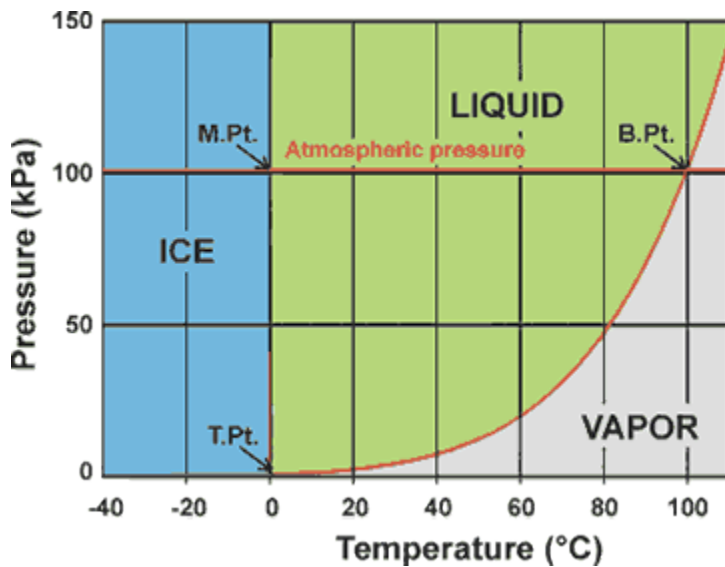


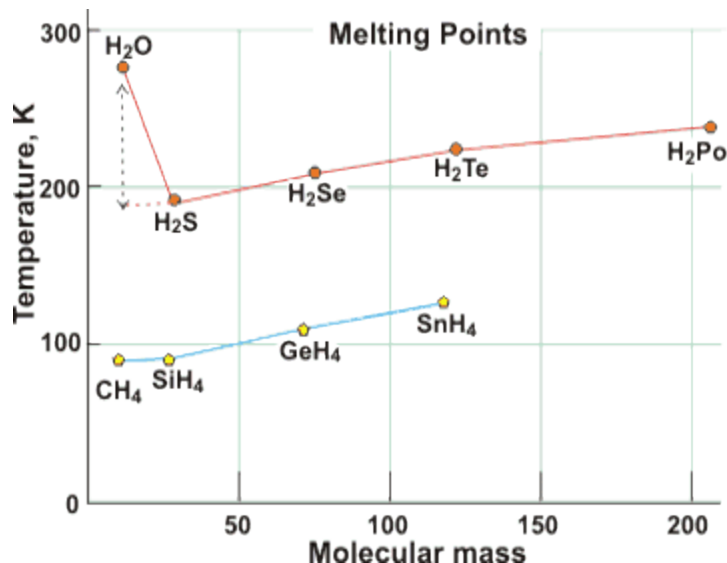
Explanation of the Phase Anomalies of Water (P1-P12)

- ✓ Water has unusually high melting point
- ✓ Water has unusually high boiling point
- ✓ Water has unusually high critical point
- ✓ Solid water exists in a wider variety of stable (and metastable) crystal and amorphous structures than other materials
- ✓ The thermal conductivity of ice reduces with increasing pressure
- ✓ The structure of liquid water changes at high pressure
- ✓ Supercooled water has two phases and a second critical point at about $-91\text{ }^{\circ}\text{C}$
- ✓ Liquid water is easily supercooled but glassified with difficulty
- ✓ Liquid water exists at very low temperatures and freezes on heating
- ✓ Liquid water may be easily superheated
- ✓ Hot water may freeze faster than cold water; the Mpemba effect
- ✓ Warm water vibrates longer than cold water
- ✓ Water molecules shrink as the temperature rises and expand as the pressure increases

P1 High melting point ($0\text{ }^{\circ}\text{C}$, compare CHCl_3 $-63\text{ }^{\circ}\text{C}$)



Partial phase diagram of water (H_2O) showing the melting (M.Pt.), boiling (B.Pt.) and triple (T.Pt) points.^a

