

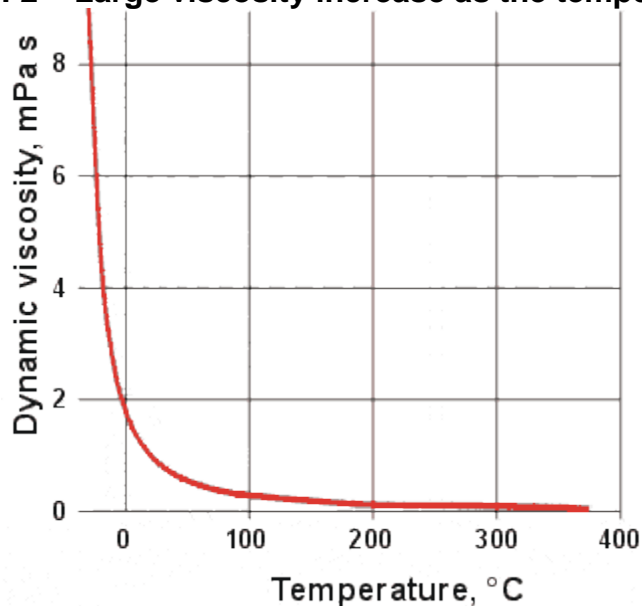
# Explanation of the Physical Anomalies of Water (F1-F9)

- ✓ Water has unusually high viscosity
- ✓ Large viscosity increase as the temperature is lowered
- ✓ Water's viscosity decreases with pressure below 33 °C
- ✓ Large diffusion decrease as the temperature is lowered
- ✓ At low temperatures, the self-diffusion of water increases as the density and pressure increase
- ✓ The thermal diffusivity rises to a maximum at about 0.8 GPa
- ✓ Water has unusually high surface tension
- ✓ Some salts give a surface tension-concentration minimum; the Jones-Ray effect
- ✓ Some salts prevent the coalescence of small bubbles
- ✓ The molar ionic volumes of salts show maxima with respect to temperature

## F1 High viscosity (0.89 cP, compare 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. It depends on the forces holding the molecules together (cohesiveness). This cohesiveness is large in water due to its extensive three-dimensional hydrogen bonding. It should be noted that although the viscosity of water is high, it is not so high that it causes too much difficulty being moved around within organisms. The Arrhenius energy of activation for viscous flow is similar to the hydrogen bond energy ( $\text{H}_2\text{O}$ ,  $21.5 \text{ kJ mol}^{-1}$ ;  $\text{D}_2\text{O}$ ,  $24.7 \text{ kJ mol}^{-1}$ ;  $\text{T}_2\text{O}$ ,  $26.2 \text{ kJ mol}^{-1}$ , all calculated from [73]; all at 0 °C and all more than doubling at -30 °C). [[◀ Anomalies page : Back to Top ▶](#)]

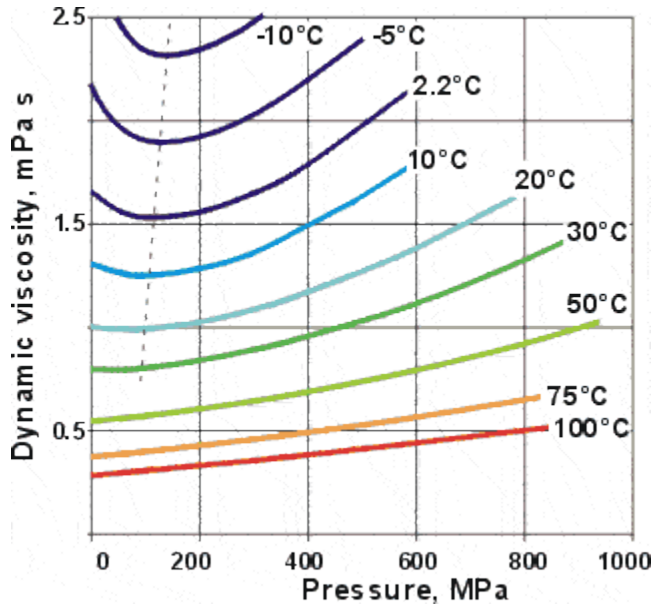
## F2 Large viscosity increase as the temperature is lowered.



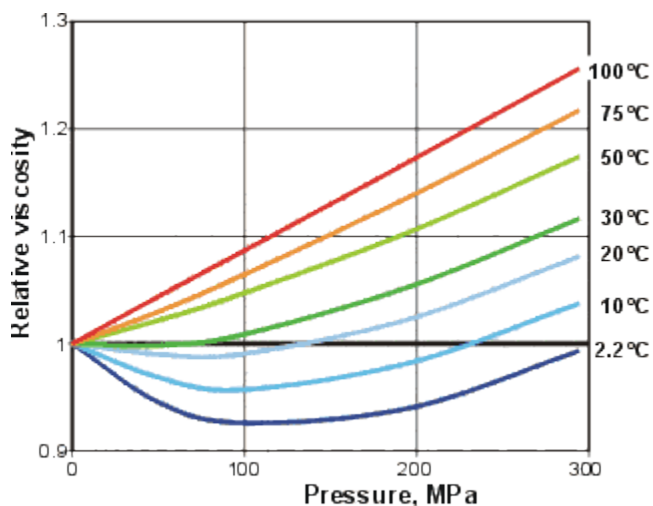
The increase in the viscosity with lower temperatures is particularly noticeable within supercooled water (see opposite). The water clusterequilibrium shifts towards the more open structure (for example, ES) as the temperature is lowered. This structure is formed by stronger hydrogen bonding. In turn, this creates larger clusters and reduces the ease of movement (increasing viscosity). [[◀ Anomalies page : Back to Top ▶](#)]

