with other liquids) to a greater e
than the contained cavities increase it. At low temperatures D$_2$O has a higher compressibility than H$_2$O (
4% higher at 10°C but only 2% higher at 40°C [188]) due its stronger hydrogen bonding producing an
ES$\rightleftharpoons$CS equilibrium shifted towards the more-open ES structure. [Back]

17   Compressibility drops as temperature increases (up to a minimum at about 46.5°C)

In a typical liquid the compressibility decreases as the structure becomes more compact due to lowered
temperature. In water, the cluster equilibrium shifts towards the more open structure (e.g. ES) as the
temperature is reduced due to it favoring the more ordered structure (DG becomes more positive). As the
water structure is more open at these lower temperatures, the capacity for it to be compressed increases. '
effect is not a simple dependency on density, however, or else the minimum at 46.5°C for isothermal (i.e.
without change in temperature) compressibility ($k_T = -[\P V/\P P]_T/V$) and the minimum at 64°C for adiabat
(i.e. without loss or gain of heat energy, also isentropic) compressibility ($k_S = -[\P V/\P P]_S/V$ [112]) would
be at the density minimum (4°C). Compressibility depends on fluctuations in the specific volume and the
will be large where water molecules fluctuate between being associated, or not, with a more open structu
and between the different environments within the water clusters. At sufficiently low temperature, there i
be a maximum in this compressibility-temperature relationship, so long as no phase change occurs. This i
expected to lie just below the minimum temperature accessible on supercooling (232 K, [215]) close to th
temperature of minimum density. [Back]

18   Water has a low thermal expansivity (0.00021/°C, c.f. CCl$_4$ 0.00124/°C at 20°C)

As the temperature increases, the cluster equilibrium shifts towards the more collapsed structure (e.g. CS

which reduces any increase in volume due to the increased kinetic energy of the molecules. Normally the higher the volume a molecule occupies, the larger is the disorder (entropy). Thermal expansivity ($a_P = [\partial V/\partial T]_P/V$) depends on the product of the fluctuations in these factors. In water, however, the more ope structure (e.g. ES) is also more ordered (i.e. has lower entropy). [Back]

19   Water's thermal expansivity reduces increasingly (becoming negative) at low temperatures.
Supercooled and cold (< 3.984°C) liquid water contracts on heating. As the temperature decreases, the cl equilibrium shifts towards the expanded, more open, structure (e.g. ES), which more than compensates fc decrease in volume due to the reduction in the kinetic energy of the molecules. It should be noted that thi behavior requires that the thermodynamic work (dW) equals -p dV rather than the usual +p dV (pressure change in volume) [404]. [Back]

20   Speed of sound increases with temperature (up to a maximum at 73°C)
Sound is a longitudinal pressure wave, whereby the energy is propagated as deformations in the media bu molecules then return to their original positions and are not propagated. The propagation of a sound wave depends on the transfer of vibration from one molecule to another. The speed ($u = [\partial r/\partial P]_S$) is inversely proportional to the square root of the adiabatic compressibility times density term. The anomalous nature both these physical properties are described above (compressibility, density). At low temperatures both compressibility and density are high, so causing a lower speed of sound. As the temperature increases the compressibility drops and goes through a minimum whereas the density goes through a maximum and th drops. Combination of these two properties leads to the maximum in the speed of sound. Increasing the pressure increases the speed of sound and shifts the maximum to higher temperatures, both in line with th effect on the density.

Water has a second anomaly (called 'fast sound') concerning the speed of sound. Over a range of high frequencies liquid water behaves as though frozen and sound travels at about twice its normal speed (~32 s^{-1}). [Back]

21   High specific heat capacity (C_V and C_P, 4.18 J g^{-1} K^{-1}) c.f. pentane 1.66 J g^{-1} K^{-1}, at 25°C)
As water is heated, the increased movement of water causes the hydrogen bonds to bend and break. As th energy absorbed in these processes is not available to increase the kinetic energy of the water, it takes considerable heat to raise water's temperature. Also, as water is a light molecule there are more molecule gram, than most simlar molecules, to absorb this energy. Heat absorbed is given out on cooling, so allowi water to act as a heat reservoir, buffering against changes in temperature. [Back]