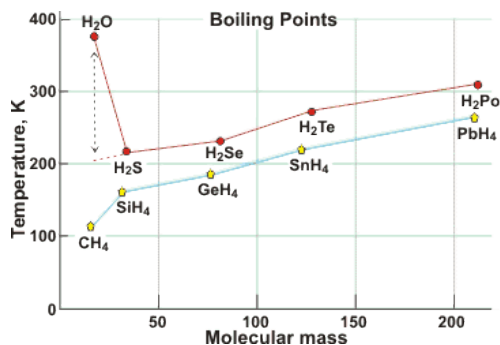


The melting point of water is over 100 K higher than expected by extrapolation of the melting points of other Group 6A hydrides, here above right shown compared with Group 4A hydrides. It is also much higher than O₂ (54 K) or H₂ (4 K). See also below for further comparisons.

In ice (I_h), all water molecules participate in four hydrogen bonds (two as donor and two as acceptor) and are held relatively static. In liquid water, some of the weaker hydrogen bonds must be broken to allow the molecules to move around. The large energy required for breaking these bonds must be supplied during the melting process and only a relatively minor amount of energy is reclaimed from the change in volume ($P\Delta V = -0.166 \text{ J mol}^{-1}$). The free energy change ($\Delta G = \Delta H - T\Delta S$, where $\Delta H = \Delta U + P\Delta V$) 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 sufficient change in the entropy term ($-T\Delta S$) to provide the energy required for the bond breaking (ΔH). The low entropy (high organization) of liquid water causes this melting point to be high.

Although ice is very difficult to superheat above its (equilibrium) melting point, tiny amounts of ice (I_h) have been superheated to 290 K (without melting) for very short periods (>250 ps) [954a] with the limit of superheating (>1 ns) established at about 330 K [954b]. [[◀ Anomalies page : Back to Top ▲](#)]

P2 High boiling point (100 °C, compare CHCl₃ 61 °C)

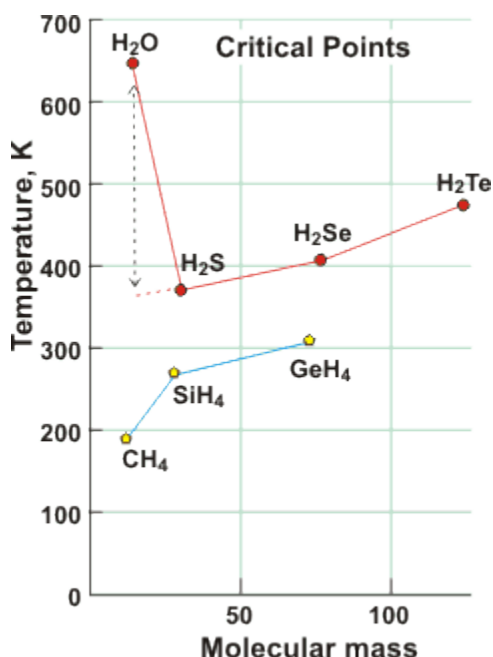


The boiling point of water is over 150 K higher than expected by extrapolation of the boiling points of other Group 6A hydrides, here shown compared with Group 4A hydrides. It is also much higher than O₂ (90 K) or H₂ (20 K). See also below for further comparisons.

There is considerable hydrogen bonding in liquid water resulting in high cohesion (water's cohesive energy density is 2.6 times that of methanol), which prevents water molecules from being easily released from the water's surface. Consequentially, the vapor pressure is reduced. As boiling cannot occur until this vapor pressure equals the external pressure (see graph), a higher temperature is required.