### F3 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 pressure increases the viscosity.



Water's pressure-viscosity behavior [534] can be explained by the increased pressure (up to about 150 MPa) causing deformation, so reducing the strength of the hydrogen-bonded network, which is also partially responsible for the viscosity. This reduction in cohesiveness more than compensates for the reduced void volume. It is thus a direct consequence of the balance between hydrogen bonding effects and the van der Waals dispersion forces [558] in water; hydrogen bonding prevailing at lower temperatures and pressures. At higher pressures (and densities), the balance between hydrogen bonding effects and the van der Waals dispersion forces is tipped in favor of the dispersion forces and the remaining hydrogen bonds are stronger due to the closer proximity of the contributing oxygen atoms [655]. Viscosity, then, increases with pressure. The dashed line (opposite) indicates the viscosity minima.



The variation of viscosity with pressure and temperature has been used as evidence that the viscosity is determined more by the extent of hydrogen bonding rather than hydrogen bonding strength [824].

Self-diffusion is also affected by pressure where (at low temperatures) both the translational and rotational motion of water anomalously increase as the pressure increases (see below). [

◀ Anomalies page : Back to Top ▲]

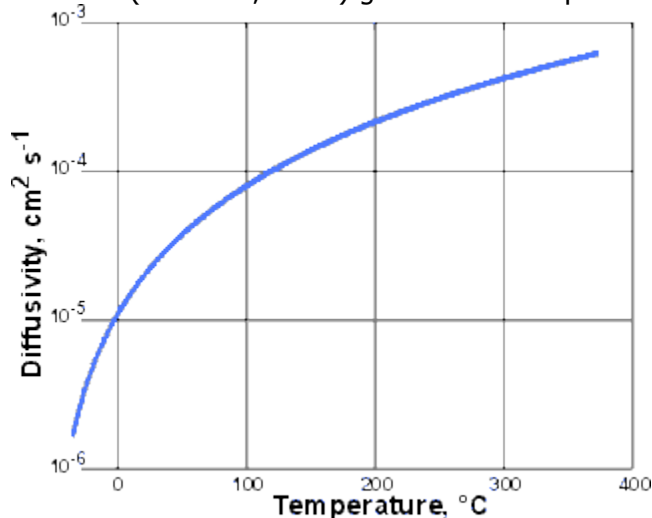
#### F4 Large diffusion decrease as the temperature is lowered.

Diffusion may be generally described by the Stokes-Einstein equation for translational diffusion

[806],  $D_t = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}$  and the Stokes-Einstein-Debye equation for rotational

diffusion,  $D_r = \frac{RT}{N} \cdot \frac{1}{8\pi\eta r^3}$ , where  $D_t$  and  $D_r$  are the translational and rotational diffusivities respectively, R is the gas constant, N is Avogadro's number,  $\eta$  is dynamic viscosity and r is water's molecular radius. The values for self-diffusion are greatly reduced at lower temperatures where they anomalously decrease as the density decreases (see below). This is unsurprising as these diffusion terms are approximately proportional to the reciprocal of the viscosity, and viscosity anomalously increases at lower temperatures. The inverse relationship between water diffusivity and dynamic viscosity, and the ratio of translational to rotational diffusivity, are almost independent of temperature between about -35 °C and +100 °C. However there is a strong divergence from these Stokes-Einstein relationships, and their ratio [1040c], at lower, supercooled, temperatures (at 225 K [1040a]) due to the differential effects of clustering [807] caused by the presence of both low and higher density aqueous phases [1040];<sup>f</sup> the extensive 'sticky' low-density clusters reducing translational freedom, whereas rotational freedom is retained within the higher density intervening spaces. Although such behavior is expected of liquids close to their glass transition, that is not the case with water where it occurs well above the glass-transition temperature.

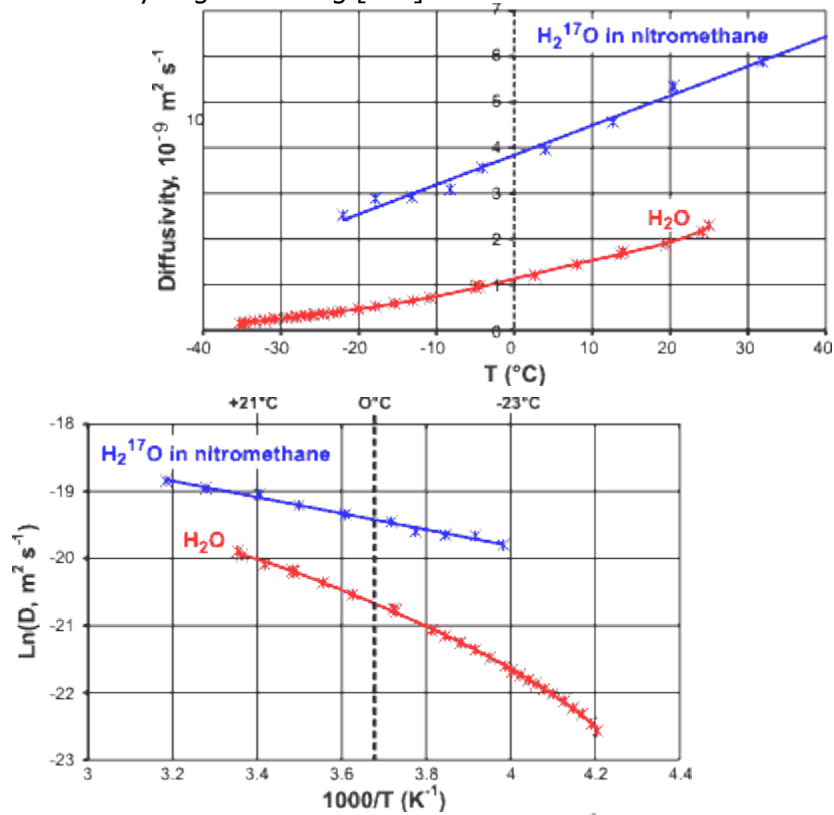
The diffusion equations (above) give unexpectedly good estimates for the radius of the water molecule ( $r = 1.1 \text{ \AA}$ , 25 °C)<sup>a</sup> given that the equations were derived for large spherical particles.