22   Water has over twice the specific heat capacity of ice or steam (c.f. benzene where $C_{P\,liquid} = 1$
$C_{P\,solid}$)
The specific heats of polar molecules do increase considerably on melting but water shows a particularly increase. As water is heated, much of the energy is used to bend the hydrogen bonds; a factor not availab the solid or gaseous phase. This extra energy causes the specific heat to be greater in liquid water. The presence of this large specific heat offers strong support for the extensive nature of the hydrogen-bonded network of liquid water. [Back]

23   Specific heat capacity (C_P) has a minimum (36°C)

The specific heat capacity has a shallow minimum at about 36°C with a particularly steep negative slope below 273°C [15]. The water cluster equilibrium shifts towards less structure (e.g. CS) and higher enthal the temperature is raised. C_P is the heat capacity at constant pressure defined by $C_P = (\P H/\P T)_P$ (change i enthalpy with temperature). The extra positive $\P H$ due to the shift in equilibrium (at low temperatures) as temperature is raised causes a higher C_P than otherwise, particularly at supercooling temperatures where much larger shift occurs. This addition to the C_P, as the temperature is lowered, is greater than the 'natur fall expected, so causing a minimum to be created. Note that C_V (the heat capacity at constant volume, C ($\P U/\P T)_V$ shows no such anomaly, as most of the anomalous enthalpy change is associated with the anomalous volume change. It is expected that the large specific heat changes with temperature at low temperatures will be reduced at higher pressures and the specific heat minimum will shift to lower temperatures. At sufficiently low temperature, there must be a maximum in this compressibility-temperat relationship, so long as no phase change occurs. This is expected to lie just below the minimum temperat accessible on supercooling (232 K, [215]).[Back]

24   NMR spin-lattice relaxation times are very small at low temperatures

NMR spin-lattice relaxation time depends on the degree of structure. As the water cluster equilibrium shi towards a stiffer, tetrahedrally organized, structure (e.g. ES) as the temperature is lowered, the NMR spin-lattice relaxation time reduces far more than would otherwise be expected. This effect can be partial reversed by increasing the pressure, which reduces the degree of structure. [Back]

25   Solutes have varying effects on properties such as density and viscosity

Solutes will interfere with the cluster equilibrium by favoring either open or collapsed structures. Any ef will cause the physical properties of the solution, such as density or viscosity, to change. Solutes have a l than expected effect on both the cryoscopic (i.e. effect of solute on freezing point depression, 1.86 K kg c.f. CCl_4 30 K kg mol^{-1}) and ebullioscopic constants. [Back]

26   Solutions are not ideal

Ideality depends on the structure of the solvent being unaffected by the solute. Water is not even close to being a homogeneous phase on the molecular level. Local clustering will be effected by the presence of solutes, so changing the nature of the water. Even solutions of HDO in H_2O do not behave ideally. [Back

27   X-ray diffraction shows an unusually detailed structure

This is simply explained by the presence of ordered clustering within the liquid phase. [Back]

28   Supercooled water has two phases and a second critical point at about -50°C

As water is supercooled it converts mainly into its expanded form (e.g. ES) at ambient pressures, which low enough temperatures (< -38°C) may result in it forming metastable low-density amorphous ice (LDA

although normally it will form hexagonal ice at this temperature). If the pressure on LDA is increased ab
about 200 MPa then LDA undergoes a 30% collapse forming metastable high-density amorphous ice (HI
but notably in a continuous process without breaking the hydrogen bonds [394].. This phase change cann
continue to higher temperatures (so creating a second critical point, [45]) as neither of these phases is sta
the presence of liquid water although they may convert into their metastable supercooled liquid forms. [E

29   Liquid water is easily supercooled

It may be expected that the directional hydrogen bonding capacity of water would reduce its tendency to
supercool as it would encourage the regular structuring in cold liquid. Liquid water, however, is easily
supercooled down to about -25°C and with more difficulty down to about -38°C with further supercoolin
possible, in tiny droplets, down to about -70°C. Water, supercooled down to -37.5°C, is sustained in storm
clouds and the condensed clouds formed by aircraft. Rather strangely, at the limit of this supercooling (al
known as the homogeneous freezing point) the water activity is always 0.305 lower than that of water me
at the same temperature [457].

Liquid water may be supercooled to about -92°C at 210 MPa. Deeply supercooled liquid water can be
produced from glassy amorphous ice between -123°C and - 149°C [74] and may coexist with cubic ice u
-63°C [137]. This behavior is particularly anomalous as the liquid (deeply supercooled water) is a 'stron
liquid (compared with supercooled water that is a 'fragile' liquid [493]) that changes to crystalline solid (
ice) on increasing the temperature whilst keeping the pressure constant.