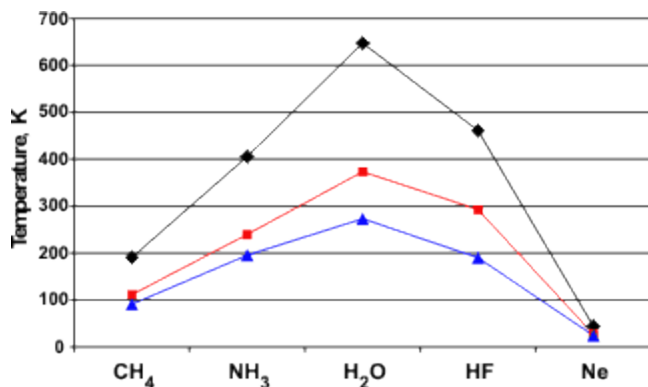
The pressure/temperature range of liquidity for water is much larger than for most other materials (for example, under ambient pressure the liquid range of water is 100 °C whereas for both H₂S and H₂Se it is about 25 °C. [[◀ Anomalies page : Back to Top ▶](#)]

P3 High critical point (374 °C, compare CH₃CH₃ 32 °C)



The critical point of water is over 250 K higher than expected by extrapolation of the critical points of other Group 6A hydrides, here shown compared with Group 4A hydrides. For example, the critical point (647 K, 22.06 MPa 322 kg m⁻³) is far higher than ethanol (514 K, 6.14 MPa 276 kg m⁻³), which also hydrogen bonds (but in chains not 3-dimensional) and is much larger and more massive.

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



The critical points (C.Pt.), boiling points (B.Pt.) and melting points (M.Pt.) of the molecules isoelectronic with water shows water to have higher values.

Ammonia and hydrogen fluoride also have somewhat raised values as they form molecular clustering, albeit with three donor H-atoms and one lone pair acceptor group or one donor H-atom and three lone pair acceptor groups, respectively; giving a maximum of two hydrogen bonds per molecule, on average. Although solid HF forms stronger hydrogen bonds, these form linear zigzag chains with no rings or polygons and hence its three-dimensional structure is weaker. The hydrogen bonds in solid NH₃ can form three-dimensional arrangements but are distorted and weakened. Water has two donor H-atoms and two lone pair acceptor groups with close to tetrahedral angles giving the possibility of four hydrogen bonds per molecule with little distortion. [[◀ Anomalies page : Back to Top ▲](#)]

P4 Solid water exists in a wider variety of stable (and metastable) crystal and amorphous structures than other materials.

The ability for water to form extensive networks of hydrogen bonds increases the number of solid phases possible to over fifteen. Both open and close-packed structures are possible. The open structure of hexagonal ice ($19.65 \text{ cm}^3 \text{ mol}^{-1}$), which contains only about $7.5 \text{ cm}^3 \text{ mol}^{-1}$ of water molecules, gives plenty of scope for different arrangements of the water molecules as the structure is compressed. For comparison, hydrogen sulfide has only four distinct solid phases [119].

Another anomaly is found as the ices change their crystalline phase. Thus there are decreases in volume when ice Ih changes to ice II ($\Delta V = 3.92 \text{ cm}^3 \text{ mol}^{-1}$), ice II changes to ice V ($\Delta V = 0.7 \text{ cm}^3 \text{ mol}^{-1}$), ice V changes to ice VI ($\Delta V = 0.7 \text{ cm}^3 \text{ mol}^{-1}$), and ice VI changes to ice VII ($\Delta V = 1.05 \text{ cm}^3 \text{ mol}^{-1}$) but in all cases this is associated with increases in internal lattice energy (79 J mol^{-1} , 1.45 kJ mol^{-1} , 423 J mol^{-1} , 2.3 kJ mol^{-1} respectively). Normally an increase in density is expected to increase the interaction between the molecules and make the internal energy more negative. These phenomena are primarily due to the changes in the hydrogen bonding strength caused by the molecular rearrangement. [[◀ Anomalies page : Back to Top ▲](#)]

P5 The thermal conductivity, shear modulus and transverse sound velocity of ice reduce with increasing pressure

Hexagonal ice shows anomalous reduction in thermal conductivity shear modulus and transverse sound velocity with increasing pressure (as do cubic ice and low-density amorphous ice but not high-density amorphous ice), which behavior is different from most crystals where these properties increase with increasing density. Low-density amorphous ice is the only glass to show this

peculiar behavior. These anomalies are due to the pressure-induced bending of the hydrogen bonding [617]. The same anomalies are found in D₂O hexagonal ice, but to a much lesser extent [1796], showing unexpectedly large isotopic effects due to the greater degree of ordering in D₂O hexagonal ice. [[◀ Anomalies page : Back to Top ▲](#)]