The activation energy for this diffusion increases to about the equivalent of two hydrogen bonds ( $44.4 \text{ kJ mol}^{-1}$ ) at 238 K where the diffusion coefficient is  $1.58 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  [653]. The importance of this activation energy disappears above about 315 K, when it appears to be less than the thermal energy [1295]. Thus, the main reason for the low diffusion at low temperatures is the three-dimensional hydrogen bond network.

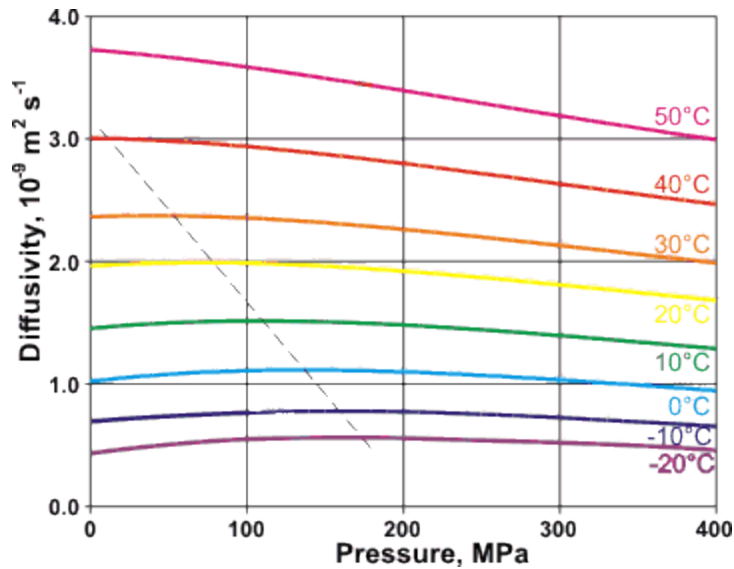
The diffusion coefficient of deeply supercooled water is  $2.2 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$  at 150 K [334].

As shown below, this anomalous diffusional behavior is not present when water diffuses in nitromethane in the absence of hydrogen bonding [652].

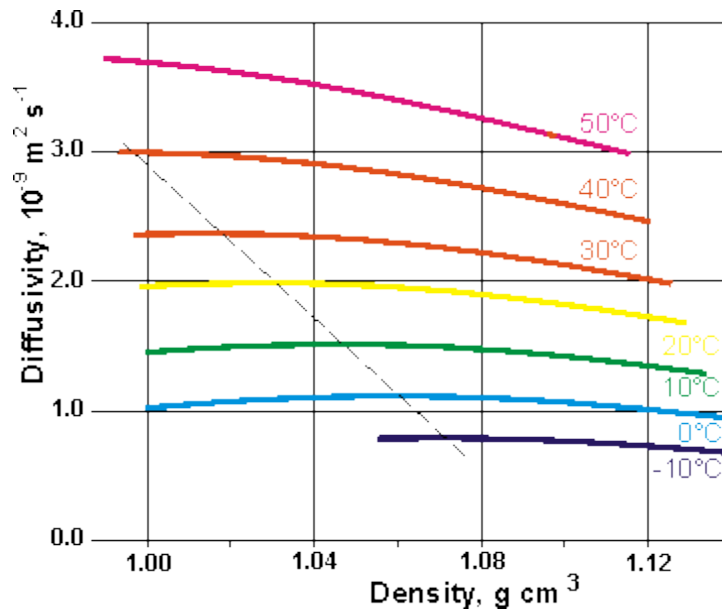


[ [◀ Anomalies page : Back to Top ▶](#) ]

**F5 At low temperatures, the self-diffusion of water increases as the density and pressure increase.**



Data for these tables was calculated from<sup>a</sup> the IAPWS viscosity data [540] or from [2081]. The dashed lines indicate the maxima.