As water is cooled, the cluster equilibrium shifts towards the more open structure (e.g. ES) with higher
viscosity. In order for crystallization to occur at least 3 - 4 unit cells worth of water molecules have to co
together in the correct orientation.[1] The formation of icosahedral clusters interferes with this process whi
not allowing cluster crystallization due to their five fold symmetry. Lowering the temperature further, wh
should encourage crystallization, is partially counteracted by the increase in icosahedral clustering. The
presence of ES clusters is, in principle, in agreement with computer simulation studies requiring the prese
of metastable states [216]. Methods that break the hydrogen bonding in these clusters, such as ultrasonics
[296], cause the supercooled water to freeze.

A possible explanation of the existence of low-temperature-range supercooled water (124-150 K) may be
formation of strands of icosahedral structures. This model can also explain the high viscosity and strong (
low specific heat) liquid behavior of this extremely supercooled water [215]. [Back]

30   Solid water exists in a wide variety of stable (and metastable) crystal and amorphous structure

The ability for water to form extensive networks of hydrogen bonds increases the number of solid phases
possible. The open structure of hexagonal ice (19.65 cm^3/mol.), which contains only about 7.5 cm^3/mol
water molecules, gives plenty of scope for different arrangements of the water molecules as the structure
compressed. For comparison, hydrogen sulfide has only four distinct solid phases [119]. [Back]

31   Hot water may freeze faster than cold water; the Mpemba effect

The ability of hot water to freeze faster than cold seems counter-intuitive as it would seem that hot water
first become cold water and therefore the time required for this will always delay its freezing relative to c
water. However experiments show that hot water (e.g. 90 °C) does often appear to freeze faster than the s
amount of cold water (e.g. 18°C) under otherwise identical conditions [158]. This has been recognised ev

far back as Aristotle in the 4th century BC but was brought to the attention of the scientific community by perseverance of a Tanzanian schoolboy (Erasto Mpemba) who refused to reject his own evidence, or bow disbelieving mockery, that he could freeze ice cream faster if he warmed it first.

A number of explanations have been put forward but the most likely scenario (described in [158]) is that the degree of supercooling is greater in initially-cold water than initially-hot water. The initially-hot water appears to freeze at a higher temperature (less supercooling) but less of the apparently frozen ice is solid and a considerable amount is trapped liquid water. Initially-cold water freezes at a lower temperature to a more completely solid ice with less included liquid water; the lower temperature causing intensive nucleation and a faster crystal growth rate. If the freezing temperature is kept about -6°C then the initially-hot water is most likely to (apparently) freeze first. If freezing is continued, initially-cold water always completely freezes before initially-hot water. Why initially-cold water supercools more is explained in terms of the clustering of water. Icosahedral clusters do not readily allow the necessary arrangement of water molecules to enable hexagonal ice crystal initiation; such clustering is the cause of the facile supercooling of water. Water that is initially-cold will have the maximum (equilibrium) concentration of such icosahedral clustering. Initially-hot water has lost much of its ordered clustering and, if the cooling time is sufficiently short, this will not be fully re-attained before freezing.
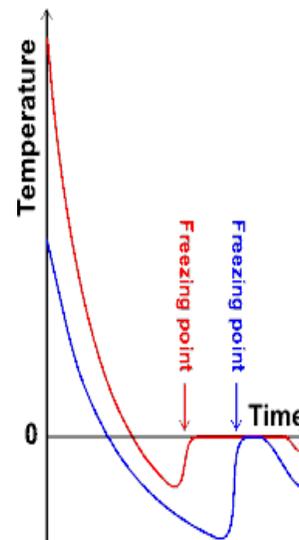
Experiments on low-density water around macromolecules has shown that such clustering processes may some time [4]. It is also possible that dissolved gases may encourage supercooling by (1) increasing the of structuring, by hydrophobic hydration, in the previously-cold water relative to the gas-reduced previously-hot water (the critical effect of low concentrations of dissolved gas on water structure is repor [294]; re-equilibration taking several days) and (2) increasing the pressure as gas comes out of solution w the water starts to crystallize, so lowering the melting point and reducing the tendency to freeze (see guestbook). Also, the presence of tiny gas bubbles (produced on heating) may increase the rate of nuclea so reducing supercooling [428]. [Back]