P6 The structure of liquid water changes at high pressure

In a similar manner to the formation of the high density crystalline (ice-five and ice seven) and amorphous (HDA) ice phases, liquid water also undergoes a significant change in structure at high pressure (about 200 MPa). The viscosity, self-diffusion, compressibility and structural properties of water all change above about 200 MPa. Other properties also change around 200 MPa, such as the loss of the density maximum, the discontinuity in fast sound in liquid water and water molecules move further away from each other. The explanation for all these effects is that there appears to be an increase in interpenetration of hydrogen bonded networks at about 200 MPa (at 290 K); interpenetration of hydrogen bonded clusters being preferred over more extreme bending or breaking of the hydrogen bonds. This structuring for liquid water at high pressures is consistent to that found by neutron scattering [1001] and indicates that liquid water structuring at high pressure has similarity to that of its high pressure ice phases [1254]. [[◀ Anomalies page : Back to Top ▲](#)]

P7 Supercooled water has two phases and a second critical point

Water below its thermodynamic melting point is 'supercooled'. The thermodynamic properties of supercooled water have been reviewed [1794]. As water is supercooled it converts mainly into its expanded form (for example, ES) at ambient pressures, which at 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 above about 200 MPa then LDA undergoes a 30% collapse forming metastable high-density amorphous ice (HDA) but notably in a continuous process without (apparently) breaking the hydrogen bonds [394]. This phase change cannot continue to higher temperatures (so creating a second critical point, [45, 1530, 1888, 2029]) as neither of these phases is stable in the presence of liquid water although they may convert into their metastable supercooled liquid forms. The presence of these low- and higher-density forms of liquid (supercooled) water leads to the breakdown of the Stokes-Einstein relationship in supercooled water [1040] occurring far above the glass-transition temperature, in contrast to many supercooled liquids where this behavior is found only at temperatures just above this transition [1040b].

It is now generally recognized that normal liquid water also consists of smaller clusters of two different states of water, related to LDA and HDA which may interconvert. [[◀ Anomalies page : Back to Top ▲](#)]

P8 Liquid water is easily supercooled but glassified with difficulty

Water freezing is not simply the reverse of ice melting [1110]. Melting is a single step process that occurs at the melting point as ice is heated whereas freezing of liquid water on cooling involves ice crystal nucleation and crystal growth that generally is initiated a few degrees below the melting point even for pure water. Liquid water below its melting point is supercooled water. 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 that may lead to a crystalline state. Liquid water, however, is easily supercooled^e down to about -25 °C and with more difficulty down to about -38 °C with further supercooling possible, in tiny droplets (~5 μm diameter), down to about -41 °C under normal atmospheric pressure and -92 °C at 200 MPa,. Supercooling increases with increasing cooling rate and decreasing volume. Water, supercooled down to -37.5 °C, is sustained in storm clouds and the condensed clouds formed by aircraft at high altitude. Rather

strangely, at the limit of this supercooling (also known as the homogeneous freezing point) the water activity is always 0.305 lower than that of water melting at the same temperature [457]. Where salts or hydrophilic solutes are present, the homogeneous freezing point is lowered about twice as much as the melting point lowering [663].

Liquid water may be maximally supercooled (T_s) to about -92 °C and 210 MPa. This amount of supercooling (about a third of the melting point (T_m , 273 K) is typical for molecular liquids, but at normal pressures the achievable supercooling is much smaller ($T_s/T_m \sim 0.15$) due to the effect of the second critical point. It should be noted that bulk water never forms a glass as its glass transition temperature ($T_g = \sim 136$ K) is far lower, relative to its melting point, than expected; $T_m/T_g \sim 2$ rather than $T_m/T_g \sim 1.3-1.5$ as for more typical liquids. Thus supercooled bulk water (*i.e.* not affected by surfaces or solutes) always crystallizes before its temperature can be sufficiently lowered, whatever the cooling rate [558]. Water glass may only be produced by extremely rapid cooling (10^5 K s⁻¹) of tiny volumes of water (< ~ 100 μm diameter).