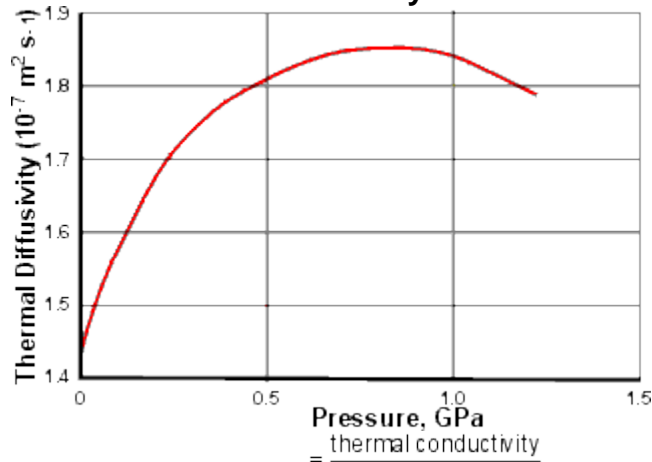
The increase in self-diffusion with density (within the range of about  $0.9 \text{ g cm}^{-3}$  up to about  $1.1 \text{ g cm}^{-3}$ , at low temperatures) is in contrast to normal liquids where increasing density decreases self-diffusion as the molecules restrict each other's movements. The density increase may be due to increasing temperature, below  $4 \text{ }^\circ\text{C}$ , at atmospheric pressure or due to increasing pressure at low temperatures. Liquids normally show reduced self-diffusion when they are squeezed but water at  $0 \text{ }^\circ\text{C}$  increases its diffusivity by 8% under a pressure of about 200 MPa [226] and the diffusivity of supercooled water at  $-30 \text{ }^\circ\text{C}$  increases by 60% with a similar pressure increase. The temperature limit for this anomalous behavior is  $\sim 42 \text{ }^\circ\text{C} \pm 5 \text{ }^\circ\text{C}$  in agreement with the limit of the compressibility anomaly [1970]. Further increase in pressure reduces the diffusivity in common with the behavior of other 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 and more complete hydrogen bonding, which reduces the self-diffusion. The strength of the hydrogen bonding is a controlling influence in this anomalous region, where the hydrogen bond angles and the intermolecular distances are strongly coupled and this order decreases on compression [169] due to the

collapse of ES structures to CS structures. Simulation studies have shown that self-diffusion goes through a minimum as the density of water is reduced below about  $0.9 \text{ g cm}^{-3}$  followed by an increase with further density reduction, as might be expected from most liquids [402], due to the disruption of the network at low density as the now-stretched hydrogen bonds are broken [626]. The maximum in the self-diffusion is brought about as at even higher pressures there is an increased packing density due to the gradual phase transition to interpenetrating hydrogen bonded networks.

For similar reasons involving the collapse of the hydrogen bonding, the ice surface diffusion coefficient at high pressure (10 MPa) is more than twice that observed at atmospheric pressure [1708].

For the same reasons, the molecular rotational movement of water (reciprocal rotational relaxation time; Debye relaxation time,  $\tau_D$ ) also varies in direct proportion to the changes in self-diffusion (translational movement). Thus rotation and translation of water are coupled [1839]. [[◀ Anomalies page : Back to Top ▲](#)]

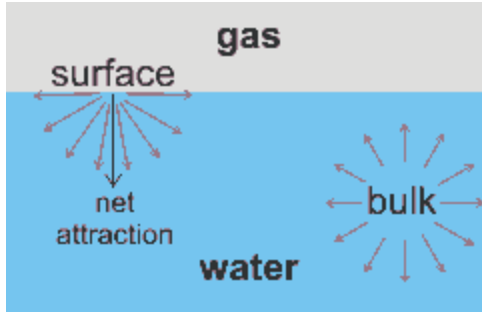
### F6 The thermal diffusivity rises to a maximum at about 0.8 GPa.



The thermal diffusivity ( $\frac{\text{thermal conductivity}}{\text{density} \times C_p}$ ),<sup>b</sup> which arises from vibrations in the water network [713], shows less anomalous temperature and pressure behavior than might be expected due to the dependence on the anomalously-behaving, but counteractive, thermal conductivity, density and specific heat capacity. There is, however, a steep increase in thermal diffusivity at low temperatures and a maximum in the low-temperature thermal diffusivity - pressure behavior at about 0.8 GPa (see left, 25 °C) [614].

It is likely that there will be a minimum in the thermal diffusivity-temperature behavior at about  $30 \pm 15 \text{ °C}$  at atmospheric pressure in line with changes in the specific heat ( $C_p$ ) and thermal conductivity. A modeling approach using TIP5P gives the minimum at  $\sim 250 \text{ K}$  [1352]. [[◀ Anomalies page : Back to Top ▲](#)]

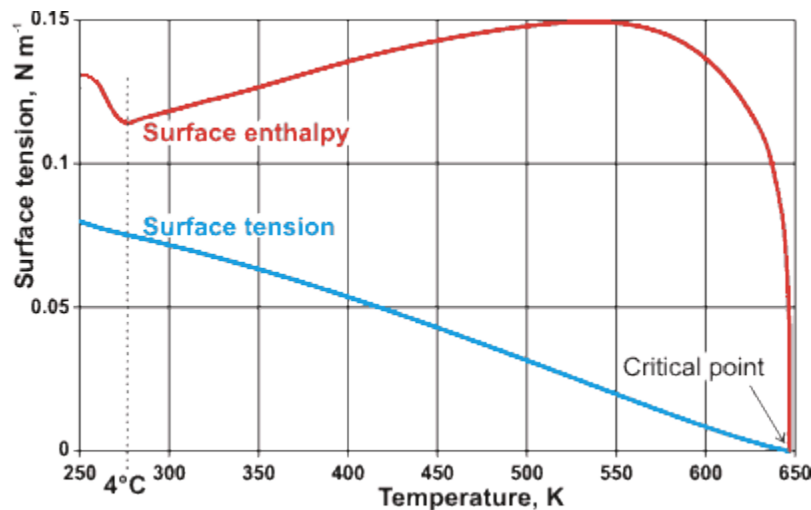
### F7 High surface tension (72.75 mJ/m<sup>2</sup>, cf. CCl<sub>4</sub> 26.6 mJ/m<sup>2</sup> at 20 °C)