32   The refractive index of water has a maximum value at just below 0°C.
The refractive index of water (l = 589.26 nm) rises from an estimated 1.33026 at -30°C to a maximum va just below 0°C (1.33434) before falling ever increasingly to 1.31854 at 100°C [310]. This may be explai by the mixture model [60] applied to the change from ES to CS as the temperature rises; ES possessing a lower refractive index than CS. Most of the effect is due to the density difference between ES and CS. Hi density produces higher refractive index such that the refractive index temperature maximum lies close t density maximum, with the small difference due to the slightly different effect of temperature on the spec refractions of ES and CS. Although not considered anomalous, it is interesting to note that ice has the lo refractive index (1.31, l = 589 nm) of any known crystal. [Back]

33   The solubilities of non-polar gases in water decrease with increasing temperature to a minimu and then rise.[2]
Non-polar gases are poorly soluble in water. Their hydration may be considered as the sum of two proces

(A) the endothermic opening of a clathrate pocket in the water, and (B) the exothermic placement of a molecule in that pocket, due to the multiple van der Waals interactions. In water at low temperatures, the energy required by process (A) is very small as such pockets may be easily formed within the water clust (by CS ® ES)[3]. The solubilization process is therefore exothermic and (as predicted by Le Chatelier's principle) solubility decreases with temperature rise. At high temperatures (often requiring high pressure) natural clustering is much reduced causing greater energy to be required for opening of the pocket in the water. The solubilization process therefore becomes endothermic and (as predicted by Le Chatelier's principle) solubility goes through a minimum before increasing with temperature rise. The more attractiv solute-water van der Waals interactions (due both to atomic number dependency and goodness of fit with the clathrate pocket), the greater the inherent exothermic nature of the process and therefore the higher th temperature minimum (e.g. He, 32°C; Ne, 50°C; Ar, 96°C; Kr, 101°C; Xe,123°C) and the greater the temperature range of negative temperature solubility coefficient. Similarly Henry's constants (= partial pressure/mole fraction) exhibit decreasing maximas at 30°C, 50°C, 90°C, 108°C and 110°C in H_2O and 5 53°C, 98°C, 108°C and 116°C in D_2O for He, Ne, Ar, Kr and Xe respectively [IAPWS]. The poor solubi of non-polar gases in water is due to positive free energy change attributed to the large negative entropy change caused by the structural enhancement of the water (ES) clusters; a conclusion reinforced by the enhanced heat capacity of these solutions. Counter-intuitively in spite of it forming stronger hydrogen bo D_2O is a better solvent than H_2O for non-polar gases, as it more easily forms the ES water clustering and therefore can accommodate the guest molecules more easily without breaking its hydrogen bonds. Additi positively hydrating salts (e.g. LiCl) that destroy the water low-density ES clustering reduce the solubility ('salt out') of the non-polar gases whereas hydrophobic hydrating salts (e.g. tetramethylammonium chlor that increase water low-density ES clustering stability also increase non-polar gas solubility ('salt in'). Sn non-polar organic molecules also behave similarly to non-polar gases, but their increased size alters the clathrate structuring. Thus benzene has a solubility minimum, at a lower temperature than expected from above, at about 20°C [210],

Interestingly, the change in solubility of non-polar gases has a maximum (and their free energy of hydrati has a minimum) with their diameter when it is about the same as that of the dodecahedral cavities (i.e. ~4 the icosahedral network [196]. The solubility behavior of larger hydrophobic molecules is discussed brief elsewhere. It should also be noted that the solvent properties of liquid superheated water also change with temperature as its dielectric permittivity reduces towards that of common organic solvents as the tempera rises towards the critical point. [Back]

34   At low temperatures, the self-diffusion of water increases as the density and pressure increase.
The increase in self-diffusion with density (within the range of about 0.9 g cm^{-3} up to about 1.1 g cm^{-3}) i contrast to normal liquids where increasing density decreases self-diffusion as the molecules restrict each other's movements. The density increase may be due to increasing temperature, below 4°C, at atmospher pressure or due to increasing pressure at low temperatures. Liquids normally show reduced self-diffusion when they are squeezed but water at 0°C increases its diffusivity by 8% under a pressure of about 200 M [226] before any further increase in pressure reduces the diffusivity in common with the behavior of othe liquids. The movement of water becomes restricted at low temperatures as the more open (lower density) structure produced on cooling (see above) is formed by stronger hydrogen bonding, which reduces the self-diffusion. The strength of the hydrogen bonding is a controlling influence in this anomalous region, the hydrogen bond angles and the inter-molecular distances are strongly coupled and this order decreases compression [169] due to the collapse of ES structures to CS structures. Simulation studies have shown t self-diffusion goes through a minimum as the density of water is reduced below about 0.9 g cm^{-3} followe

an increase with further density reduction, as might be expected from most liquids [402], due to the disru
of the network as the now-stretched hydrogen bonds are broken. For the same reasons, the molecular
rotational movement of water (reciprocal rotational relaxation time) also varies in direct proportion to the
changes in self-diffusion (translational movement). [Back]