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 come together in the correct orientation.^b The formation of whole or part icosahedral clusters interferes with this process whilst not allowing cluster crystallization due to their fivefold symmetry. Lowering the temperature further, which 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 presence of metastable states [216]. Methods that break the hydrogen bonding in these clusters, such as ultrasonics [296], cause the supercooled water to immediately freeze.

There are earlier [569] and more recent [1794] comprehensive reviews of the properties of supercooled water . [[◀ Anomalies page : Back to Top ▶](#)]

P9 Liquid water exists at very low temperatures and freezes on heating

Deeply supercooled liquid water can be produced from glassy amorphous ice between -123 °C and -149 °C [74] and may coexist with cubic ice up to -63 °C [137]. This behavior is particularly anomalous as the liquid (deeply supercooled water) is a 'strong' liquid (compared with 'normal' supercooled water that is a 'fragile' liquid [493]) that changes to crystalline solid (cubic ice) on increasing the temperature whilst keeping the pressure constant. Such a 'strong' to 'fragile' (Arrhenius to non-Arrhenius) change in a liquid is not normal. Deeply supercooled water exists in the liquid state where it appears to be too cold to diffuse sufficiently quickly to crystallize noticeably. A possible explanation of this low-temperature-range liquid water may be the formation of strands of icosahedral structures. This model can also explain the high viscosity and strong(that is, low specific heat) liquid behavior of this extremely supercooled water [215]. The unusual behavior of this liquid (that is, deeply supercooled water), by solidifying on heating, has been found with other liquids (for example, methyl cellulose and some cyclodextrin solutions [1026]). [[◀ Anomalies page : Back to Top ▶](#)]

P10 Liquid water may be easily superheated

Liquid water can be easily superheated above its boiling point away from its surface with the atmosphere [1128, 1184]. This may be particularly important when heating foods and drinks in a microwave oven where explosive production of steam from the superheated water may cause severe injuries. Superheating is also causes the boiling point of water to vary, in much the same way as its freezing point, and of irregular boiling, that is, 'bumping' [1184]. Liquid water may be superheated to about +240 °C to +280 °C in capillaries or small droplets within high-boiling

immiscible solvents (the limit of superheating, also called the spinodal temperature, is about 330 °C [1646]). Degassing water increases its tendency to superheat [1825].

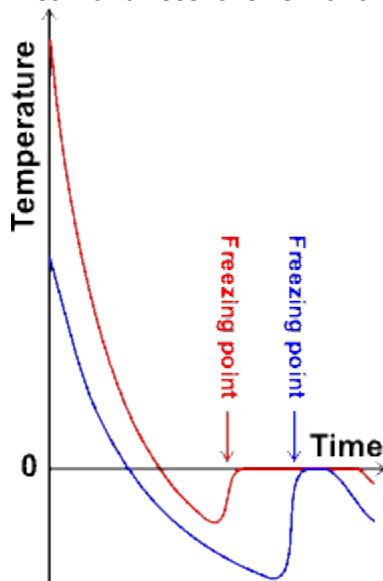
Superheating is also apparent at low temperatures but at negative pressures (i.e. stretched water). Water may be superheated by reducing the pressure to below -100 MPa at 20 °C [1128]. Superheating is facilitated by dissolved gas that may increase its hydrogen-bonded order [821] but prevented by the presence of gas bubbles or nanobubbles (that is, cavities) that act as initiation sites for vaporization.

Water vapor (gas) may easily be cooled below its condensation temperature (dew point) for its partial pressure (*i.e.* its boiling point) in the absence of dust, or other, particles or surfaces that help the nucleation process [1184].