$$\gamma = \left( \frac{dG}{dA} \right)_{T, P_n}$$

Surface tension (surface free energy,  $\gamma = \left( \frac{dG}{dA} \right)_{T, P_n}$ ) at a gas liquid interface is produced by the attraction between the molecules being directed away from the surface as surface molecules are more attracted to the molecules within the liquid than they are to molecules of the gas at the surface. In contrast, molecules of water in the bulk are equally attracted in all directions. In order to achieve the greatest possible interaction energy, surface tension causes the maximum number of surface molecules to enter the bulk of the liquid and, hence, the surface area is minimized.

Water has an abnormally high surface tension <sup>c</sup> and surface enthalpy <sup>d</sup> with an abnormally tightly packed surface compared to bulk liquid water.<sup>e</sup> Water molecules at the liquid-gas surface have lost potential hydrogen bonds directed at the gas phase and are pulled towards the underlying bulk liquid water by the remaining stronger hydrogen bonds [214]. Energy is required to increase the surface area (removing a molecule from a well hydrogen bonded interior bulk water to the lesser hydrogen bonded surface), 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 other molecules, and the water molecules are very small, the surface tension is large. Lowering the temperature greatly increases the hydrogen bonding in the bulk causing increased surface tension.



Although there is no clear anomaly in the surface tension/temperature behavior [IAPWS], there are inflection points at about +4 °C [865] and 262 °C [427]. The inflection in the data at low temperatures has been explained by use of a two-state mixture model involving low-density and higher density water clusters [866]. The surface enthalpy/ temperature behavior is anomalous, however, with a clear minimum at the temperature of maximum density.<sup>9</sup> This is a consequence of the minimum in the surface entropy/ temperature behavior. An interesting, if usually ignored,

phenomenon is the linear reduction of surface tension with increasing relative humidity;  $\sim 0.1\%$  drop per 1% increase in humidity at 5 °C [1854].

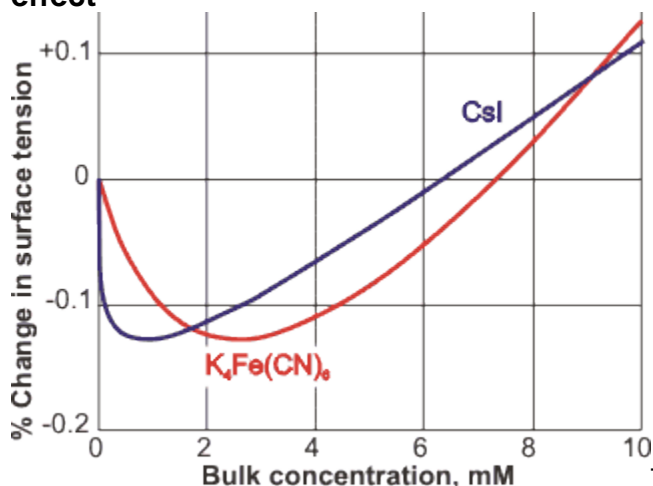
Surface tension changes differently from bulk water properties due to surface enrichment with water clusters.

The greater than expected drop in surface tension with temperature increase ( $0.155 \text{ mJ m}^{-2} \text{ K}^{-1}$  at 25 °C) is one of the highest known and similar to that of the liquid metals. It has been quantitatively explained using spherically symmetrical water clustering [376]. The thermodynamic change in surface tension with pressure is very high at 25 °C [1280].<sup>e</sup>

It is interesting to note that surfactants lower the surface tension because they prefer to sit in the surface, attracting the surface water molecules in competition to the bulk water hydrogen bonding and so reducing the net forces away from the surface (that is, the surface tension). Many organic molecules, both hydrophilic (ethanol) and hydrophobic (neopentane), prefer the surface of water to its bulk [1889].

The high surface tension of water endows it with some rather unexpected properties. Thus, water drops may rise up an inclined plate, against gravity, if subjected to symmetrical vibrations of about 100 Hz [1311]. This is due to the unequal changes in contact angle at the top and bottom surfaces, creating upwards forces greater than that due to gravity, and the non-linear friction effects. Also, if a small drop of water (typically 1 mm diameter) is coated in a fine (typically 20  $\mu\text{m}$  diameter) hydrophobic dust then the drop can roll and bounce without leakage [225], and the aqueous spheres can even float on water. Capillarity holds the dust at the air-liquid interface with the elasticity being due to the high surface tension. Similar material is known as 'dry water', behaving as a dry powder but releasing  $\sim 95\%$ - $98\%$  liquid water on mechanical action such as rubbing on the skin in cosmetics [1660]. This 'dry water' powder is able to efficiently take up and hold large amounts of  $\text{CO}_2$  as its clathrate ( $\sim 25\%$   $\text{CO}_2$  by weight) [1929]. [◀ Anomalies page : Back to Top ▶]