35   The thermal conductivity of water rises to a maximum at about 130°C and then falls.

For most liquids the thermal conductivity (the rate at which energy is transferred down a temperature gra
falls with increasing temperature but this occurs only above about 130°C in liquid water [188]. As the
temperature of water is lowered, the rate at which energy is transferred is reduced to an ever-increasing e
Instead of the energy being transferred between molecules, it is stored in the hydrogen bonding fluctuatic
within the increasingly large clusters that occur at lower temperatures. Effectively the energy is used to sl
the ES$\rightleftharpoons$CS equilibrium towards the CS structure, which possesses greater flexibility and has a greater
number of bent hydrogen bonds, rather than the transference of kinetic energy. [Back]

36   Proton and hydroxide ion mobilities are anomalously fast in an electric field.

The ionic mobilities of hydrogen ions and hydroxide ions at 362 and 206 (nm s^{-1})/(V m^{-1}) at 25°C are ve
high compared with values for other small ions such as lithium (40(nm s^{-1})/(V m^{-1})) and fluoride (57(nm
s^{-1})/(V m^{-1})). This is explained by the Grotthuss mechanism. [Back]

37 The heat of fusion of water with temperature exhibits a maximum at -17°C [15].

This strange behavior has been determined from the variation in ice and water specific heat capacities (C$_{\text{p}}$
is due to changes in the structuring of supercooled water. As the temperature is lowered from 0°C the
hydrogen-bond strength of ice increases due to the reduction in their vibrational energy and this gives ris
an increasing difference (as temperature is lowered) between the enthalpy of the water and ice. At low
temperatures (below about -17°C) the continued shift, with lowering temperature, in the supercooled wa
CS$\rightleftharpoons$ES equilibrium towards the ES structure reduces the enthalpy of the liquid water relative to the ice
to the consequent increase in hydrogen-bond strength and this causes the drop in the heat of fusion with
lowering temperature. [Back]

38 The dielectric constant is high (78.4 at 25°C).

Polar molecules, where the centers of positive and negative charge are separated, possess dipole moment
means that in an applied electric field, polar molecules tend to align themselves with the field. Although
is a polar molecule, its hydrogen-bonded network tends to oppose this alignment. The degree to which a
substance does this is called its dielectric constant and, because water is exceptionally cohesive, it has a h
dielectric constant. This allows it to act as a solvent for ionic compounds, where the attractive electric fie
between the oppositely charged ions is reduced by about 80-fold, allowing thermal motion to separate the
into solution. On heating, the dielectric constant drops, and liquid water becomes far less polar, down to
value of about 6 at the critical point. The dielectric constant similarly reduces if the hydrogen bonding is
broken by other means, such as strong electric fields.

Perhaps this property of water should not be considered anomalous as other small polar molecules form
liquids also having high dielectric constants (e.g. the dielectric constant of liquid HCN is 158). [Back]

[1] Theoretical considerations concerning the ice nucleation site size gives estimates of 45,000 water mole
at -5°C down to 70 water molecules at -40°C [265]. Molecular dynamics studies show that these do not n
to form a crystalline structure for crystallization to occur [347]. [Back]

[2] Although this behaviour is encountered with some other solute-solvent combinations (e.g. methane in
n-heptane), the behavior is a more general property of water and deserves comment. [Back]

[3] There is evidence [157, 269, 274] that the first (clathrate) shell possesses stronger hydrogen bonding an
weakens the hydrogen bonding out to the next shell. [Back]

[4] Pipes burst due to the rapid formation of a network of feathery dendritic ice enclosing water which then
expands on freezing within a now restricted volume to generate the required pressure [354]. [Back]

Please submit any other explanations of water anomalies.

This page was last updated by Martin Chaplin
on **27 July, 2003**

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