An interesting, if unrelated effect (the Leidenfrost effect), is that water droplets remain far longer on a hotplate just above 200 °C than if the hotplate was just above 100 °C. (see [960] for an amusing scientific answer to how water boils). If the hotplate surface is made superhydrophobic, then the droplets remain even at lower temperatures (22 °C - >300 °C) [1926]. On heated curved surfaces larger quantities of fluid, not just droplets, can be suspended [1957]. [[◀ Anomalies page : Back to Top ▲](#)]

P11 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 must first become cold water and therefore the time required for this will always delay its freezing relative to cold water. However experiments show that hot water (for example, 90 °C) does often (but by no means always) appear to freeze faster than the same amount of cold water (for example, 18 °C) under otherwise identical conditions [158]. This has been recognized even as far back as Aristotle^g in the 4th century BC but was brought to the attention of the scientific community by the perseverance of Erasto Mpemba [1388] a Tanzanian schoolboy,^c who refused to reject his own evidence, or bow to disbelieving mockery, that he could freeze ice cream faster if he warmed it first. For a recent review of the Mpemba effect, see [959].^f



A number of explanations have been put forward [1921]. One that has gained some support is that there is sufficient evaporation from the hot water that this causes faster cooling plus a reduction in

mass, so faster cooling (even to the extent of the existence of a cross-over temperature between, initially hot and initially colder, cooling curves [1716]) and freezing [1390]. There does not seem to be sufficient mass lost in experiments to support such an explanation as the sole cause, however, and the effect is apparent even when the vessel has a lid. Related to this explanation, part of the cause may be due to the larger and more persistent convective currents created when hot water cools; however the effect is again evident even if the vessel has an insulated base and lid. The most likely scenario (described in [158], disputed [1415], but later supported [2047].) is that the degree of supercooling is greater, under some circumstances, 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. After coming to this conclusion, it was found that this explanation for the Mpemba effect was first experimentally determined in 1775 [1861].

Why initially-cold water supercools more is explained in terms of the gas concentration and the clustering of water. Certainly, water behaves differently, and possesses a different structuring, at the same temperature depending upon whether it is being heated or cooled [1697]. 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 have shown that such clustering processes may take some time [4]. Also of relevance here is that the formation of clathrate ices, which have structures closely related to the icosahedral clusters, behaves in an opposite manner. Thus, their supercooling (before clathrate ice formation) from hot water is far greater than that from cold water [1391].^d Recently, it has been discovered that the charge on the liquid interface affects the freezing point of supercooled water [1737]. As the surface of nanobubbles is thought to be negative, the presence of such nanobubbles, with their extensive surface area are expected to increase supercooling. Heating water containing nanobubbles is expected to destroy nanobubbles as they grow in size, due to the lower gas solubility at higher temperatures, and dissipate. The Mpemba effect is then simply explained by the loss of nanobubbles in the hot water which are kinetically too slow to reform on cooling.

It is also possible that dissolved gases may encourage supercooling by (1) increasing the degree 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 reported in [294]; re-equilibration taking several days) and (2) increasing the pressure as gas comes out of solution when the water starts to crystallize, so lowering the melting point and reducing the tendency to freeze (see guest book). Also, the presence of tiny gas bubbles (cavities produced on heating) may increase the rate of nucleation, so reducing supercooling [428]. Recently another possibility has been described depending on changes in dissolved material with temperature (such as the reduction in bicarbonate in heated 'hard' water), but this has not yet been experimentally tested [1014]. The rationale for the Mpemba effect in this case concerns differences in the solute concentration at the ice-liquid interface causing a localized lowering of the melting point [1014]. [