### F8 Some salts give a surface tension-concentration minimum; the Jones-Ray effect



The affinity of chaotropic ions for the expanded and weakly hydrogen bonded surface water structure (aided by the excess of 'lone pair' electrons directed towards the bulk [594]) may help explain the shallow minima in their surface tension at very low ionic concentrations (that is, the Jones-Ray effect [674]; first dismissed erroneously as an artifact by Irving Langmuir [1518]). For example, at low concentration ( $< 1 \text{ mM}$ ) the surface tension of KCl solutions drops ( $\sim -0.01\%$  change) with increasing concentration. The increase in surface



tension with higher concentrations of salt is thought due to the relative depletion of salt within the surface, which means that when ions do adsorb at the surface a depletion layer must be created deeper in. Also, higher concentrations of such salts must disproportionately increase the bulk salt concentration so adding to the attractive forces on the surface water molecules, consequently adding to the increase in the surface tension. Kosmotropic cations and anions prefer to be fully hydrated in the bulk liquid water and so increase the surface tension by the latter mechanism at all concentrations [1885]. This partitioning is noticeable in NaCl solutions, such as seawater; the weakly chaotropic  $\text{Cl}^-$  occupying surface sites whereas the weakly kosmotropic  $\text{Na}^+$  only resides in the bulk water [928]. The polarizability of large chaotropic anions (such as  $\text{I}^-$ ) is accentuated due to the asymmetric solvent distribution at the surface and increases the strength of chaotrope-solvent interactions when at the surface [989]. Similarly to chaotropic ions, hydroxyl radicals also prefer to reside at air-water interfaces [939]; the radicals donating one hydrogen bond but accepting less than two [943]. The ionic surface tension increments,  $k_i = d\gamma/dc_i$  ( $\text{mN m}^{-1} \text{M}^{-1}$ ) have been tabulated [1981] for higher molar concentrations.

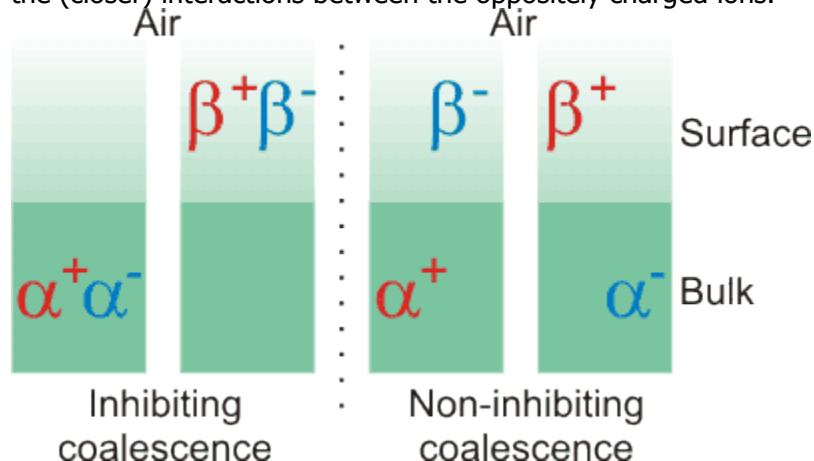
The supposed preference of  $\text{H}_3\text{O}^+$  for the surface in some acid solutions (presumed due to its likely surface active nature, as its O atom is not hydrogen bonded) is indicated by the drop in surface tension with high HCl,  $\text{HNO}_3$  and  $\text{HClO}_4$  acid concentrations. However, the anion is important as the same effect is not shown by  $\text{H}_2\text{SO}_4$ ; thus the  $\text{H}_3\text{O}^+$  ions in  $\text{H}_2\text{SO}_4$  solutions show no preference for the surface. Also,  $\text{NH}_4\text{OH}$  (but not  $\text{NH}_4\text{Cl}$ , nor  $\text{NaOH}$ ) shows a much more marked reduction in surface tension with concentration than these acids, which by a similar, if possibly equally erroneous argument, might indicate a greater preference of hydroxide ion for the surface.<sup>h</sup> The surface active nature of these acids and bases is more easily and more consistently explained by the formation of uncharged species (for example, HCl,  $\text{NH}_3$ ) at the surface, coincident with their volatility.

Interestingly the surface tension of pure (no  $\text{CO}_2$ ) water does not change with pH over the range of pH 1 - 13 on adjusting using just HCl or NaOH, except for a small local minimum around pH 4, which has been attributed as a probable manifestation of the Jones-Ray effect [2073]. [[◀ Anomalies](#) page : [Back to Top ▲](#)]

### **F9 Some salts prevent the coalescence of small bubbles.**

Higher concentrations (often about 0.1M) of many, but not all, salts prevent the coalescence of small gas bubbles (reviewed [672]) in contrast to the expectation from the raised surface tension and reduced surface charge double layer effects (DLVO theory<sup>j</sup>). Higher critical concentrations are required for smaller bubble size [599]. This is the reason behind the foam that is found on the seas (salt water) but not on lakes (fresh water). The salts do not directly follow the Hofmeister effects (that are primarily described in terms of the individual cations or anions) with both the anion and cation having importance together with one preferentially closer to the interface than the other; for example, excess hydrogen ions [1205] tend to negate the effect of halides [622]. The explanation for this unexpected phenomenon is that bubble coalescence entails a reduction in the net gas-liquid surface. The reduction in this surface is preferred when it gives rise to an increase in

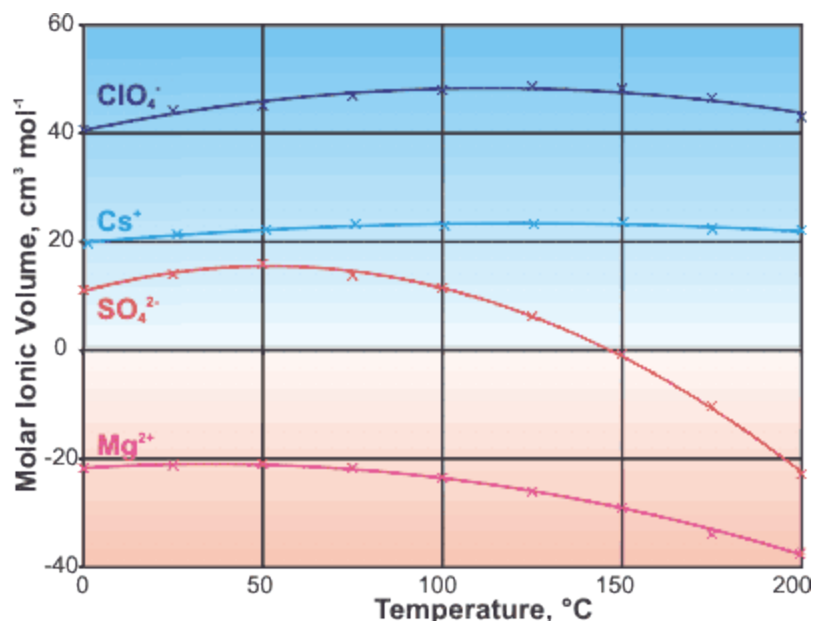
the (closer) interactions between the oppositely charged ions.



It has recently been proposed that anions and cations may be divided into two groups  $\alpha$  and  $\beta$  with  $\alpha$  cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ) and  $\alpha$  anions ( $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ) avoiding the surface and  $\beta$  anions ( $\text{ClO}_4^-$ ,  $\text{CH}_3\text{CO}_2^-$ ,  $\text{SCN}^-$ ) and  $\beta$  cations ( $\text{H}^+$ ,  $(\text{CH}_3)_4\text{N}^+$ ) attracted to the interface;  $\alpha\alpha$  and  $\beta\beta$  anion-cation pairs then cause inhibition of bubble coalescence whereas  $\alpha\beta$  and  $\beta\alpha$  pairs do not [1657].<sup>†</sup> Bubble coalescence is inhibited when a bulk solvated or a surface active ion pair is present in solution ( $\alpha\alpha$  or  $\beta\beta$ , respectively), creating an effectively uncharged interface [1657]. These groupings do not behave as bulk-phase ionic kosmotropes and chaotropes, which indicates the different properties of bulk water to that at the gas-liquid surface. It is likely that the ions reside in the interfacial region, between the exterior surface layer and interior bulk water molecules, where the hydrogen bonding is naturally most disrupted [605]. A similar phenomenon is the bubble (cavity) attachment to microscopic salt particles used in microflotation, where chaotropic anions encourage bubble formation [758].

Interestingly, the concentration of salt in our bodies corresponds to the minimum required for optimal prevention of bubble coalescence [622]. As small bubbles are much less harmful than large bubbles, this fact is very useful. [[◀ Anomalies page : Back to Top ▶](#)]

**F10 The molar ionic volumes of salts show maxima with respect to temperature.**



The molar ionic volumes, at infinite dilution, of salts depend on both the positive intrinsic volume of the ions and the negative volume change of the water due to the ion's electric field pulling on their neighboring water molecules. Their behavior with respect to temperature is thus mostly derived from how they are able to disrupt the structuring in water (i.e. contract its clustering). Shown opposite is the behavior of two ionkosmotropes,  $\text{SO}_4^{2-}$  (intrinsic volume  $52.94 \text{ cm}^3 \text{ mol}^{-1}$ ) and  $\text{Mg}^{2+}$  (intrinsic volume  $1.62 \text{ cm}^3 \text{ mol}^{-1}$ ) and two ionic chaotropes,  $\text{ClO}_4^-$  (intrinsic volume  $60.15 \text{ cm}^3 \text{ mol}^{-1}$ ) and  $\text{Cs}^+$  (intrinsic volume  $21.38 \text{ cm}^3 \text{ mol}^{-1}$ ) [1599, 1912]. They all are able to hold water increasingly strongly (relative to water holding itself) at higher temperatures (where water-water hydrogen bonding is more disrupted) and as the temperature is lowered at low temperatures (where the salt interacts with the clathrate clustering).

Additionally, kosmotropes and chaotropes behave differently with the chaotropes' molar volumes changing less with temperature and reaching their maxima at higher temperatures [1599, 1912]. [

◀ Anomalies page : Back to Top ▶]

## Footnotes

<sup>a</sup> If the equation for 'slip boundary' solutes, where the solute diffusion does not involve the fixed

$$D = \frac{RT}{N} \cdot \frac{1}{4\pi\eta r}$$

shell of solvent molecules assumed in the above equation, is used then the water hydrodynamic radius is close to correct at  $1.64 \text{ \AA}$  at  $25 \text{ }^\circ\text{C}$ . [Back]

<sup>b</sup> At temperatures between  $100 \text{ }^\circ\text{C}$  and  $400 \text{ }^\circ\text{C}$ , the thermal diffusivity scales as the square root of the absolute temperature (Diffusivity/ $\sqrt{T} \propto$  density [614]). [Back]

<sup>c</sup> A freshly exposed surface of water would be expected to have much higher surface energy ( $\sim 0.180 \text{ J m}^{-2}$  [1255]), with the surface tension reducing as hydroxide ions build up at the water-air interface [1905]. [Back]