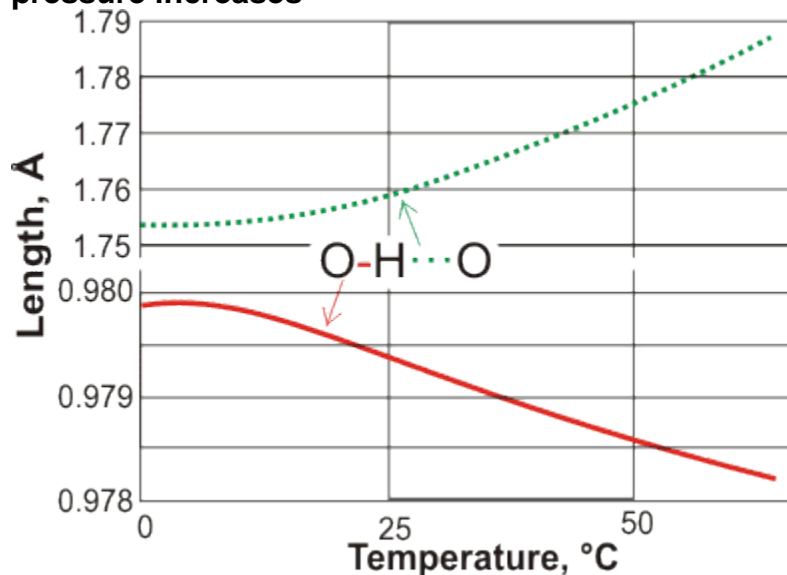
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P12 Warm water vibrates longer than cold water

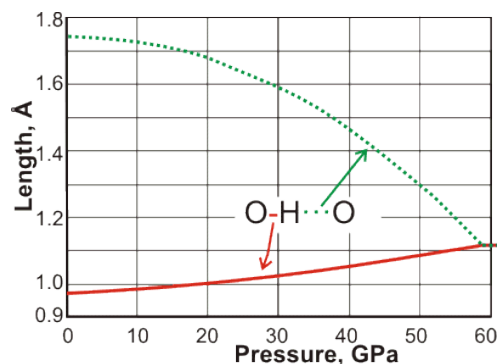
It is expected that the lifetime of an excited molecular vibration should decrease as the temperature increases as the energy and likelihood of interactions with other molecules also both increase. For example, the lifetime of the excited liquid HCl stretch vibration decreases from 2.1 ns at 173 K to 1.0 ns at 248 K.

In liquid water, the excited OH-stretch vibration has a lifetime of 0.26 ps at 298 K and this lifetime increases to 0.32 ps at 358 K [592]. The reason for this is due to the effects of the hydrogen-bonded network. The OH-stretch vibration normally relaxes by transferring energy to an overtone of the H-O-H bending vibration. However, as the temperature increases the hydrogen bonds of water get weaker, which leads to an increase of the frequency of the stretch vibration and a decrease of the frequency of the bending vibration. As a result, the overtone of the bending mode shifts out of resonance with the stretching mode, thereby making the energy transfer less likely. [[Anomalies](#) page : [Back to Top](#) ▲]

P13 Water molecules shrink as the temperature rises and expand as the pressure increases



It is expected that molecular bond lengths will increase and bonds will bend more as the temperature increases, giving rise to slight increases in the volume of individual molecules. However, as the temperature rises (> 4°C) the water molecules move away from each other and the hydrogen bonds weaken. This causes the O-H covalent bonds (shown blue right, lower curve) to shrink and stiffen, so reducing the volume of individual water molecules [2044].



As covalent bonds generally reduce under high pressure, a further anomalous change is that the O-H covalent bond length of water (shown red left, lower curve) , in liquid and solid phases, increases as the pressure increases. This is due to the hydrogen bond shortening under pressure. The variation of bond lengths with pressure for ice is shown on the right [1809].

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Footnotes

^a The surface temperature on Mars lies below the triple point of water and its atmospheric pressure is close to this value, such that no liquid water may be found there. [Back]

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

^c Erasto Mpemba is now enjoying his retirement from being Principal Game Officer in Tanzania. He describes his discovery on YouTube. [Back]

^d The gas-hydrate clathrate ices also show an anomalously low dissociation rate [1539] that fits well with this hypothesis. [Back]

^e The ease of supercooling water was noted by Fahrenheit. [Back]

^f The winning entry in the Royal Society of Chemistry competition concerning the Mpemba effect is given here. [Back]

^g "The fact that the water has previously been warmed contributes to its freezing quickly: for so it cools sooner" Aristotle [2043]. [Back]

Source:<http://www1.lsbu.ac.uk/water/explan.html>