<sup>d</sup> Surface enthalpy (also known as the total surface energy) may be calculated from the binding energy lost per unit surface area (= molecules per surface area x binding energy lost per molecule). If the surface is only half occupied with water molecules that have lost about a third of their

hydrogen bonds, the surface enthalpy should be  $= 0.5 \times (10^{19} \text{ molecule m}^{-2}) \times (1/6.022 \times 10^{23} \text{ mol molecule}^{-1}) \times 1/3 \times (45 \text{ kJ mol}^{-1}) = \sim 0.125 \text{ J m}^{-2}$  (compare with the actual value of  $0.118 \text{ J m}^{-2}$  at  $25 \text{ }^\circ\text{C}$ ). [Back]

<sup>e</sup> The influence of pressure on the surface tension of water, as with other liquids, is not straightforward. There are two clear effects. Firstly, the thermodynamic relationship relating surface

tension to pressure  $\left(\frac{d\gamma}{dP}\right)_{T,P_n}$  has been shown to equal the change in volume associated with

forming more surface,  $\left(\frac{dV}{dA}\right)_{T,P_n}$  [1283].  $\left(\frac{dA}{dV}\right)_{T,P_n}$  may be taken as a measure of the difference in density of the liquid in the bulk compared with that at its surface and is therefore generally positive (that is, the surface tension should increase with pressure about  $+0.7 \text{ mJ m}^{-2} \text{ MPa}^{-1}$  for water at  $25$

$^\circ\text{C}$ ). The pressure coefficient of the surface tension  $\left(\frac{d\gamma}{dP}\right)_{T,P_n} = \text{surface enthalpy/internal+external pressure}$ ,  $= 0.696 \text{ nm}$  at  $25 \text{ }^\circ\text{C}$ ) is generally much higher than for other liquids; for example, methanol ( $0.159 \text{ nm}$ ), diethyl ether ( $0.176 \text{ nm}$ ), benzene ( $0.178 \text{ nm}$ ) and even mercury ( $0.398 \text{ nm}$ ) [1280]. This high value for water indicates that the density at the surface of water is more similar to the bulk liquid than occurs in most other liquids (see the thermodynamic derivatization). Anomalously amongst liquids, the densities of surface and bulk water are equal at  $3.984 \text{ }^\circ\text{C}$  (at atmospheric pressure, as calculated from the equations given in [1280]) and below this temperature the bulk liquid is less dense than the surface liquid.

The thermodynamic relationship does not hold for real liquid-gas systems, however, where the application of pressure will cause water vapor to condense and gas molecules to adsorb on to the liquid-gas interface. The adsorption of gas molecules to the surface of liquid water lowers the surface tension by a greater extent than the thermodynamic effect outlined above (except perhaps for helium). Thus, the surface tension of water, in contact with other molecules in the gas phase, drops with increase in pressure due to the surface activity of surface-absorbed gas molecules [1282]. The extent of this lowering depends upon the gas involved and is much greater for hydrophilic gasses, such as  $\text{CO}_2$  ( $-7.7 \text{ mJ m}^{-2} \text{ MPa}^{-1}$ ), than nonpolar gasses such as  $\text{N}_2$  and  $\text{O}_2$  ( $-0.8 \text{ mJ m}^{-2} \text{ MPa}^{-1}$ ). [Back]

<sup>f</sup> A similar effect occurs in kosmotropic salt solutions such as  $\text{MgCl}_2$ . As the concentration of salt increases the glass transition temperature increases as does the disparity between the rotational and translational diffusivities. With the rotational diffusivity almost independent of the viscosity, this involves a breakdown of the Stokes-Einstein relationship [1451]. This is explained, in a manner similar to the explanation for the effect in deeply supercooled pure water, as sticky clusters (here, hydrated salt ions) constantly jamming into each other (thus high viscosity) but with intervening space where water molecules can rotate unimpeded. [Back]

<sup>g</sup> The surface enthalpy/temperature curve was calculated from a combination of sixth power fits to four ranges of surface tension data, given in [865] and [IAPWS]; and assuming the effect of changes in pressure on the change in surface tension with temperature was insignificant. Due to noise in the data and the lack of data below  $250 \text{ K}$ , the form of the curve at very low temperatures is error-prone. [Back]

<sup>h</sup> It has been proposed that the lesser hydration energy of  $\text{OH}^-$ , relative to  $\text{H}_3\text{O}^+$ , results in  $\text{OH}^-$  preferring the surface over the  $\text{H}_3\text{O}^+$  [1025], which also has some, but less, preference for the

surface [1205,1308], and biases a pure aqueous interface to give it a negative potential [1205c, 1308]. This phenomena, even if correct, cannot be the whole story as ions with even lower hydration energy do not seem to readily replace hydroxide ions at the interface [1505]. [Back]

<sup>i</sup> Originally, it was proposed that  $\beta$  anions ( $\text{ClO}_4^-$ ,  $\text{CH}_3\text{CO}_2^-$ ,  $\text{SCN}^-$ ) avoided the surface and  $\alpha$  anions ( $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) were attracted to the interface [1305]. [Back]

<sup>j</sup> The DLVO theory does not hold at short distances ( $\sim < 2\text{nm}$ ) in liquid water due to hydrated surfaces with long range secondary hydration forces [1726]. Kosmotropic and chaotropic ions behave differently within any hydrated surface layer [Back]

Source:<http://www1.lsbu.ac.uk/water/explan5.html>